

Instructor's Solutions Manual for Physical Chemistry

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Preface

This *Instructor's Solutions Manual* has a twofold purpose. First, and most obvious, is to provide worked solutions for the use of instructors. Second, but equally important, is to provide examples of good problem-solving techniques and strategies that will benefit your students if you share these solutions with them.

Most education researchers believe that it is more beneficial for students to study a smaller number of carefully chosen problems in detail, including variations, than to race through a larger number of poorly understood calculations. The solutions presented here are intended to provide a basis for this practice.

Please note that Benjamin Cummings has copyrighted the *Instructor's Solutions Manual* and permits posting these solutions to password-protected sites only. Posting of these solutions to open-access sites is forbidden in order to prevent dissemination of the solutions via the Internet. Should you have any questions concerning this policy, please direct them to the Chemistry Editor at Benjamin Cummings.

We have made every effort to be accurate and correct in these solutions. However, if you do find errors or ambiguities, we would be very grateful to hear from you. Please contact us at: pchem@chem.washington.edu.

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Chapter 1: Fundamental Concepts of Thermodynamics

Problem numbers in italics indicate that the solution is included in the *Student's Solutions Manual*.

Questions on Concepts

Q1.1) The location of the boundary between the system and the surroundings is a choice that must be made by the thermodynamicist. Consider a beaker of boiling water in an airtight room. Is the system open or closed if you place the boundary just outside the liquid water? Is the system open or closed if you place the boundary just inside the walls of the room?

If the system boundaries are just outside of the liquid water, the system is open because water can escape from the top surface. The system is closed if the boundary is just inside the walls, because the room is airtight.

Q1.2) Real walls are never totally adiabatic. Order the following walls in increasing order with respect to being diathermal: 1-cm-thick concrete, 1-cm-thick vacuum, 1-cm-thick copper, 1-cm-thick cork.

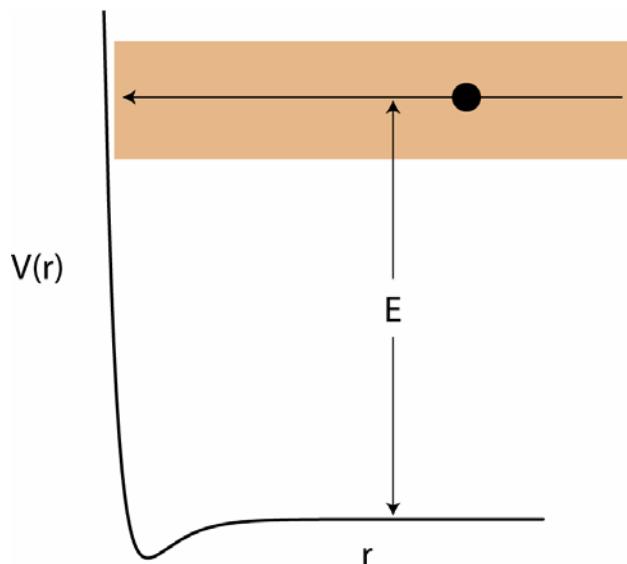
1-cm-thick vacuum < 1-cm-thick cork < 1-cm-thick concrete < 1-cm-thick copper

Q1.3) Why is the possibility of exchange of matter or energy appropriate to the variable of interest a necessary condition for equilibrium between two systems?

Equilibrium is a dynamic process in which the rates of two opposing processes are equal. However, if the rate in each direction is zero, no exchange is possible, and therefore the system can not reach equilibrium.

Q1.4) At sufficiently high temperatures, the van der Waals equation has the form $P \approx \frac{RT}{V_m - b}$. Note that the attractive part of the potential has no influence in this expression. Justify this behavior using the potential energy diagram in Figure 1.6.

At high temperatures, the energy of the molecule is large as indicated by the colored rectangular area in the figure below.



In this case, the well depth is a small fraction of the total energy. Therefore, the particle is unaffected by the attractive part of the potential.

Q1.5) The parameter a in the van der Waals equation is greater for H₂O than for He. What does this say about the form of the potential function in Figure 1.6 for the two gases?

It says that the depth of the attractive potential is greater for H₂O than for He.

Problems

P1.1) A sealed flask with a capacity of 1.00 dm³ contains 5.00 g of ethane. The flask is so weak that it will burst if the pressure exceeds 1.00×10^6 Pa. At what temperature will the pressure of the gas exceed the bursting temperature?

$$T = \frac{PV}{nR} = \frac{1.00 \times 10^6 \text{ Pa} \times 10^{-3} \text{ m}^3}{\frac{5.00 \times \text{g}}{30.07 \text{ g mol}^{-1}} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}} = 723 \text{ K}$$

P1.2) Consider a gas mixture in a 2.00-dm³ flask at 27.0°C. For each of the following mixtures, calculate the partial pressure of each gas, the total pressure, and the composition of the mixture in mole percent.

- a) 1.00 g H₂ and 1.00 g O₂
- b) 1.00 g N₂ and 1.00 g O₂
- c) 1.00 g CH₄ and 1.00 g NH₃

a)

$$P_{H_2} = \frac{n_{H_2}RT}{V} = \frac{1.00/2.016 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{2.00 \times 10^{-3} \text{ m}^3} = 6.24 \times 10^5 \text{ Pa}$$

$$P_{O_2} = \frac{n_{O_2}RT}{V} = \frac{1.00/32.00 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{2.00 \times 10^{-3} \text{ m}^3} = 3.90 \times 10^4 \text{ Pa}$$

$$P_{total} = 6.57 \times 10^5 \text{ Pa}$$

$$\text{mol \% H}_2 = 100 \times \frac{\text{mol H}_2}{\text{mol H}_2 + \text{mol O}_2} = 100 \times \frac{1.00/2.016}{1.00/2.016 + 1.00/32.00} = 94.1\%$$

$$\text{mol \% O}_2 = 100 \times \frac{\text{mol O}_2}{\text{mol H}_2 + \text{mol O}_2} = 100 \times \frac{1.00/32.00}{1.00/2.016 + 1.00/32.00} = 5.9\%$$

b)

$$P_{N_2} = \frac{n_{N_2}RT}{V} = \frac{1.00/28.02 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{2.00 \times 10^{-3} \text{ m}^3} = 4.45 \times 10^4 \text{ Pa}$$

$$P_{O_2} = \frac{n_{O_2}RT}{V} = \frac{1.00/32.00 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{2.00 \times 10^{-3} \text{ m}^3} = 3.90 \times 10^4 \text{ Pa}$$

$$P_{total} = 8.35 \times 10^4 \text{ Pa}$$

$$\text{mol \% N}_2 = 100 \times \frac{\text{mol N}_2}{\text{mol N}_2 + \text{mol O}_2} = 100 \times \frac{1.00/28.02}{1.00/28.02 + 1.00/32.00} = 53.3\%$$

$$\text{mol \% O}_2 = 100 \times \frac{\text{mol O}_2}{\text{mol N}_2 + \text{mol O}_2} = 100 \times \frac{1.00/32.00}{1.00/28.02 + 1.00/32.00} = 46.7\%$$

c)

$$P_{NH_3} = \frac{n_{NH_3}RT}{V} = \frac{1.00/17.03 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{2.00 \times 10^{-3} \text{ m}^3} = 7.32 \times 10^4 \text{ Pa}$$

$$P_{CH_4} = \frac{n_{CH_4}RT}{V} = \frac{1.00/16.04 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{2.00 \times 10^{-3} \text{ m}^3} = 7.77 \times 10^4 \text{ Pa}$$

$$P_{total} = 1.51 \times 10^5 \text{ Pa}$$

$$\text{mol \% NH}_3 = 100 \times \frac{\text{mol NH}_3}{\text{mol NH}_3 + \text{mol CH}_4} = 100 \times \frac{1.00/17.03}{1.00/17.03 + 1.00/16.04} = 48.5\%$$

$$\text{mol \% O}_2 = 100 \times \frac{\text{mol CH}_4}{\text{mol NH}_3 + \text{mol CH}_4} = 100 \times \frac{1.00/16.04}{1.00/17.03 + 1.00/16.04} = 51.5\%$$

P1.3) Suppose that you measured the product PV of one mole of a dilute gas and found that $PV = 22.98 \text{ L atm}$ at 0°C and 31.18 L atm at 100°C . Assume that the ideal gas law is valid, with $T = t(\text{ }^\circ\text{C}) + a$, and that the value of R is not known. Determine R and a from the measurements provided.

Expressing the ideal gas law in the form $PV = R(t + a) = m(t + a)$,

$$m = \frac{\Delta PV}{\Delta t} = \frac{(31.18 - 22.98) \text{ l atm mol}^{-1}}{(100 - 0)^\circ \text{C}} = 0.08200 \text{ atm mol}^{-1} \text{ } ^\circ\text{C}^{-1} = R$$

$$a = \frac{PV}{R} - t = \frac{31.18 \text{ l atm mol}^{-1}}{0.08200 \text{ atm mol}^{-1} \text{ } ^\circ\text{C}^{-1}} - 100^\circ \text{C} = 280.2^\circ \text{C}$$

P1.4) A compressed cylinder of gas contains 1.50×10^3 g of N₂ gas at a pressure of 2.00×10^7 Pa and a temperature of 17.1°C . What volume of gas has been released into the atmosphere if the final pressure in the cylinder is 1.80×10^5 Pa? Assume ideal behavior and that the gas temperature is unchanged.

Let n_i and n_f be the initial and final number of mols of N₂ in the cylinder.

$$\frac{n_i RT}{P_i} = \frac{n_f RT}{P_f}$$

$$n_f = n_i \frac{P_f}{P_i} = \frac{1.50 \times 10^3 \text{ g}}{28.01 \text{ g mol}^{-1}} \times \frac{1.80 \times 10^5 \text{ Pa}}{2.00 \times 10^7 \text{ Pa}} = 0.482 \text{ mol}$$

$$n_i = \frac{1.50 \times 10^3 \text{ g}}{28.01 \text{ g mol}^{-1}} = 53.55 \text{ mol}$$

The volume of gas released into the atmosphere is given by

$$V = \frac{(n_f - n_i) RT}{P} = \frac{(53.55 - 0.482) \text{ mol} \times 8.2057 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} \times 290.2 \text{ K}}{1 \text{ atm}} \\ = 1.26 \times 10^3 \text{ L}$$

P1.5) A balloon filled with 10.50 L of Ar at 18.0°C and 1 atm rises to a height in the atmosphere where the pressure is 248 Torr and the temperature is -30.5°C . What is the final volume of the balloon?

$$V_f = \frac{P_i}{P_f} \frac{T_f}{T_i} V_i = \frac{760 \text{ Torr} \times (273.15 - 30.5) \text{ K}}{248 \text{ Torr} \times (273.15 + 18.0) \text{ K}} \times 10.50 \text{ L} = 26.8 \text{ L}$$

P1.6) Consider a 20.0-L sample of moist air at 60°C and 1 atm in which the partial pressure of water vapor is 0.120 atm. Assume that dry air has the composition 78.0 mole percent N₂, 21.0 mole percent O₂, and 1.00 mole percent Ar.

a) What are the mole percentages of each of the gases in the sample?

b) The percent relative humidity is defined as % RH = $\frac{P_{H_2O}}{P_{H_2O}^*}$ where P_{H_2O} is the partial pressure of water in the sample and $P_{H_2O}^* = 0.197$ atm is the equilibrium vapor pressure of water at 60°C . The gas is compressed at 60°C until the relative humidity is 100%. What volume does the mixture now occupy?

c) What fraction of the water will be condensed if the total pressure of the mixture is isothermally increased to 200 atm?

a)

$$\text{mol \% N}_2 = 100 \times \frac{P_{N_2}}{P_{\text{total}}} = 100 \times \frac{0.78 \times 0.88 \text{ atm}}{1 \text{ atm}} = 68.6\%$$

$$\text{mol \% O}_2 = 100 \times \frac{P_{O_2}}{P_{\text{total}}} = 100 \times \frac{0.21 \times 0.88 \text{ atm}}{1 \text{ atm}} = 18.5\%$$

$$\text{mol \% Ar} = 100 \times \frac{P_{Ar}}{P_{\text{total}}} = 100 \times \frac{0.01 \times 0.88 \text{ atm}}{1 \text{ atm}} = 0.9\%$$

$$\text{mol \% H}_2\text{O} = 100 \times \frac{P_{H_2O}}{P_{\text{total}}} = 100 \times \frac{0.12 \text{ atm}}{1 \text{ atm}} = 12.0\%$$

b)

$$P_{H_2O}V = \frac{n_{H_2O}RT}{V}$$

$P'_{H_2O}V' = P_{H_2O}V$ where the primed quantities refer to 100% RH

$$V' = \frac{P_{H_2O}V}{P'_{H_2O}} = \frac{0.12 \text{ atm} \times 20.0 \text{ L}}{0.197 \text{ atm}} = 12.2 \text{ L}$$

c)

If all the water remained in the gas phase, the partial pressure of water at a total pressure of 200 atm would be

$$P_{H_2O} = P_{\text{total}} \times \text{mol fraction H}_2\text{O} = 200 \text{ atm} \times 0.12 = 24.0 \text{ atm}$$

However, the partial pressure of water cannot be greater than 0.197 atm, and the excess will condense. The fraction that condenses is given by

$$\text{fraction condensed} = \frac{24.0 \text{ atm} - 0.197 \text{ atm}}{24.0 \text{ atm}} = 0.992$$

P1.7) A mixture of 2.50×10^{-3} g of O₂, 3.51×10^{-3} mol of N₂, and 4.67×10^{20} molecules of CO are placed into a vessel of volume 3.50 L at 5.20°C.

- Calculate the total pressure in the vessel.
- Calculate the mole fractions and partial pressures of each gas.

a)

$$n_{O_2} = \frac{2.50 \times 10^{-3} \text{ g}}{32.0 \text{ g mol}^{-1}} = 7.81 \times 10^{-5} \text{ mol}; n_{CO} = \frac{4.67 \times 10^{20} \text{ molecules}}{6.022 \times 10^{23} \text{ molecules mol}^{-1}} = 7.75 \times 10^{-4} \text{ mol}$$

$$n_{\text{total}} = n_{O_2} + n_{N_2} + n_{CO} = 7.81 \times 10^{-5} \text{ mol} + 3.51 \times 10^{-3} \text{ mol} + 7.75 \times 10^{-4} \text{ mol} = 4.36 \times 10^{-3} \text{ mol}$$

$$P_{\text{total}} = \frac{nRT}{V} = \frac{4.36 \times 10^{-3} \text{ mol} \times 8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 278.3 \text{ K}}{3.50 \text{ L}} = 2.88 \times 10^{-2} \text{ bar}$$

b)

$$x_{O_2} = \frac{7.81 \times 10^{-5} \text{ mol}}{4.36 \times 10^{-3} \text{ mol}} = 0.0179; x_{N_2} = \frac{3.51 \times 10^{-3} \text{ mol}}{4.36 \times 10^{-3} \text{ mol}} = 0.803;$$

$$x_{CO} = \frac{7.75 \times 10^{-4} \text{ mol}}{4.36 \times 10^{-3} \text{ mol}} = 0.178$$

$$P_{O_2} = x_{O_2} P_{total} = 0.0179 \times 2.88 \times 10^{-2} \text{ bar} = 5.16 \times 10^{-4} \text{ bar}$$

$$P_{N_2} = x_{N_2} P_{total} = 0.803 \times 2.88 \times 10^{-2} \text{ bar} = 2.31 \times 10^{-2} \text{ bar}$$

$$P_{CO} = x_{CO} P_{total} = 0.177 \times 2.88 \times 10^{-2} \text{ bar} = 5.10 \times 10^{-3} \text{ bar}$$

P1.8) Liquid N₂ has a density of 875.4 kg m⁻³ at its normal boiling point. What volume does a balloon occupy at 18.5°C and a pressure of 1.00 atm if 2.00 × 10⁻³ L of liquid N₂ is injected into it?

$$n_{N_2} = \frac{\rho_{N_2} V_{liq}}{M_{N_2}}$$

$$V_{N_2} = \frac{n_{N_2} RT}{P} = \frac{\rho_{N_2} V_{liq} RT}{M_{N_2} P}$$

$$= \frac{875.4 \text{ g L}^{-1} \times 2.00 \times 10^{-3} \text{ L} \times 8.2057 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1} \times (273.15 + 18.5) \text{ K}}{28.01 \text{ g mol}^{-1} \times 1 \text{ atm}}$$

$$= 1.50 \text{ L}$$

P1.9) A rigid vessel of volume 0.500 m³ containing H₂ at 20.5°C and a pressure of 611 × 10³ Pa is connected to a second rigid vessel of volume 0.750 m³ containing Ar at 31.2°C at a pressure of 433 × 10³ Pa. A valve separating the two vessels is opened and both are cooled to a temperature of 14.5°C. What is the final pressure in the vessels?

$$n_{H_2} = \frac{PV}{RT} = \frac{611 \times 10^3 \text{ Pa} \times 0.500 \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (273.15 + 20.5) \text{ K}} = 125 \text{ mol}$$

$$n_{Ar} = \frac{PV}{RT} = \frac{433 \times 10^3 \text{ Pa} \times 0.750 \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (273.15 + 31.2) \text{ K}} = 128 \text{ mol}$$

$$P = \frac{nRT}{V} = \frac{(125 + 128) \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (273.15 + 14.5) \text{ K}}{(0.500 + 0.750) \text{ m}^3} = 4.84 \times 10^5 \text{ Pa}$$

P1.10) A sample of propane (C₃H₈) placed in a closed vessel together with an amount of O₂ that is 3.00 times the amount needed to completely oxidize the propane to CO₂ and H₂O at constant temperature. Calculate the mole fraction of each component in the resulting mixture after oxidation assuming that the H₂O is present as a gas.

The reaction is C₃H₈(g) + 5O₂(g) → 3CO₂(g) + 4H₂O(g). If *m* mol of propane are present initially, there must be 15*m* mol of O₂. After the reaction is complete, there are 3*m* mol of CO₂, 4*m* mol of H₂O, and 10*m* mol of O₂.

$$x_{CO_2} = \frac{3m}{17m} = 0.176; x_{H_2O} = \frac{4m}{17m} = 0.235; x_{O_2} = \frac{10m}{17m} = 0.588$$

P1.11) A glass bulb of volume 0.136 L contains 0.7031 g of gas at 759.0 Torr and 99.5°C. What is the molar mass of the gas?

$$n = \frac{m}{M} = \frac{PV}{RT}; M = m \frac{RT}{PV}$$

$$M = 0.7031 \text{ g} \times \frac{8.2057 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1} \times (273.15 + 99.5) \text{ K}}{\frac{759}{760} \text{ atm} \times 0.136 \text{ L}} = 158 \text{ amu}$$

P1.12) The total pressure of a mixture of oxygen and hydrogen is 1.00 atm. The mixture is ignited and the water is removed. The remaining gas is pure hydrogen and exerts a pressure of 0.400 atm when measured at the same values of T and V as the original mixture. What was the composition of the original mixture in mole percent?

2H ₂ (g)	+	O ₂ (g) → 2H ₂ O(l)
initial moles	$n_{H_2}^\circ$	$n_{O_2}^\circ$ 0
at equilibrium	$n_{H_2}^\circ - 2\alpha$	$n_{O_2}^\circ - \alpha$ 2α

If the O₂ is completely consumed, $n_{O_2}^\circ - \alpha = 0$ or $\alpha = n_{O_2}^\circ$. The number of moles of H₂ remaining is $n_{H_2}^\circ - 2\alpha = n_{H_2}^\circ - 2n_{O_2}^\circ$.

Let P_1 be the initial total pressure and P_2 be the total pressure after all the O₂ is consumed.

$$P_1 = (n_{H_2}^\circ + n_{O_2}^\circ) \frac{RT}{V} \text{ and } P_2 = (n_{H_2}^\circ - 2n_{O_2}^\circ) \frac{RT}{V}$$

Dividing the second equation by the first

$$\begin{aligned} \frac{P_2}{P_1} &= \frac{n_{H_2}^\circ}{n_{H_2}^\circ + n_{O_2}^\circ} - 2 \frac{n_{O_2}^\circ}{n_{H_2}^\circ + n_{O_2}^\circ} = x_{H_2} - 2x_{O_2} = 1 - x_{O_2} - 2x_{O_2} = 1 - 3x_{O_2} \\ x_{O_2} &= \frac{1}{3} \left(1 - \frac{P_2}{P_1} \right) = \frac{1}{3} \left(1 - \frac{0.400 \text{ atm}}{1.00 \text{ atm}_1} \right) = 0.20; \quad x_{H_2} = 0.80 \end{aligned}$$

P1.13) A gas sample is known to be a mixture of ethane and butane. A bulb of 200.0-cm³ capacity is filled with the gas to a pressure of 100.0×10^3 Pa at 20.0°C. If the weight of the gas in the bulb is 0.3846 g, what is the mole percent of butane in the mixture?

Chapter 1/Fundamental Concepts of Thermodynamics

n_1 = moles of ethane n_2 = moles of butane

$$n_1 + n_2 = \frac{PV}{RT} = \frac{100.0 \times 10^3 \text{ Pa} \times 0.200 \times 10^{-3} \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 293 \text{ K}} = 8.21 \times 10^{-3} \text{ mol}$$

The total mass is

$$n_1 M_1 + n_2 M_2 = 0.3846 \text{ g}$$

Dividing this equation by $n_1 + n_2$

$$\frac{n_1 M_1}{n_1 + n_2} + \frac{n_2 M_2}{n_1 + n_2} = \frac{0.3846 \text{ g}}{8.21 \times 10^{-3} \text{ mol}} = 46.87 \text{ g mol}^{-1}$$

$$x_1 M_1 + x_2 M_2 = (1 - x_2) M_1 + x_2 M_2 = 46.87 \text{ g mol}^{-1}$$

$$x_2 = \frac{46.87 \text{ g mol}^{-1} - M_1}{M_2 - M_1} = \frac{46.87 \text{ g mol}^{-1} - 30.069 \text{ g mol}^{-1}}{58.123 \text{ g mol}^{-1} - 30.069 \text{ g mol}^{-1}} = 0.599$$

mole % = 59.9%

P1.14) When Julius Caesar expired, his last exhalation had a volume of 500 cm^3 and contained 1.00 mole percent argon. Assume that $T = 300 \text{ K}$ and $P = 1.00 \text{ atm}$ at the location of his demise. Assume further that T and P currently have the same values throughout the Earth's atmosphere. If all of his exhaled CO_2 molecules are now uniformly distributed throughout the atmosphere (which for our calculation is taken to have a thickness of 1.00 km), how many inhalations of 500 cm^3 must we make to inhale one of the Ar molecules exhaled in Caesar's last breath? Assume the radius of the Earth to be $6.37 \times 10^6 \text{ m}$. [Hint: Calculate the number of Ar atoms in the atmosphere in the simplified geometry of a plane of area equal to that of the Earth's surface and a height equal to the thickness of the atmosphere. See Problem P1.15 for the dependence of the barometric pressure on the height above the Earth's surface.]

The total number of Ar atoms in the atmosphere is $N_{Ar} = \int_0^{\infty} \tilde{N}_{Ar}^{\circ} A dz$ where \tilde{N}_{Ar}° is the number of Ar atoms per m^3 at the surface of the earth. \tilde{N}_{Ar}° is given by

$$\tilde{N}_{Ar}^{\circ} = \frac{N_A P_{Ar}}{RT} = \frac{6.023 \times 10^{23} \times 0.0100 \times 1 \times 10^5 \text{ Pa}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}} = 2.41 \times 10^{23} \text{ m}^{-3}$$

The total number of Ar atoms in the atmosphere is

$$\begin{aligned} N_{Ar} &= \int_0^{\infty} \tilde{N}_{Ar}^{\circ} A dz = \tilde{N}_{Ar}^{\circ} \int_0^{\infty} e^{-\frac{M_{Ar}g z}{RT}} A dz = \tilde{N}_{Ar}^{\circ} A \frac{RT}{M_{Ar}g} \\ &= \frac{2.41 \times 10^{23} \text{ m}^{-3} \times 4\pi \times (6.37 \times 10^6 \text{ m})^2 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{39.9 \times 10^{-3} \text{ kg} \times 9.81 \text{ m s}^{-2}} \\ &= 7.85 \times 10^{41} \end{aligned}$$

The fraction of these atoms that came from Caesar's last breath, f , is given by

$$f = \frac{\tilde{N}_{Ar}^{\circ} V}{N_{Ar}} = \frac{2.41 \times 10^{23} \text{ m}^{-3} \times 0.500 \times 10^{-3} \text{ m}^3}{7.85 \times 10^{41}} = 1.53 \times 10^{-22}$$

The number of Ar atoms that we inhale with each breath is

$$N = N_A \frac{PV}{RT} = 6.023 \times 10^{23} \times \frac{10^{-2} \times 1 \times 10^5 \text{ Pa} \times 0.500 \times 10^{-3} \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}} = 1.21 \times 10^{20}$$

The number of these that came from Caesar's last breath is fN

$$fN = 1.53 \times 10^{-22} \times 1.21 \times 10^{20} = 1.85 \times 10^{-2}$$

The reciprocal of this result, or 54, is the number of breaths needed to inhale one Ar atom that Caesar exhaled in his last breath.

P1.15) The barometric pressure falls off with height above sea level in the Earth's atmosphere as $P_i = P_i^0 e^{-\frac{M_i g z}{RT}}$ where P_i is the partial pressure at the height z , P_i^0 is the partial pressure of component i at sea level, g is the acceleration of gravity, R is the gas constant, and T is the absolute temperature. Consider an atmosphere that has the composition $x_{N_2} = 0.600$ and $x_{CO_2} = 0.400$ and that $T = 300 \text{ K}$. Near sea level, the total pressure is 1.00 bar. Calculate the mole fractions of the two components at a height of 50.0 km. Why is the composition different from its value at sea level?

$$P_{N_2} = P_{N_2}^0 e^{-\frac{M_{N_2} g z}{RT}} = 0.600 \times 1.0125 \times 10^5 \text{ Pa} \exp\left(-\frac{28.04 \times 10^{-3} \text{ kg} \times 9.81 \text{ m s}^{-2} \times 50 \times 10^3 \text{ m}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}\right)$$

$$= 242 \text{ Pa}$$

$$P_{CO_2} = P_{CO_2}^0 e^{-\frac{M_{CO_2} g z}{RT}} = 0.400 \times 1.0125 \times 10^5 \text{ Pa} \exp\left(-\frac{44.04 \times 10^{-3} \text{ kg} \times 9.81 \text{ m s}^{-2} \times 50 \times 10^3 \text{ m}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}\right)$$

$$= 6.93 \text{ Pa}$$

$$x_{CO_2} = \frac{P_{CO_2}}{P_{CO_2} + P_{N_2}} = \frac{6.93}{6.93 + 242} = 0.028 \quad x_{N_2} = 1 - x_{CO_2} = 0.972$$

The mole fraction of CO₂ at the high altitude is much reduced relative to its value at sea level because it has a larger molecular mass than N₂.

P1.16) Assume that air has a mean molar mass of 28.9 g mol⁻¹ and that the atmosphere has a uniform temperature of 25.0°C. Calculate the barometric pressure at Denver, for which $z = 1600 \text{ m}$. Use the information contained in Problem P1.15.

$$P = P^0 e^{-\frac{M g z}{RT}} = 10^5 \text{ Pa} \exp\left(-\frac{28.9 \times 10^{-3} \text{ kg} \times 9.81 \text{ m s}^{-2} \times 1600 \text{ m}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}\right) = 8.34 \times 10^4 \text{ Pa}$$

P1.17) Calculate the pressure exerted by Ar for a molar volume 1.42 L at 300 K using the van der Waals equation of state. The van der Waals parameters a and b for Ar are

1.355 bar dm⁶ mol⁻² and 0.0320 dm³ mol⁻¹, respectively. Is the attractive or repulsive portion of the potential dominant under these conditions?

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$= \frac{8.314 \times 10^{-2} \text{ bar dm}^3 \text{ mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{1.42 \text{ dm}^3 \text{ mol}^{-1} - 0.0321 \text{ dm}^3 \text{ mol}^{-1}} - \frac{1.355 \text{ bar dm}^6 \text{ mol}^{-2}}{(1.42 \text{ dm}^3 \text{ mol}^{-1})^2} = 17.3 \text{ bar}$$

$$P_{ideal} = \frac{RT}{V} = \frac{8.3145 \times 10^{-2} \times \text{L bar mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{1.42 \text{ L}} = 17.6 \text{ bar}$$

Because $P < P_{ideal}$, the attractive part of the potential dominates.

P1.18) Calculate the pressure exerted by benzene for a molar volume 1.42 L at 790 K using the Redlich-Kwong equation of state:

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}} \frac{1}{V_m(V_m + b)} = \frac{nRT}{V - nb} - \frac{n^2 a}{\sqrt{T}} \frac{1}{V(V + nb)}$$

The Redlich-Kwong parameters a and b for benzene are 452.0 bar dm⁶ mol⁻² K^{1/2} and 0.08271 dm³ mol⁻¹, respectively. Is the attractive or repulsive portion of the potential dominant under these conditions?

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}} \frac{1}{V_m(V_m + b)}$$

$$= \frac{8.314 \times 10^{-2} \text{ bar dm}^3 \text{ mol}^{-1} \text{ K}^{-1} \times 790 \text{ K}}{1.42 \text{ dm}^3 \text{ mol}^{-1} - 0.08271 \text{ dm}^3 \text{ mol}^{-1}}$$

$$- \frac{452.0 \text{ bar dm}^6 \text{ mol}^{-2} \text{ K}^{\frac{1}{2}}}{\sqrt{790 \text{ K}}} \times \frac{1}{1.42 \text{ dm}^3 \text{ mol}^{-1} \times (1.42 \text{ dm}^3 \text{ mol}^{-1} + 0.08271 \text{ dm}^3 \text{ mol}^{-1})}$$

$$P = 41.6 \text{ bar}$$

$$P_{ideal} = \frac{RT}{V} = \frac{8.3145 \times 10^{-2} \times \text{L bar mol}^{-1} \text{ K}^{-1} \times 790 \text{ K}}{1.42 \text{ L}} = 46.3 \text{ bar}$$

Because $P < P_{ideal}$, the attractive part of the potential dominates.

P1.19) Devise a temperature scale, abbreviated G, for which the magnitude of the ideal gas constant is 1.00 J G⁻¹ mol⁻¹.

Let T and T' represent the Kelvin and G scales, and R and R' represent the gas constant in each of these scales. Then

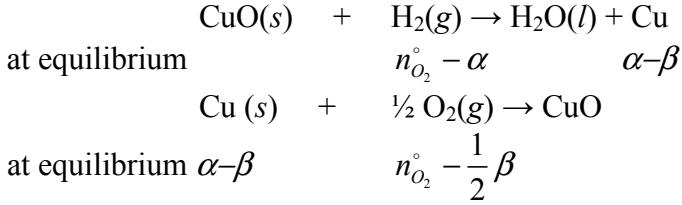
$$PV = nRT = nR'T'$$

$$T' = \frac{R}{R'} T = 8.314 T$$

The temperature on the G scale is the value in K multiplied by 8.314.

P1.20) A mixture of oxygen and hydrogen is analyzed by passing it over hot copper oxide and through a drying tube. Hydrogen reduces the CuO according to the reaction $\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$ and oxygen reoxidizes the copper formed according to $\text{Cu} + 1/2 \text{O}_2 \rightarrow \text{CuO}$. At 25°C and 750 Torr, 100.0 cm³ of the mixture yields 84.5 cm³ of dry oxygen measured at 25°C and 750 Torr after passage over CuO and the drying agent. What is the original composition of the mixture?

Two equilibria must be considered:



In the final state, only O₂ is present. Therefore $\alpha = n_{\text{O}_2}^\circ$. In an excess of O₂, all the copper is oxidized. Therefore $\alpha - \beta = 0$ or $\beta = n_{\text{O}_2}^\circ$. We conclude that $n_{\text{O}_2} = n_{\text{O}_2}^\circ - \frac{1}{2}n_{\text{H}_2}^\circ$.

Let V_1 and V_2 be the initial and final volumes.

$$V_1 = (n_{\text{H}_2}^\circ + n_{\text{O}_2}^\circ) \frac{RT}{P} \quad V_2 = \left(n_{\text{O}_2}^\circ - \frac{1}{2}n_{\text{H}_2}^\circ \right) \frac{RT}{P}$$

Dividing the second equation by the first yields

$$\begin{aligned} \frac{V_2}{V_1} &= \frac{n_{\text{O}_2}^\circ}{n_{\text{H}_2}^\circ + n_{\text{O}_2}^\circ} - \frac{1}{2} \frac{n_{\text{H}_2}^\circ}{n_{\text{H}_2}^\circ + n_{\text{O}_2}^\circ} = x_{\text{O}_2}^\circ - \frac{1}{2}x_{\text{H}_2}^\circ = 1 - x_{\text{H}_2}^\circ - \frac{1}{2}x_{\text{H}_2}^\circ = 1 - \frac{3}{2}x_{\text{H}_2}^\circ \\ x_{\text{H}_2}^\circ &= \frac{2}{3} \left(1 - \frac{V_2}{V_1} \right) = \frac{2}{3} \left(1 - \frac{84.5 \text{ cm}^3}{100.0 \text{ cm}^3} \right) = 0.103; \quad x_{\text{O}_2}^\circ = 1 - x_{\text{H}_2}^\circ = 0.897 \end{aligned}$$

Questions on Concepts

Q2.1) Electrical current is passed through a resistor immersed in a liquid in an adiabatic container. The temperature of the liquid is raised by 1°C. The system consists solely of the liquid. Does heat or work flow across the boundary between the system and surroundings? Justify your answer.

Although work is done on the resistor, this work is done in the surroundings. Heat flows across the boundary between the surroundings and the system because of the temperature difference between them.

Q2.2) Explain how a mass of water in the surroundings can be used to determine q for a process. Calculate q if the temperature of 1.00 kg of water in the surroundings increases by 1.25°C. Assume that the surroundings are at a constant pressure.

If heat flows across the boundary between the system and the surroundings, it will lead to a temperature change in the surroundings given by $\Delta T = \frac{q}{C_p}$. For the case of interest,

$$q = -q_{surroundings} = -mC_p\Delta T = -1000 \text{ g} \times 4.19 \text{ J g}^{-1}\text{K}^{-1} \times 1.25 \text{ K} = -5.24 \times 10^3 \text{ J}.$$

Q2.3) Explain the relationship between the terms *exact differential* and *state function*.

In order for a function $f(x,y)$ to be a state function, it must be possible to write the total differential df in the form $df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$. If the form df as written exists, it is an exact differential.

Q2.4) Why is it incorrect to speak of the heat or work associated with a system?

Heat and work are transients that exist only in the transition between equilibrium states. Therefore, a state at equilibrium is not associated with values of heat or work.

Q2.5) Two ideal gas systems undergo reversible expansion starting from the same P and V . At the end of the expansion, the two systems have the same volume. The pressure in the system that has undergone adiabatic expansion is lower than in the system that has undergone isothermal expansion. Explain this result without using equations.

In the system undergoing adiabatic expansion, all the work done must come through the lowering of ΔU , and therefore of the temperature. By contrast, some of the work done in the isothermal expansion can come at the expense of the heat that has flowed across the boundary between the system and surroundings.

Q2.6) A cup of water at 278 K (the system) is placed in a microwave oven and the oven is turned on for one minute, during which it begins to boil. Which of q , w , and ΔU are positive, negative or zero?

The heat q is positive because heat flows across the system-surrounding boundary into the system. The work w is negative because the vaporizing water does work on the surroundings. ΔU is positive because the temperature increases and some of the liquid is vaporized.

Q2.7) What is wrong with the following statement?: *Because the well insulated house stored a lot of heat, the temperature didn't fall much when the furnace failed.* Rewrite the sentence to convey the same information in a correct way.

Heat can't be stored because it exists only as a transient. A possible rephrasing follows. Because the house was well insulated, the walls were nearly adiabatic. Therefore, the temperature of the house did not fall as rapidly when in contact with the surroundings at a lower temperature as would have been the case if the walls were diathermal.

Q2.8) What is wrong with the following statement?: *Burns caused by steam at 100°C can be more severe than those caused by water at 100°C because steam contains more heat than water.* Rewrite the sentence to convey the same information in a correct way.

Heat is not a substance that can be stored. When steam is in contact with your skin, it condenses to the liquid phase. In doing so, energy is released that is absorbed by the skin. Hot water does not release as much energy in the same situation, because no phase change occurs.

Q2.9) Describe how reversible and irreversible expansions differ by discussing the degree to which equilibrium is maintained between the system and the surroundings.

In a reversible expansion, the system and surroundings are always in equilibrium with one another. In an irreversible expansion, they are not in equilibrium with one another.

Q2.10) A chemical reaction occurs in a constant volume enclosure separated from the surroundings by diathermal walls. Can you say whether the temperature of the surroundings increase, decrease, or remain the same in this process? Explain.

No. The temperature will increase if the reaction is exothermic, decrease if the reaction is endothermic, and not change if no energy is evolved in the reaction.

Problems

P2.1) 3.00 moles of an ideal gas at 27.0°C expands isothermally from an initial volume of 20.0 dm³ to a final volume of 60.0 dm³. Calculate *w* for this process a) for expansion against a constant external pressure of 1.00 × 10⁵ Pa, and b) for a reversible expansion.

a) $w = -P_{\text{external}} \Delta V = -1.00 \times 10^5 \text{ Pa} \times (60.0 - 20.0) \times 10^{-3} \text{ m}^3 = -4.00 \times 10^3 \text{ J}$

b)

$$w_{\text{reversible}} = -nRT \ln \frac{V_f}{V_i} = -3.00 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K} \times \ln \frac{60.0 \text{ dm}^3}{20.0 \text{ dm}^3} = -8.22 \times 10^3 \text{ J}$$

P2.2) 3.00 moles of a gas are compressed isothermally from 60.0 L to 20.0 L using a constant external pressure of 5.00 atm. Calculate *q*, *w*, ΔU , and ΔH .

$$\begin{aligned} w &= -P_{\text{external}} \Delta V \\ &= -5 \times 1.013 \times 10^5 \text{ Pa} \times (60 \times 10^{-3} \text{ L} - 20 \times 10^{-3} \text{ L}) = -2.03 \times 10^4 \text{ J} \end{aligned}$$

$\Delta U = 0$ and $\Delta H = 0$ because $\Delta T = 0$

$$q = -w = 2.03 \times 10^4 \text{ J}$$

P2.3) A system consisting of 57.5 g of liquid water at 298 K is heated using an immersion heater at a constant pressure of 1.00 bar. If a current of 1.50 A passes through the 10.0 Ohm resistor for 150 s, what is the final temperature of the water? The heat capacity for water can be found in the Data Tables in Appendix A.

$$\begin{aligned} q &= I^2 R t = nC_{P,m} (T_f - T_i); T_f = \frac{I^2 R t + nC_{P,m} T_i}{nC_{P,m}} \\ T_f &= \frac{(1.50 \text{ A})^2 \times 10.0 \text{ Ohm} \times 150 \text{ s} + \frac{57.5 \text{ g}}{18.02 \text{ g mol}^{-1}} \times 75.291 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{\frac{57.5 \text{ g}}{18.02 \text{ g mol}^{-1}} \times 75.291 \text{ J mol}^{-1} \text{ K}^{-1}} = 312 \text{ K} \end{aligned}$$

P2.4) For one mole of an ideal gas, $P_{\text{external}} = P = 200 \times 10^3 \text{ Pa}$. The temperature is changed from 100°C to 25.0°C at constant pressure. $C_{V,m} = 3/2 R$. Calculate *q*, *w*, ΔU , and ΔH .

$$\Delta U = nC_{V,m} \Delta T = \frac{3}{2} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (298 \text{ K} - 373 \text{ K}) = -935 \text{ J}$$

$$\begin{aligned} \Delta H &= nC_{P,m} \Delta T = n(C_{V,m} + R) \Delta T \\ &= \frac{5}{2} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (298 \text{ K} - 373 \text{ K}) \\ &= -1.56 \times 10^3 \text{ J} \\ &= q_P \end{aligned}$$

$$w = \Delta U - q_p = -935 \text{ J} + 1.56 \times 10^3 \text{ J} = 624 \text{ J}$$

P2.5) Consider the isothermal expansion of 5.25 moles of an ideal gas at 450 K from an initial pressure of 15.0 bar to a final pressure of 3.50 bar. Describe the process that will result in the greatest amount of work being done by the system with

$P_{\text{external}} \geq 3.50 \text{ bar}$ and calculate w . Describe the process that will result in the least amount of work being done by the system $P_{\text{external}} \geq 3.50 \text{ bar}$ and calculate w . What is the least amount of work done without restrictions on the external pressure?

The greatest amount of work is done in a reversible expansion. The work is given by

$$\begin{aligned} w_{\text{reversible}} &= -nRT \ln \frac{V_f}{V_i} = -nRT \ln \frac{P_i}{P_f} = -5.25 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 450 \text{ K} \times \ln \frac{15.0 \text{ bar}}{3.50 \text{ bar}} \\ &= -28.6 \times 10^3 \text{ J} \end{aligned}$$

The least amount of work is done in a single stage expansion at constant pressure with the external pressure equal to the final pressure. The work is given by

$$\begin{aligned} w &= -P_{\text{external}} (V_f - V_i) = -nRTP_{\text{external}} \left(\frac{1}{P_f} - \frac{1}{P_i} \right) \\ &= -5.25 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 450 \text{ K} \times 3.50 \text{ bar} \times \left(\frac{1}{3.50 \text{ bar}} - \frac{1}{15.0 \text{ bar}} \right) = -15.1 \times 10^3 \text{ J} \end{aligned}$$

The least amount of work done without restrictions on the pressure is zero, which occurs when $P_{\text{external}} = 0$.

P2.6) Calculate ΔH and ΔU for the transformation of one mole of an ideal gas from 27.0°C and 1.00 atm to 327°C and 17.0 atm if

$$C_{P,m} = 20.9 + 0.042 \frac{T}{K} \text{ in units of J K}^{-1}\text{mol}^{-1}.$$

$$\begin{aligned} \Delta H &= n \int_{T_i}^{T_f} C_{P,m} dT \\ &= \int_{300K}^{600K} \left(20.9 + 0.42 \frac{T'}{K} \right) dT' \\ &= 20.9 \times (600 \text{ K} - 300 \text{ K}) \text{ J} + \left[0.21T^2 \right]_{300K}^{600K} \text{ J} \\ &= 6.27 \times 10^3 \text{ J} + 56.7 \times 10^3 \text{ J} \\ &= 63.0 \times 10^3 \text{ J} \end{aligned}$$

$$\begin{aligned}\Delta U &= \Delta H - \Delta(PV) = \Delta H - nR\Delta T \\ &= 63.0 \times 10^3 \text{ J} - 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \\ &= 60.5 \times 10^3 \text{ J}\end{aligned}$$

P2.7) Calculate w for the adiabatic expansion of one mole of an ideal gas at an initial pressure of 2.00 bar from an initial temperature of 450 K to a final temperature of 300 K. Write an expression for the work done in the isothermal reversible expansion of the gas at 300 K from an initial pressure of 2.00 bar. What value of the final pressure would give the same value of w as the first part of this problem? Assume that $C_{P,m} = 5/2 R$.

$$w_{ad} = \Delta U = n(C_{P,m} - R)\Delta T = -\frac{3}{2} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 150 \text{ K} = -1.87 \times 10^3 \text{ J}$$

$$\begin{aligned}w_{reversible} &= -nRT \ln \frac{P_i}{P_f}; \ln \frac{P_i}{P_f} = \frac{-w_{reversible}}{nRT} \\ \ln \frac{P_i}{P_f} &= \frac{nRT}{w_{reversible}} = \frac{1.87 \times 10^3 \text{ J}}{1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}} = 0.7497 \\ P_f &= 0.472P_i = 0.944 \text{ bar}\end{aligned}$$

P2.8) In the adiabatic expansion of one mole of an ideal gas from an initial temperature of 25°C, the work done on the surroundings is 1200 J. If $C_{V,m} = 3/2R$, calculate q , w , ΔU , and ΔH .

$q = 0$ because the process is adiabatic

$$\Delta U = w = -1200 \text{ J}$$

$$\begin{aligned}\Delta U &= nC_{V,m}(T_f - T_i) \\ T_f &= \frac{\Delta U + nC_{V,m}T_i}{nC_{V,m}} \\ &= \frac{-1200 \text{ J} + 7.5 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{1.5 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \\ &= 202 \text{ K} \\ \Delta H &= nC_{P,m}(T_f - T_i) = n(C_{V,m} + R)(T_f - T_i) \\ &= 2.5 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} (202 \text{ K} - 298 \text{ K}) \\ &= -2.00 \times 10^3 \text{ J}\end{aligned}$$

P2.9) An ideal gas undergoes an expansion from the initial state described by P_i , V_i , T to a final state described by P_f , V_f , T in a) a process at the constant external pressure P_f , and b) in a reversible process. Derive expressions for the largest mass that can be lifted through a height h in the surroundings in these processes.

$$a) \quad w = mgh = -P_f(V_f - V_i); \quad m = \left| -\frac{P_f(V_f - V_i)}{gh} \right|$$

$$b) \quad w = mgh = -nRT \ln \frac{V_f}{V_i}; \quad m = \left| -\frac{nRT}{gh} \ln \frac{V_f}{V_i} \right|$$

P2.10) An automobile tire contains air at $320 \times 10^3 \text{ Pa}$ at 20°C . The stem valve is removed and the air is allowed to expand adiabatically against the constant external pressure of $100 \times 10^3 \text{ Pa}$ until $P = P_{\text{external}}$. For air, $C_{V,m} = 5/2 R$. Calculate the final temperature of the gas in the tire. Assume ideal gas behavior.

because $q = 0$, $\Delta U = w$

$$nC_{V,m}(T_f - T_i) = -P_{\text{ext}}(V_f - V_i)$$

$$nC_{V,m}(T_f - T_i) = -P_{\text{ext}} \left(\frac{nRT_f}{P_f} - \frac{nRT_i}{P_i} \right)$$

The factor n cancels out. Rearranging the equation

$$\begin{aligned} \left(C_{V,m} + \frac{RP_{\text{ext}}}{P_f} \right) T_f &= \left(C_{V,m} + \frac{RP_{\text{ext}}}{P_i} \right) T_i \\ \frac{T_f}{T_i} &= \frac{C_{V,m} + \frac{RP_{\text{ext}}}{P_i}}{C_{V,m} + \frac{RP_{\text{ext}}}{P_f}} \\ &= \frac{2.5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} + \frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 10^5 \text{ Pa}}{3.20 \times 10^5 \text{ Pa}}}{2.5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} + \frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 10^5 \text{ Pa}}{10^5 \text{ Pa}}} \end{aligned}$$

$$T_f = 0.804 T_i \quad T_f = 235 \text{ K}$$

P2.11) 3.50 moles of an ideal gas is expanded from 450 K and an initial pressure of 5.00 bar to a final pressure of 1.00 bar. $C_{P,m} = 5/2R$. Calculate w for the following two cases.

- a) The expansion is isothermal and reversible.
- b) The expansion is adiabatic and reversible.

Without resorting to equations, explain why the result to part b) is greater than (or less than) the result to part a).

a)

$$w = -nRT \ln \frac{V_f}{V_i} = -nRT \ln \frac{P_i}{P_f}$$

$$= -3.50 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 450 \text{ K} \times \ln \frac{5.00 \text{ bar}}{1.00 \text{ bar}} = -21.1 \times 10^3 \text{ J}$$

b) Because $q = 0$, $w = \Delta U$. In order to calculate ΔU , we first calculate T_f .

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i} \right)^{1-\gamma} = \left(\frac{T_f}{T_i} \right)^{1-\gamma} \left(\frac{P_i}{P_f} \right)^{1-\gamma}; \left(\frac{T_f}{T_i} \right)^\gamma = \left(\frac{P_i}{P_f} \right)^{1-\gamma}; \frac{T_f}{T_i} = \left(\frac{P_i}{P_f} \right)^{\frac{1-\gamma}{\gamma}}$$

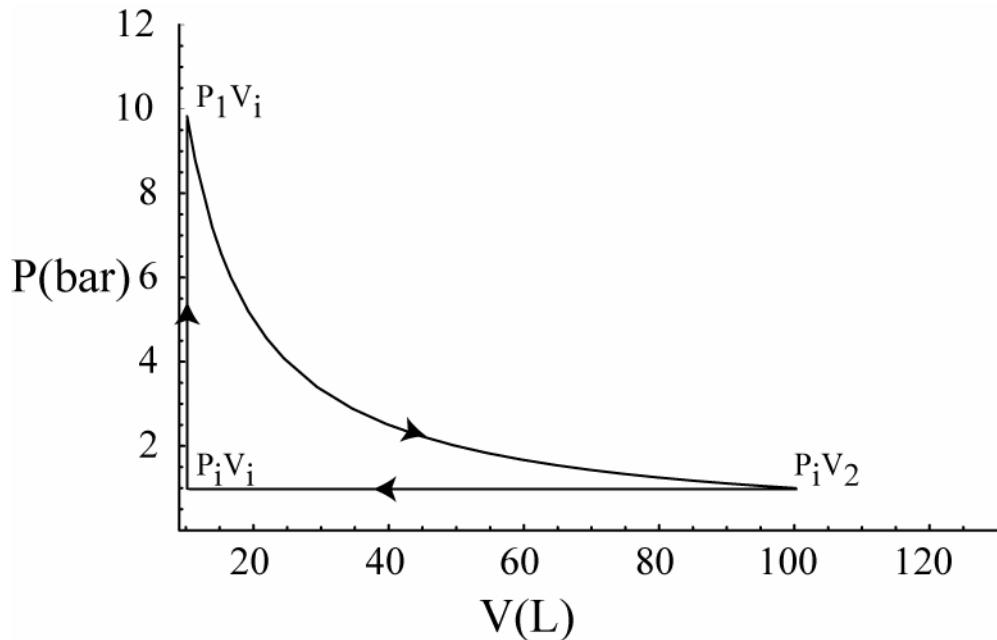
$$\frac{T_f}{T_i} = \left(\frac{5.00 \text{ bar}}{1.00 \text{ bar}} \right)^{\frac{5}{3}} = 0.525$$

$$T_f = 0.525 \times 450 \text{ K} = 236 \text{ K}$$

$$w = \Delta U = nC_{V,m}\Delta T = 3.50 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{2} \times (236 \text{ K} - 450 \text{ K}) = -9.34 \times 10^3 \text{ J}$$

Less work is done on the surroundings in part b) because in the adiabatic expansion, the temperature falls and therefore the final volume is less than that in part a).

P2.12) An ideal gas described by $T_i = 300 \text{ K}$, $P_i = 1.00 \text{ bar}$ and $V_i = 10.0 \text{ L}$ is heated at constant volume until $P = 10.0 \text{ bar}$. It then undergoes a reversible isothermal expansion until $P = 1.00 \text{ bar}$. It is then restored to its original state by the extraction of heat at constant pressure. Depict this closed cycle process in a P - V diagram. Calculate w for each step and for the total process. What values for w would you calculate if the cycle were traversed in the opposite direction?



$$n = \frac{PV_i}{RT_i} = \frac{1.00 \text{ bar} \times 10.0 \text{ L}}{8.3145 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}} = 0.401 \text{ mol}$$

The process can be described by

step 1: $P_i, V_i, T_i \rightarrow P_1 = 10.0 \text{ bar}, V_i, T_1$

step 2: $P_1, V_i, T_1 \rightarrow P_i, V_2, T_1$

step 3: $P_i, V_2, T_1 \rightarrow P_i, V_i, T_i$.

In step 1, $P_i, V_i, T_i \rightarrow P_1, V_i, T_1$, $w = 0$ because V is constant.

In step 2, $P_1, V_i, T_1 \rightarrow P_i, V_2, T_1$

Before calculating the work in step 2, we first calculate T_1 .

$$T_1 = T_i \frac{P_1}{P_i} = 300 \text{ K} \times \frac{10.0 \text{ bar}}{1.00 \text{ bar}} = 3000 \text{ K}$$

$$w = -nRT_1 \ln \frac{V_f}{V_i} = -nRT_1 \ln \frac{P_i}{P_f}$$

$$= -0.401 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 3000 \text{ K} \times \ln \frac{10.0 \text{ bar}}{1.00 \text{ bar}} = -23.0 \times 10^3 \text{ J}$$

In step 3,

$$P_1 V_i = P_i V_2; \quad V_2 = \frac{P_1 V_i}{P_i} = 10 V_i = 100 \text{ L}$$

$$w = -P_{\text{external}} \Delta V = -1.00 \text{ bar} \times \frac{10^5 \text{ Pa}}{\text{bar}} \times (10 \text{ L} - 100 \text{ L}) \times \frac{10^{-3} \text{ m}^3}{\text{L}} = 9.00 \times 10^3 \text{ J}$$

$$w_{\text{cycle}} = 0 - 23.0 \times 10^3 \text{ J} + 9.00 \times 10^3 \text{ J} = -14.0 \times 10^3 \text{ J}$$

If the cycle were traversed in the opposite direction, the magnitude of each work term would be unchanged, but all signs would change.

P2.13) 3.00 moles of an ideal gas with $C_{V,m} = 3/2 R$, initially at a temperature $T_i = 298 \text{ K}$ and $P_i = 1.00 \text{ bar}$, is enclosed in an adiabatic piston and cylinder assembly. The gas is compressed by placing a 625 kg mass on the piston of diameter 20.0 cm. Calculate the work done in this process and the distance that the piston travels. Assume that the mass of the piston is negligible.

$$P_{\text{external}} = \frac{F}{A} = \frac{mg}{\pi r^2} = \frac{625 \text{ kg} \times 9.81 \text{ m s}^{-2}}{\pi \times (0.100 \text{ m})^2} = 1.95 \times 10^5 \text{ Pa}$$

$$V_i = \frac{nRT}{P_i} = \frac{3.00 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{10^5 \text{ Pa}} = 7.43 \times 10^{-2} \text{ m}^3 = 74.3 \text{ L}$$

Following Example Problem 2.6,

$$T_f = T_i \left(\frac{C_{V,m} + \frac{RP_{external}}{P_i}}{C_{V,m} + \frac{RP_{external}}{P_f}} \right) = 298 \text{ K} \times \left(\frac{12.47 \text{ J mol}^{-1}\text{K}^{-1} + \frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 1.95 \times 10^5 \text{ Pa}}{1.00 \times 10^5 \text{ Pa}}}{12.47 \text{ J mol}^{-1}\text{K}^{-1} + \frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 1.95 \times 10^5 \text{ Pa}}{1.95 \times 10^5 \text{ Pa}}} \right)$$

$$= 411 \text{ K}$$

$$V_f = \frac{nRT}{P_f} = \frac{3.00 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 411 \text{ K}}{1.95 \times 10^5 \text{ Pa}} = 5.25 \times 10^{-2} \text{ m}^3$$

$$w = -P_{external} (V_f - V_i) = -1.95 \times 10^5 \text{ Pa} \times (5.25 \times 10^{-2} \text{ m}^3 - 7.43 \times 10^{-2} \text{ m}^3) = 4.25 \times 10^3 \text{ J}$$

$$h = \frac{w}{mg} = \frac{4.25 \times 10^3 \text{ J}}{625 \text{ kg} \times 9.81 \text{ m s}^{-2}} = 0.69 \text{ m}$$

P2.14) A bottle at 21.0°C contains an ideal gas at a pressure of $126.4 \times 10^3 \text{ Pa}$. The rubber stopper closing the bottle is removed. The gas expands adiabatically against $P_{external} = 101.9 \times 10^3 \text{ Pa}$, and some gas is expelled from the bottle in the process. When $P = P_{external}$, the stopper is quickly replaced. The gas remaining in the bottle slowly warms up to 21.0°C. What is the final pressure in the bottle for a monatomic gas, for which $C_{V,m} = 3/2 R$ and a diatomic gas, for which $C_{V,m} = 5/2 R$?

In this adiabatic expansion, $\Delta U = w$

$$nC_{V,m} (T_f - T_i) = -P_{ext} (V_f - V_i)$$

$$nC_{V,m} (T_f - T_i) = -P_{ext} \left(\frac{nRT}{V_f} - \frac{nRT}{V_i} \right)$$

$$\left(C_{V,m} + \frac{RP_{ext}}{P_f} \right) T_f = \left(C_{V,m} + \frac{RP_{ext}}{P_i} \right) T_i$$

$$\frac{T_f}{T_i} = \frac{C_{V,m} + \frac{RP_{ext}}{P_i}}{C_{V,m} + \frac{RP_{ext}}{P_f}}$$

$$= \frac{1.5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} + \frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 101.9 \times 10^3 \text{ Pa}}{126.4 \times 10^3 \text{ Pa}}}{1.5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} + \frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 101.9 \times 10^3 \text{ Pa}}{101.9 \times 10^3 \text{ Pa}}}$$

$$\frac{T_f}{T_i} = 0.923, \quad T_f = 271 \text{ K}$$

Once the stopper is put in place, the gas makes a transformation from

$T_i = 214 \text{ K}$, $P_i = 101.9 \times 10^3 \text{ Pa}$ to $T_f = 294 \text{ K}$ and P_f

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}, \text{ but } V_i = V_f$$

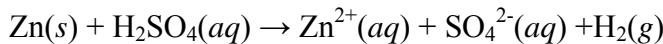
$$P_f = \frac{T_f}{T_i} P_i = \frac{294 \text{ K}}{271 \text{ K}} \times 101.9 \times 10^3 \text{ Pa} = 110.5 \times 10^3 \text{ Pa}$$

The same calculation carried out for $C_{V,m} = \frac{5}{2}R$ gives

$$\frac{T_f}{T_i} = 0.945, \quad T_f = 278 \text{ K}$$

$$P_f = 107.8 \times 10^3 \text{ Pa}$$

P2.15) A pellet of Zn of mass 10.0 g is dropped into a flask containing dilute H_2SO_4 at a pressure $P = 1.00 \text{ bar}$ and temperature $T = 298 \text{ K}$. What is the reaction that occurs? Calculate w for the process.



The volume of H_2 produced is given by

$$V = \frac{10.0 \text{ g}}{65.39 \text{ g}(\text{mol Zn})^{-1}} \times \frac{1 \text{ mol H}_2}{1 \text{ mol Zn}} \times \frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K}}{1 \times 10^5 \text{ Pa}} = 3.79 \times 10^{-3} \text{ m}^3$$

$$w = -P_{\text{external}} \Delta V$$

$\Delta V \approx$ volume of H_2 produced.

$$w = -1 \times 10^5 \text{ Pa} \times 3.79 \times 10^{-3} \text{ m}^3 = -379 \text{ J}$$

P2.16) One mole of an ideal gas for which $C_{V,m} = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$ is heated from an initial temperature of 0°C to a final temperature of 275°C at constant volume. Calculate q , w , ΔU and ΔH for this process.

$w = 0$ because $\Delta V = 0$.

$$\Delta U = q = C_V \Delta T = 20.8 \text{ J mol}^{-1}\text{K}^{-1} \times 275 \text{ K} = 5.72 \times 10^3 \text{ J}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + R\Delta T = 5.72 \times 10^3 \text{ J} + 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 275 \text{ K} = 8.01 \times 10^3 \text{ J}$$

P2.17) One mole of an ideal gas, for which $C_{V,m} = 3/2 R$, initially at 20.0°C and $1.00 \times 10^6 \text{ Pa}$ undergoes a two stage transformation. For each of the stages described below, calculate the final pressure, as well as q , w , ΔU and ΔH . Also calculate q , w , ΔU and ΔH for the complete process.

a) The gas is expanded isothermally and reversibly until the volume doubles.

b) Beginning at the end of the first stage, the temperature is raised to 80.0°C at constant volume.

$$\text{a)} P_2 = \frac{P_1 V_1}{V_2} = \frac{P_1}{2} = 0.500 \times 10^6 \text{ Pa}$$

$$w = -nRT \ln \frac{V_2}{V_1} = -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln 2 = -1.69 \times 10^3 \text{ J}$$

$$\Delta U = 0 \text{ and } \Delta H = 0 \text{ because } \Delta T = 0$$

$$q = -w = 1.69 \times 10^3 \text{ J}$$

$$\text{b)} \frac{T_1}{P_1} = \frac{T_2}{P_2}; P_2 = \frac{T_2 P_1}{T_1} = \frac{353 \text{ K} \times 0.500 \times 10^6 \text{ Pa}}{293 \text{ K}} = 6.02 \times 10^5 \text{ Pa}$$

$$\Delta U = nC_{V,m}\Delta T = 1.5 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (353 \text{ K} - 293 \text{ K}) = 748 \text{ J}$$

$$w = 0 \text{ because } \Delta V = 0$$

$$q = \Delta U = 748 \text{ J}$$

$$\begin{aligned} \Delta H &= nC_{P,m}\Delta T = n(C_{V,m} + R)\Delta T = \frac{3}{2} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (353 \text{ K} - 293 \text{ K}) \\ &= 1.25 \times 10^3 \text{ J} \end{aligned}$$

For the overall process,

$$q = 1.69 \times 10^3 \text{ J} + 748 \text{ J} = 2.44 \times 10^3 \text{ J}$$

$$w = -1.69 \times 10^3 \text{ J} + 0 = -1.69 \times 10^3 \text{ J}$$

$$\Delta U = 0 + 748 \text{ J} = 748 \text{ J}$$

$$\Delta H = 0 + 1.25 \times 10^3 \text{ J} = 1.25 \times 10^3 \text{ J}$$

P2.18) One mole of an ideal gas with $C_{V,m} = 3/2R$ initially at 298 K and $1.00 \times 10^5 \text{ Pa}$ undergoes a reversible adiabatic compression. At the end of the process, the pressure is $1.00 \times 10^6 \text{ Pa}$. Calculate the final temperature of the gas. Calculate q , w , ΔU and ΔH for this process.

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i} \right)^{1-\gamma} = \left(\frac{T_f}{T_i} \right)^{1-\gamma} \left(\frac{P_i}{P_f} \right)^{1-\gamma}; = \left(\frac{T_f}{T_i} \right)^\gamma = \left(\frac{P_i}{P_f} \right)^{\frac{1-\gamma}{\gamma}}; \frac{T_f}{T_i} = \left(\frac{P_i}{P_f} \right)^{\frac{1-\gamma}{\gamma}}$$

$$\frac{T_f}{T_i} = \left(\frac{1.00 \times 10^5 \text{ Pa}}{1.00 \times 10^6 \text{ Pa}} \right)^{\frac{1-\gamma}{\gamma}} = (0.100)^{-0.4} = 2.51$$

$$T_f = 2.51 \times 298 \text{ K} = 749 \text{ K}$$

$q = 0$ because the process is adiabatic.

$$w = \Delta U = nC_{V,m}\Delta T = 1 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times (749 \text{ K} - 298 \text{ K}) = 5.62 \times 10^3 \text{ J}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + R\Delta T = 5.62 \times 10^3 \text{ J} + 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times (749 \text{ K} - 298 \text{ K})$$

$$\Delta H = 9.37 \times 10^3 \text{ J}$$

P2.19) One mole of an ideal gas, for which $C_{V,m} = 3/2R$, is subjected to two successive changes in state:

- a) From 25.0°C and $100 \times 10^3 \text{ Pa}$, the gas is expanded isothermally against a constant pressure of $20.0 \times 10^3 \text{ Pa}$ to twice the initial volume.
- b) At the end of the previous process, the gas is cooled at constant volume from 25.0°C to -25.0°C .

Calculate q , w , ΔU and ΔH for each of the stages. Also calculate q , w , ΔU and ΔH for the complete process.

$$\text{a)} \quad V_i = \frac{nRT}{P_i} = \frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K}}{100R \times 10^3 \text{ Pa}} = 2.48 \times 10^{-2} \text{ m}^3$$

$$V_f = 2V_i = 4.96 \times 10^{-2} \text{ m}^3$$

$$w = -P_{ext}(V_f - V_i) = -20.0 \times 10^3 \text{ Pa} \times (4.96 \times 10^{-2} \text{ m}^3 - 2.48 \times 10^{-2} \text{ m}^3) = -496 \text{ J}$$

$$\Delta U \text{ and } \Delta H = 0 \text{ because } \Delta T = 0$$

$$q = -w = 496 \text{ J}$$

$$\text{b)} \quad \Delta U = nC_{V,m}(T_f - T_i) = 1.5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times (248 \text{ K} - 298 \text{ K}) = -623 \text{ J}$$

$$w = 0 \text{ because } \Delta V = 0$$

$$q = \Delta U = -623 \text{ J}$$

$$\Delta H = nC_{P,m}(T_f - T_i) = n(C_{V,m} + R)(T_f - T_i)$$

$$= 2.5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times (248 \text{ K} - 298 \text{ K})$$

$$= -1.04 \times 10^3 \text{ J}$$

$$\Delta U_{total} = 0 - 623 \text{ J} = 623 \text{ J}$$

$$w_{total} = 0 - 496 \text{ J} = -496 \text{ J}$$

$$q_{total} = 496 \text{ J} - 623 \text{ J} = -127 \text{ J}$$

$$\Delta H_{total} = 0 - 1.04 \times 10^3 \text{ J} = -1.04 \times 10^3 \text{ J}$$

P2.20) The temperature of one mole of an ideal gas increases from 18.0°C to 55.1°C as the gas is compressed adiabatically. Calculate q , w , ΔU and ΔH for this process assuming that $C_{V,m} = 3/2 R$.

$q = 0$ because the process is adiabatic.

$$w = \Delta U = nC_{V,m}\Delta T = 1 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times (55.1^\circ\text{C} - 18.0^\circ\text{C}) = 463 \text{ J}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + R\Delta T = 463 \text{ J} + 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times (55.1^\circ\text{C} - 18.0^\circ\text{C})$$

$$\Delta H = 771 \text{ J}$$

P2.21) A one mole sample of an ideal gas, for which $C_{V,m} = 3/2R$, undergoes the following two-step process.

- a) From an initial state of the gas described by $T = 28.0^\circ\text{C}$ and $P = 2.00 \times 10^4 \text{ Pa}$, the gas undergoes an isothermal expansion against a constant external pressure of $1.00 \times 10^4 \text{ Pa}$ until the volume has doubled.
- b) Subsequently, the gas is cooled at constant volume. The temperature falls to -40.5°C . Calculate q , w , ΔU and ΔH for each step and for the overall process.

a) For the first step, $\Delta U = \Delta H = 0$ because the process is isothermal.

$$V_i = \frac{nRT_i}{P_i} = \frac{1 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times (273.15 + 28.0) \text{ K}}{2.00 \times 10^4 \text{ Pa}} = 1.25 \times 10^{-2} \text{ m}^3$$

$$w = -q = -P_{\text{external}}\Delta V = -1.00 \times 10^4 \text{ Pa} \times 0.125 \times 10^{-2} \text{ m}^3 = -1.25 \times 10^3 \text{ J}$$

b) For the second step, $w = 0$ because $\Delta V = 0$.

$$q = \Delta U = C_V\Delta T = 1 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times (28.0^\circ\text{C} + 40.5^\circ\text{C}) = 854 \text{ J}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + R\Delta T = 854 \text{ J} + 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times (28.0^\circ\text{C} + 40.5^\circ\text{C})$$

$$\Delta H = 1.42 \times 10^3 \text{ J}$$

For the overall process, $w = -1.25 \times 10^3 \text{ J}$, $q = 854 + 1.25 \times 10^3 \text{ J} = 2.02 \times 10^3 \text{ J}$, $\Delta U = 854 \text{ J}$, and $\Delta H = 1.42 \times 10^3 \text{ J}$.

P2.22) A cylindrical vessel with rigid adiabatic walls is separated into two parts by a frictionless adiabatic piston. Each part contains 50.0 L of an ideal monatomic gas with $C_{V,m} = 3/2R$. Initially, $T_i = 298 \text{ K}$ and $P_i = 1.00 \text{ bar}$ in each part. Heat is slowly introduced into the left part using an electrical heater until the piston has moved sufficiently to the right to result in a final pressure $P_f = 7.50 \text{ bar}$ in the right part. Consider the compression of the gas in the right part to be a reversible process.

- a) Calculate the work done on the right part in this process, and the final temperature in the right part.
- b) Calculate the final temperature in the left part and the amount of heat that flowed into this part.

The number of moles of gas in each part is given by

$$n = \frac{PV_i}{RT_i} = \frac{1.00 \text{ bar} \times 50.0 \text{ L}}{8.3145 \times 10^{-2} \text{ L bar mol}^{-1}\text{K}^{-1} \times 298 \text{ K}} = 2.02 \text{ mol}$$

a) We first calculate the final temperature in the right side.

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i} \right)^{1-\gamma} = \left(\frac{T_f}{T_i} \right)^{1-\gamma} \left(\frac{P_i}{P_f} \right)^{1-\gamma}; = \left(\frac{T_f}{T_i} \right)^\gamma = \left(\frac{P_i}{P_f} \right)^{1-\gamma}; \frac{T_f}{T_i} = \left(\frac{P_i}{P_f} \right)^{\frac{1-\gamma}{\gamma}}$$

$$\frac{T_f}{T_i} = \left(\frac{1.00 \text{ bar}}{7.50 \text{ bar}} \right)^{\frac{1-\frac{5}{3}}{\frac{5}{3}}} = 2.24$$

$$T_f = 2.24 \times 298 \text{ K} = 667 \text{ K}$$

$$\Delta U = w = nC_{V,m}\Delta T = 2.02 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times (667 \text{ K} - 298 \text{ K}) = 9.30 \times 10^3 \text{ J}$$

b) We first calculate the final volume of the right part.

$$V_{rf} = \frac{nRT_{rf}}{P_f} = \frac{2.02 \text{ mol} \times 8.314 \times 10^{-2} \text{ L bar mol}^{-1}\text{K}^{-1} \times 667 \text{ K}}{7.50 \text{ bar}} = 14.9 \text{ L}$$

Therefore, $V_{lf} = 100.0 \text{ L} - 14.9 \text{ L} = 85.1 \text{ L}$.

$$T_{lf} = \frac{P_{lf}V_{lf}}{nR} = \frac{7.50 \text{ bar} \times 85.1 \text{ L}}{2.02 \text{ mol} \times 8.314 \times 10^{-2} \text{ L bar mol}^{-1}\text{K}^{-1}} = 3.80 \times 10^3 \text{ K}$$

$$\Delta U = nC_{V,m}\Delta T = 2.02 \text{ mol} \times 3/2 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times (3.80 \times 10^3 \text{ K} - 298 \text{ K}) = 88.2 \times 10^3 \text{ J}$$

From part a), $w = -9.30 \times 10^3 \text{ J}$

$$q = \Delta U - w = 88.2 \times 10^3 \text{ J} + 9.30 \times 10^3 \text{ J} = 97.5 \times 10^3 \text{ J}$$

P2.23) A vessel containing one mole of an ideal gas with $P_i = 1.00 \text{ bar}$ and $C_{P,m} = 5/2R$ is in thermal contact with a water bath. Treat the vessel, gas and water bath as being in thermal equilibrium, initially at 298 K, and as separated by adiabatic walls from the rest of the universe. The vessel, gas and water bath have an average heat capacity of $C_p = 7500 \text{ J/K}$. The gas is compressed reversibly to $P_f = 10.5 \text{ bar}$. What is the temperature of the system after thermal equilibrium has been established?

Assume initially that the temperature rise is so small that the reversible compression can be thought of as an isothermal reversible process. If the answer substantiates this assumption, it is valid.

$$\begin{aligned} w &= -nRT_1 \ln \frac{V_f}{V_i} = -nRT_1 \ln \frac{P_i}{P_f} \\ &= -1 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K} \times \ln \frac{1.00 \text{ bar}}{10.5 \text{ bar}} = 5.83 \times 10^3 \text{ J} \end{aligned}$$

$$\Delta U_{\text{combined system}} = C_p \Delta T$$

$$\Delta T = \frac{\Delta U_{\text{combined system}}}{C_p} = \frac{5.83 \times 10^3 \text{ J}}{7500 \text{ J K}^{-1}} = 0.777 \text{ K}$$

$$T_f \approx 299 \text{ K}$$

The result justifies the assumption.

P2.24) The heat capacity of solid lead oxide is given by

$C_{p,m} = 44.35 + 1.47 \times 10^{-3} \frac{T}{K}$ in units of $\text{J K}^{-1}\text{mol}^{-1}$. Calculate the change in enthalpy of 1 mol of $\text{PbO}(s)$ if it is cooled from 500 K to 300 K at constant pressure.

$$\begin{aligned}\Delta H &= n \int_{T_i}^{T_f} C_{p,m} dT \\ &= \int_{500}^{300} \left(44.35 + 1.47 \times 10^{-3} \frac{T}{\text{K}} \right) d\left(\frac{T}{\text{K}}\right) \\ &= 44.35 \times (300 \text{ K} - 500 \text{ K}) \\ &\quad + \left[\frac{1.47 \times 10^{-3}}{2} \left(\frac{T}{\text{K}} \right)^2 \right]_{500 \text{ K}}^{300 \text{ K}} \\ &= -8870 \text{ J} - 117 \text{ J} \\ &= -8.99 \times 10^3 \text{ J}\end{aligned}$$

P2.25) Consider the adiabatic expansion of 0.500 moles of an ideal monatomic gas with $C_{V,m} = 3/2R$. The initial state is described by $P = 3.25$ bar and $T = 300$ K.

- a) Calculate the final temperature if the gas undergoes a reversible adiabatic expansion to a final pressure $P = 1.00$ bar.
 - b) Calculate the final temperature if the same gas undergoes an adiabatic expansion against an external pressure of to $P = 1.00$ bar to a final pressure $P = 1.00$ bar.
- Explain the difference in your results for parts a) and b).

a)

$$\begin{aligned}\frac{T_f}{T_i} &= \left(\frac{V_f}{V_i} \right)^{1-\gamma} = \left(\frac{T_f}{T_i} \right)^{1-\gamma} \left(\frac{P_i}{P_f} \right)^{1-\gamma}; = \left(\frac{T_f}{T_i} \right)^\gamma = \left(\frac{P_i}{P_f} \right)^{1-\gamma}; \frac{T_f}{T_i} = \left(\frac{P_i}{P_f} \right)^{\frac{1-\gamma}{\gamma}} \\ \frac{T_f}{T_i} &= \left(\frac{3.25 \text{ bar}}{1.00 \text{ bar}} \right)^{\frac{1-\frac{5}{3}}{\frac{5}{3}}} = 0.626 \\ T_f &= 0.626 \times 300 \text{ K} = 188 \text{ K}\end{aligned}$$

b)

$$\Delta U = nC_{V,m} (T_f - T_i) = -P_{\text{external}} (V_f - V_i)$$

$$nC_{V,m}(T_f - T_i) = -nRP_{external} \left(\frac{T_f}{P_f} - \frac{T_i}{P_i} \right)$$

$$T_f \left(nC_{V,m} + \frac{nRP_{external}}{P_f} \right) = T_i \left(nC_{V,m} + \frac{nRP_{external}}{P_i} \right)$$

$$T_f = T_i \left(\frac{\frac{C_{V,m} + \frac{RP_{external}}{P_i}}{C_{V,m} + \frac{RP_{external}}{P_f}}}{\frac{C_{V,m} + \frac{RP_{external}}{P_i}}{C_{V,m} + \frac{RP_{external}}{P_f}}} \right) = 300 \text{ K} \times \left(\frac{1.5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} + \frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 1.00 \text{ bar}}{3.25 \text{ bar}}}{1.5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} + \frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 1.00 \text{ bar}}{1.00 \text{ bar}}} \right)$$

$$T_f = 217 \text{ K}$$

More work is done on the surroundings in the reversible expansion, and therefore ΔU and the temperature decrease more than for the irreversible expansion.

P2.26) An ideal gas undergoes a single stage expansion against a constant external pressure $P_{external}$ from T, P_i, V_i , to T, P_f, V_f .

- a) What is the largest mass, m , that can be lifted through the height h in this expansion?
- b) The system is restored to its initial state in a single state compression. What is the smallest mass, m' that must fall through the height h to restore the system to its initial state?
- c) If $h = 10.0 \text{ cm}$, $P_i = 1.00 \times 10^6 \text{ Pa}$, $P_f = 0.500 \times 10^6 \text{ Pa}$, $T = 300 \text{ K}$, and $n = 1.00 \text{ mole}$, calculate the values of the masses in parts a and b.

Consider the expansion

$$\text{a)} \quad w = mgh = -P_{ext}(V_f - V_i)$$

$$m = \left| \frac{-P_{ext}(V_f - V_i)}{gh} \right|$$

for the final volume to be V_f , the external pressure can be no bigger than P_f

$$m_{\max} = \left| \frac{-P_f(V_f - V_i)}{gh} \right|$$

b) Consider the compression

$$m' = \left| \frac{-P_{ext}(V_i - V_f)}{gh} \right|$$

for the final volume to be V_i , the pressure can be no smaller than P_i

$$m_{\min} = \left| \frac{-P_i(V_i - V_f)}{gh} \right|$$

c)

$$V_i = \frac{nRT}{P_i} = \frac{1.00 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 300 \text{ K}}{1.00 \times 10^6 \text{ Pa}} = 2.49 \times 10^{-3} \text{ m}^3$$

$$P_f V_f = P_i V_i$$

$$V_f = \frac{P_i V_i}{P_f} = \frac{1.00 \times 10^6 \text{ Pa} \times 2.49 \times 10^{-3} \text{ m}^3}{0.500 \times 10^6 \text{ Pa}} = 4.98 \times 10^{-3} \text{ m}^3$$

$$m_{\max} = \left| \frac{-0.500 \times 10^6 \text{ Pa} \times (4.98 \times 10^{-3} \text{ m}^3 - 2.49 \times 10^{-3} \text{ m}^3)}{9.81 \text{ m s}^{-2} \times 0.100 \text{ m}} \right| = 1.27 \times 10^3 \text{ kg}$$

$$m'_{\min} = \left| \frac{-1.00 \times 10^6 \text{ Pa} \times (2.49 \times 10^{-3} \text{ m}^3 - 4.98 \times 10^{-3} \text{ m}^3)}{9.81 \text{ m s}^{-2} \times 0.100 \text{ m}} \right| = 2.54 \times 10^3 \text{ kg}$$

P2.27) Calculate q , w , ΔU and ΔH if 1.00 mole of an ideal gas with $C_{V,m} = 3/2R$ undergoes a reversible adiabatic expansion from an initial volume $V_i = 5.25 \text{ m}^3$ to a final volume $V_f = 25.5 \text{ m}^3$. The initial temperature is 300 K.

$q = 0$ because the process is adiabatic.

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i} \right)^{1-\gamma}$$

$$\frac{T_f}{T_i} = \left(\frac{25.5 L}{5.25 L} \right)^{\frac{5}{3}} = 0.349$$

$$T_f = 0.349 \times 300 \text{ K} = 105 \text{ K}$$

$$\Delta U = w = nC_{V,n}\Delta T = 1.00 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times (105 \text{ K} - 300 \text{ K}) = -2.43 \times 10^3 \text{ J}$$

$$\Delta H = \Delta U + nR\Delta T = -2.43 \times 10^3 \text{ J} + 1.00 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times (105 \text{ K} - 300 \text{ K})$$

$$\Delta H = -4.05 \times 10^3 \text{ J}$$

P2.28) A nearly flat bicycle tire becomes noticeably warmer after it has been pumped up. Approximate this process as a reversible adiabatic compression. Take the initial pressure and temperature of the air before it is put in the tire to be $P_i = 1.00 \text{ bar}$ and $T_i = 298 \text{ K}$. The final volume of the air in the tire is $V_f = 1.00 \text{ L}$ and the final pressure is $P_f = 5.00 \text{ bar}$. Calculate the final temperature of the air in the tire. Assume that $C_{V,m} = 5/2 R$.

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i} \right)^{1-\gamma} = \left(\frac{T_f}{T_i} \right)^{1-\gamma} \left(\frac{P_i}{P_f} \right)^{1-\gamma}; = \left(\frac{T_f}{T_i} \right)^\gamma = \left(\frac{P_i}{P_f} \right)^{1-\gamma}; \frac{T_f}{T_i} = \left(\frac{P_i}{P_f} \right)^{\frac{1-\gamma}{\gamma}}$$

$$\frac{T_f}{T_i} = \left(\frac{1.00 \text{ bar}}{5.00 \text{ bar}} \right)^{\frac{1-\gamma}{\gamma}} = (0.200)^{-0.285} = 1.58$$

$$T_f = 1.58 \times 298 \text{ K} = 472 \text{ K}$$

P2.29) One mole of an ideal gas with $C_{V,m} = 3/2R$ is expanded adiabatically against a constant external pressure of 1.00 bar. The initial temperature and pressure are $T_i = 300 \text{ K}$ and $P_i = 25.0 \text{ bar}$. The final pressure is $P_f = 1.00 \text{ bar}$. Calculate q , w , ΔU and ΔH for the process.

$$\Delta U = nC_{V,m}(T_f - T_i) = -P_{\text{external}}(V_f - V_i) = w$$

$q = 0$ because the process is adiabatic.

$$nC_{V,m}(T_f - T_i) = -nRP_{\text{external}} \left(\frac{T_f}{P_f} - \frac{T_i}{P_i} \right)$$

$$T_f \left(nC_{V,m} + \frac{nRP_{\text{external}}}{P_f} \right) = T_i \left(nC_{V,m} + \frac{nRP_{\text{external}}}{P_i} \right)$$

$$T_f = T_i \left(\frac{C_{V,m} + \frac{RP_{\text{external}}}{P_i}}{C_{V,m} + \frac{RP_{\text{external}}}{P_f}} \right) = 300 \text{ K} \times \left(\frac{1.5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} + \frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 1.00 \text{ bar}}{25.0 \text{ bar}}}{1.5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} + \frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 1.00 \text{ bar}}{1.00 \text{ bar}}} \right)$$

$$T_f = 185 \text{ K}$$

$$\Delta U = w = nC_{V,n}\Delta T = 1.00 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times (185 \text{ K} - 300 \text{ K}) = -1.43 \times 10^3 \text{ J}$$

$$\Delta H = \Delta U + nR\Delta T = -1.43 \times 10^3 \text{ J} + 1.00 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times (185 \text{ K} - 300 \text{ K})$$

$$\Delta H = -2.39 \times 10^3 \text{ J}$$

P2.30) One mole of N₂ in a state defined by $T_i = 300 \text{ K}$ and $V_i = 2.50 \text{ L}$ undergoes an isothermal reversible expansion until $V_f = 23.0 \text{ L}$. Calculate w assuming a) that the gas is described by the ideal gas law, and b) that the gas is described by the van der Waals equation of state. What is the percent error in using the ideal gas law instead of the van der Waals equation? The van der Waals parameters for N₂ are tabulated in Appendix A.

a) for the ideal gas

$$w_{reversible} = -nRT \ln \frac{V_f}{V_i} = -1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K} \times \ln \frac{23.0 \text{ L}}{2.50 \text{ L}} = -5.54 \times 10^3 \text{ J}$$

for the van der Waals gas

$$\begin{aligned} w &= - \int_{V_i}^{V_f} P_{external} dV = - \int_{V_i}^{V_f} \left(\frac{RT}{V_m - b} - \frac{a}{V_m^2} \right) dV \\ &= - \int_{V_i}^{V_f} \left(\frac{RT}{V_m - b} \right) dV + \int_{V_i}^{V_f} \left(\frac{a}{V_m^2} \right) dV \end{aligned}$$

The first integral is solved by making the substitution $y = V_m - b$.

$$- \int_{V_i}^{V_f} \left(\frac{RT}{V_m - b} \right) dV = - \int_{y_i}^{y_f} \left(\frac{RT}{y} \right) dy = -RT \left[\ln(V_f + b) - \ln(V_i + b) \right]$$

Therefore, the work is given by

$$\begin{aligned} w &= -nRT \ln \frac{(V_f - b)}{(V_i - b)} + a \left(\frac{1}{V_i} - \frac{1}{V_f} \right) \\ &= -1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K} \times \ln \frac{23.0 \text{ L} - 0.0380 \text{ L}}{2.50 \text{ L} - 0.0380 \text{ L}} \\ &\quad + 1.366 \text{ L}^2 \text{ bar} \times \frac{10^5 \text{ Pa}}{\text{bar}} \times \frac{10^{-6} \text{ m}^6}{\text{L}^2} \left(\frac{1}{2.50 \times 10^{-3} \text{ m}^3} - \frac{1}{23.0 \times 10^{-3} \text{ m}^3} \right) \end{aligned}$$

$$w = -5.56 \times 10^3 \text{ J} + 48.7 \text{ J} = -5.52 \times 10^3 \text{ J}$$

$$\text{Percent error} = 100 \times \frac{-5.52 \times 10^3 \text{ J} + 5.54 \times 10^3 \text{ J}}{-5.52 \times 10^3 \text{ J}} = -0.4\%$$

Chapter 3: The Importance of State Functions: Internal Energy and Enthalpy

Problem numbers in italics indicate that the solution is included in the *Student's Solutions Manual*.

Questions on Concepts

Q3.1) Why is $C_{P,m}$ a function of temperature for ethane, but not for argon?

Argon has only translational degrees of freedom, which are fully excited at very low temperatures because $\Delta E_{translational} \ll kT$, where $\Delta E_{translational}$ is the spacing between translational levels. The translational degrees of freedom for ethane are also fully excited at 298 K. This condition is not fulfilled for the spacing between vibrational levels for ethane, and $C_{P,m}$ increases with temperature as the vibrational degrees of freedom become excited.

Q3.2) Why is $q_V = \Delta U$ only for a constant volume process? Is this formula valid if work other than $P-V$ work is possible?

Because $\Delta U = q + w$, $q_V = \Delta U$ only if w is zero. Therefore, the formula is not valid if work other than $P-V$ work is possible.

Q3.3) Refer to Figure 1.6 and explain why $\left(\frac{\partial U}{\partial V}\right)_T$ is generally small for a real gas.

The depth of the minimum in the potential is generally very small. Therefore, it takes very little energy to separate the atoms or molecules that make up the gas.

Q3.4) Explain without using equations why $\left(\frac{\partial H}{\partial P}\right)_T$ is generally small for a real gas.

The variation of H with P is a measure of how the energy of a gas changes with the spacing between the molecules of the gas. Because the depth of the minimum in the potential in Figure 1.6 is generally very small, it takes very little energy to separate the atoms or molecules that make up the gas.

Q3.5) Why is it reasonable to write $dH \approx C_p dT + VdP$ for a liquid or solid sample?

This approximation is valid because $T\left(\frac{\partial U}{\partial V}\right)_T \ll V$ for a liquid or solid.

Q3.6) Why is the equation $\Delta H = \int_{T_i}^{T_f} C_p(T) dT = n \int_{T_i}^{T_f} C_{P,m}(T) dT$ valid for an ideal gas even if P is not constant in the process? Is this equation also valid for a real gas? Why or why not?

It is valid because for an ideal gas, H is a function of T only, and is not a function of V or P . The formula is not accurate for a real gas, because H is a weak function of V and P .

Q3.7) Heat capacity $C_{P,m}$ is less than $C_{V,m}$ for $\text{H}_2\text{O}(l)$ between 4° and 5°C . Explain this result.

This unusual behavior occurs because the density of water decreases with temperature in this range. Therefore, work is done by the surroundings on the system as water is heated at constant P between 4°C and 5°C .

Q3.8) What is the physical basis for the experimental result that U is a function of V at constant T for a real gas? Under what conditions will U decrease as V increases?

U is a function of V for a real gas because of the interaction potential between gas molecules. U decreases as V increases if the density is such that the gas is dominated by the repulsive part of the potential.

Q3.9) Why does the relation $C_P > C_V$ always hold for a gas? Can $C_P < C_V$ be valid for a liquid?

This is the case because the volume of a real gas always increases with increasing T . Therefore, heating a real gas at constant P results in the system doing work on the surroundings. $C_P < C_V$ is valid for a liquid if V decreases with T at constant P . Although unusual, this condition is satisfied for water between 4°C and the freezing point.

Q3.10) Can a gas be liquefied through an isoenthalpic expansion if $\mu_{J-T} = 0$?

No. The gas would not be cooled if $\mu_{J-T} = 0$.

Problems

P3.1) A differential $dz = f(x, y)dx + g(x, y)dy$ is exact if the integral $\int f(x, y)dx + \int g(x, y)dy$ is independent of the path. Demonstrate that the differential $dz = 2xydx + x^2dy$ is exact by integrating dz along the paths $(1,1) \rightarrow (5,1) \rightarrow (5,5)$ and $(1,1) \rightarrow (3,1) \rightarrow (3,3) \rightarrow (5,3) \rightarrow (5,5)$. The first number in each set of parentheses is the x coordinate, and the second number is the y coordinate.

$$\int dz = \int 2xy dx + \int x^2 dy$$

Path 1

$$\int dz = 2 \int_1^5 x dx + 25 \int_1^5 dy = [x^2]_1^5 + 25[y]_1^5 = (25 - 1) + 25(5 - 1) = 124$$

Path 2

$$\begin{aligned} \int dz &= 2 \int_1^3 x dx + 9 \int_1^3 dy + 6 \int_3^5 x dx + 25 \int_3^5 dy = [x^2]_1^3 + 9[y]_1^3 + 3[x^2]_3^5 + 25[y]_3^5 \\ &= (9 - 1) + 9(3 - 1) + 3(25 - 9) + 25(5 - 3) = 124 \end{aligned}$$

P3.2) The function $f(x,y)$ is given by $f(x,y) = xy \sin 5x + x^2 \sqrt{y} \ln y + 3e^{-2x^2} \cos y$.

Determine $\left(\frac{\partial f}{\partial x}\right)_y, \left(\frac{\partial f}{\partial y}\right)_x, \left(\frac{\partial^2 f}{\partial x^2}\right)_y, \left(\frac{\partial^2 f}{\partial y^2}\right)_x, \left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x$ and $\left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y$.

Is $\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y$? Obtain an expression for the total differential df .

$$\left(\frac{\partial f}{\partial x}\right)_y = 5xy \cos 5x + y \sin 5x - 12xe^{-2x^2} \cos y + 2x\sqrt{y} \ln y$$

$$\left(\frac{\partial f}{\partial y}\right)_x = x \sin 5x + \frac{x^2}{\sqrt{y}} + \frac{x^2 \ln y}{2\sqrt{y}} - 3e^{-2x^2} \sin y$$

$$\left(\frac{\partial^2 f}{\partial x^2}\right)_y = 10y \cos 5x - 25xy \sin 5x - 12e^{-2x^2} \cos y + 48e^{-2x^2} x^2 \cos y + 2\sqrt{y} \ln y$$

$$\left(\frac{\partial^2 f}{\partial y^2}\right)_x = -3e^{-2x^2} \cos y - \frac{x^2 \ln y}{4y^{\frac{3}{2}}}$$

$$\left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = \frac{2x}{\sqrt{y}} + \frac{x \ln y}{\sqrt{y}} + \sin 5x + 5x \cos 5x + 12e^{-2x^2} x \sin y$$

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = 5x \cos 5x + 12e^{-2x^2} x \sin y + \frac{2x}{\sqrt{y}} + \frac{x \ln y}{\sqrt{y}} + \sin 5x = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y$$

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = \left(5xy \cos 5x + y \sin 5x - 12xe^{-2x^2} \cos y + 2x\sqrt{y} \ln y\right) dx$$

$$+ \left(x \sin 5x + \frac{x^2}{\sqrt{y}} + \frac{x^2 \ln y}{2\sqrt{y}} - 3e^{-2x^2} \sin y\right) dy$$

P3.3) This problem will give you practice in using the cyclic rule. Use the ideal gas law to obtain the three functions $P = f(V, T)$, $V = g(P, T)$, and $T = h(P, V)$. Show that the

cyclic rule $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$ is obeyed.

$$P = \frac{nRT}{V}; \quad V = \frac{nRT}{P}; \quad T = \frac{PV}{nR}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT}{V^2}; \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}; \quad \left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{nR}$$

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = \left(-\frac{nRT}{V^2}\right) \left(\frac{nR}{P}\right) \left(\frac{V}{nR}\right) = \frac{-nRT}{PV} = -1$$

P3.4) Using the chain rule for differentiation, show that the isobaric expansion

$$\text{coefficient expressed in terms of density is given by } \beta = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T}\right)_P.$$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{\rho}{m} \left(\frac{\partial \frac{m}{\rho}}{\partial T}\right)_P = \frac{\rho}{m} \left(\frac{\partial \frac{m}{\rho}}{\partial \rho}\right)_P \left(\frac{\partial \rho}{\partial T}\right)_P = \frac{\rho}{m} \left(-\frac{m}{\rho^2}\right) \left(\frac{\partial \rho}{\partial T}\right)_P = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T}\right)_P$$

P3.5) A vessel is filled completely with liquid water and sealed at 25.0°C and a pressure of 1.00 bar. What is the pressure if the temperature of the system is raised to 60.0°C ?

Under these conditions, $\beta_{\text{water}} = 2.04 \times 10^{-4} \text{ K}^{-1}$, $\beta_{\text{vessel}} = 1.02 \times 10^{-4} \text{ K}^{-1}$, and $\kappa_{\text{water}} = 4.59 \times 10^{-5} \text{ bar}^{-1}$.

$$\Delta P = \int \frac{\beta_{\text{water}}}{\kappa} dT - \int \frac{1}{\kappa V} dV \approx \frac{\beta_{\text{water}}}{\kappa} \Delta T - \frac{1}{\kappa} \ln \frac{V_f}{V_i}$$

$$= \frac{\beta_{\text{water}}}{\kappa} \Delta T - \frac{1}{\kappa} \ln \frac{V_i(1 + \beta_{\text{vessel}} \Delta T)}{V_i} \approx \frac{\beta_{\text{water}}}{\kappa} \Delta T - \frac{1}{\kappa} \frac{V_i \beta_{\text{vessel}} \Delta T}{V_i} = \frac{(\beta_{\text{water}} - \beta_{\text{vessel}})}{\kappa} \Delta T$$

$$= \frac{(2.07 - 1.02) \times 10^{-4} (\text{ }^\circ\text{C})^{-1}}{4.59 \times 10^{-5} (\text{bar})^{-1}} \times 60.0 \text{ }^\circ\text{C} = 77.8 \text{ bar}$$

$$P_i + \Delta P = 78.8 \text{ bar}$$

P3.6) Because U is a state function, $\left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V}\right)_T\right)_V$. Using this

relationship, show that $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$ for an ideal gas.

For an ideal gas, by definition, $\left(\frac{\partial U}{\partial V}\right)_T = 0$. Because

the order of differentiation can be changed for a state function,

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V = 0$$

P3.7) Because V is a state function, $\left(\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)_T\right)_P$. Using this relationship, show that the isothermal compressibility and isobaric expansion coefficient are related by $\left(\frac{\partial \beta}{\partial P}\right)_T = -\left(\frac{\partial \kappa}{\partial T}\right)_P$.

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)_T\right)_P$$

$$\text{Because } \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \text{ and } \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial [V\beta]}{\partial P}\right)_T = -\left(\frac{\partial [V\kappa]}{\partial T}\right)_P \text{ or } \left(\frac{\partial \beta}{\partial P}\right)_T = -\left(\frac{\partial \kappa}{\partial T}\right)_P$$

P3.8) Integrate the expression $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$ assuming that β is independent of pressure. By doing so, obtain an expression for V as a function of P and β .

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

$$\frac{dV}{V} = \beta dT$$

$$\int \frac{dV}{V} = \int \beta dT \text{ or } \ln \frac{V_f}{V_i} = \beta (T_f - T_i)$$

if β can be assumed constant in the temperature interval of interest.

P3.9) The molar heat capacity $C_{P,m}$ of $\text{SO}_2(g)$ is described by the following equation over the range $300 \text{ K} < 1700 \text{ K}$.

Chapter 3/ The Importance of State Functions: Internal Energy and Enthalpy

$\frac{C_{P,m}}{R} = 3.093 + 6.967 \times 10^{-3} \frac{T}{K} - 45.81 \times 10^{-7} \frac{T^2}{K^2} + 1.035 \times 10^{-9} \frac{T^3}{K^3}$. In this equation, T is the absolute temperature in Kelvin. The ratios $\frac{T^n}{K^n}$ ensure that $C_{P,m}$ has the correct dimension. Assuming ideal gas behavior, calculate q , w , ΔU , and ΔH if 1 mol of $\text{SO}_2(\text{g})$ is heated from 75° to 1350°C at a constant pressure of 1 bar. Explain the sign of w .

$$\begin{aligned}\Delta H &= q = n \int_{T_i}^{T_f} C_{P,m} dT = 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \int_{348.15}^{1623.15} \left(3.093 + 6.967 \times 10^{-3} \frac{T}{K} - 45.81 \times 10^{-7} \frac{T^2}{K^2} + 1.035 \times 10^{-9} \frac{T^3}{K^3} \right) d \frac{T}{K} \\ &= 1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \times \left[3.093 \frac{T}{K} + 0.0034835 \frac{T^2}{K^2} - 1.527 \times 10^{-6} \frac{T^3}{K^3} + 2.5875 \times 10^{-10} \frac{T^4}{K^4} \right]_{348.15}^{1623.15} \\ &= \left(1 \text{ mol} \times 3.279 \times 10^4 \text{ J mol}^{-1} + 7.279 \times 10^4 \text{ J mol}^{-1} - 5.375 \times 10^4 \text{ J mol}^{-1} + 1.490 \times 10^4 \text{ J mol}^{-1}\text{K}^{-1} \right) \\ &= 6.67 \times 10^4 \text{ J}\end{aligned}$$

$$\begin{aligned}\Delta U &= \Delta H - \Delta(PV) = \Delta H - nR\Delta T \\ &= 6.673 \times 10^4 \text{ J} - 1 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times (1623.15 \text{ K} - 348.15 \text{ K}) \\ &= 5.61 \times 10^4 \text{ J} \\ w &= \Delta U - q = 5.613 \times 10^4 \text{ J} - 6.673 \times 10^4 \text{ J} = -1.06 \times 10^4 \text{ J}\end{aligned}$$

Because the gas is heated, it expands. Therefore $\Delta V > 0$ and $w < 0$.

P3.10) Starting with the van der Waals equation of state, find an expression for the total differential dP in terms of dV and dT . By calculating the mixed partial derivatives

$\left(\frac{\partial}{\partial T} \left(\frac{\partial P}{\partial V} \right)_T \right)_V$ and $\left(\frac{\partial}{\partial V} \left(\frac{\partial P}{\partial T} \right)_V \right)_T$, determine if dP is an exact differential.

$$\left(\frac{\partial}{\partial V} \left[\frac{RT}{V_m - b} - \frac{a}{V_m^2} \right] \right)_T = \frac{2a}{V_m^3} - \frac{RT}{(V_m - b)^2}$$

$$\left(\frac{\partial}{\partial T} \left[\frac{RT}{V_m - b} - \frac{a}{V_m^2} \right] \right)_V = \frac{R}{(V_m - b)}$$

$$dP = \left(\frac{2a}{V_m^3} - \frac{RT}{(V_m - b)^2} \right) dV + \frac{R}{(V_m - b)} dT$$

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial P}{\partial V} \right)_T \right)_V = \left(\frac{\partial}{\partial T} \left[\frac{2a}{V_m^3} - \frac{RT}{(V_m - b)^2} \right] \right)_V = -\frac{R}{(V_m - b)^2}$$

$$\left(\frac{\partial}{\partial V} \left(\frac{\partial P}{\partial T} \right)_V \right)_T = \left(\frac{\partial}{\partial V} \left[\frac{R}{(V_m - b)} \right] \right)_T = -\frac{R}{(V_m - b)^2}$$

Therefore, dP is an exact differential.

P3.11) Obtain an expression for the isothermal compressibility $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$ for a

van der Waals gas.

$$\kappa = -\frac{1}{V_m} \left(\frac{\partial V_m}{\partial P} \right)_T = -\frac{1}{V_m \left(\frac{\partial P}{\partial V_m} \right)_T} = -\frac{1}{V_m \left(\left(\frac{\partial}{\partial V_m} \left[\frac{RT}{V_m - b} - \frac{a}{V_m^2} \right] \right) \right)_T}$$

$$\kappa = -\frac{1}{V_m \left[\frac{2a}{V_m^3} - \frac{RT}{(V_m - b)^2} \right]}$$

P3.12) Regard the enthalpy as a function of T and P . Use the cyclic rule to obtain the

$$\text{expression } C_P = -\frac{\left(\frac{\partial H}{\partial P} \right)_T}{\left(\frac{\partial T}{\partial P} \right)_H}.$$

$$\left(\frac{\partial H}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_H \left(\frac{\partial T}{\partial H} \right)_P = -1$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = -\left(\frac{\partial H}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_H = -\frac{\left(\frac{\partial H}{\partial P} \right)_T}{\left(\frac{\partial T}{\partial P} \right)_H}$$

P3.13) Equation (3.38), $C_P = C_V + TV \frac{\beta^2}{\kappa}$, links C_P and C_V with β and κ . Use this equation to evaluate $C_P - C_V$ for an ideal gas.

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \frac{nR}{P}; \quad \kappa = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{nRT}{VP^2} = \frac{1}{P}$$

$$C_P - C_V = TV \frac{\beta^2}{\kappa} = TV \left(\frac{1}{V} \frac{nR}{P} \right)^2 P = TV \frac{n^2 R^2}{V^2 P} = nR$$

P3.14) Use Equation (3.58), $\left(\frac{\partial U}{\partial V} \right)_T = \frac{\beta T - \kappa P}{\kappa}$ to calculate $\left(\frac{\partial U}{\partial V} \right)_T$ for an ideal gas.

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \frac{nR}{P}; \quad \kappa = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{nRT}{VP^2} = \frac{1}{P}$$

$$\left(\frac{\partial U}{\partial V} \right)_T = \frac{\beta T - \kappa P}{\kappa} = \frac{\frac{1}{V} \frac{nRT}{P} - 1}{\frac{1}{P}} = P(1 - \frac{1}{nRT}) = 0$$

P3.15) An 80.0-g piece of gold at 650 K is dropped into 100.0 g of H₂O(l) at 298 K in an insulated container at 1 bar pressure. Calculate the temperature of the system once equilibrium has been reached. Assume that $C_{P,m}$ for Au and H₂O is constant at their values for 298 K throughout the temperature range of interest.

$$n_{Au} C_{P,m}^{Au} (T_f - T_i^{Au}) + n_{H_2O} C_{P,m}^{H_2O} (T_f - T_i^{H_2O}) = 0$$

$$T_f = \frac{n_{Au} C_{P,m}^{Au} T_i^{Au} + n_{H_2O} C_{P,m}^{H_2O} T_i^{H_2O}}{n_{Au} C_{P,m}^{Au} + n_{H_2O} C_{P,m}^{H_2O}}$$

$$= \frac{\frac{80.0 \text{ g Au}}{196.97 \text{ g Au mol}^{-1}} \times 25.42 \text{ JK}^{-1}\text{mol}^{-1} \times 650 \text{ K} + \frac{100.0 \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.291 \text{ JK}^{-1}\text{mol}^{-1} \times 298 \text{ K}}{\frac{80.0 \text{ g Au}}{196.97 \text{ g Au mol}^{-1}} \times 25.42 \text{ JK}^{-1}\text{mol}^{-1} + \frac{100.0 \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.291 \text{ JK}^{-1}\text{mol}^{-1}}$$

$$T_f = 306 \text{ K}$$

P3.16) A mass of 35.0 g of H₂O(s) at 273 K is dropped into 180.0 g of H₂O(l) at 325 K in an insulated container at 1 bar of pressure. Calculate the temperature of the system once equilibrium has been reached. Assume that $C_{P,m}$ for H₂O is constant at its values for 298 K throughout the temperature range of interest.

$$\begin{aligned}
 n_{ice} \Delta H_{fusion}^{ice} + n_{ice} C_{P,m}^{H_2O} (T_f - T_i^{ice}) + n_{H_2O} C_{P,m}^{H_2O} (T_f - T_i^{H_2O}) &= 0 \\
 T_f = \frac{n_{Au} C_{P,m}^{Au} T_i^{Au} + n_{H_2O} C_{P,m}^{H_2O} T_i^{H_2O} - n_{ice} \Delta H_{fusion}^{ice}}{n_{Au} C_{P,m}^{Au} + n_{H_2O} C_{P,m}^{H_2O}} = \\
 \frac{\frac{35.0 \text{ g ice}}{18.02 \text{ g ice mol}^{-1}} \times 75.291 \text{ JK}^{-1}\text{mol}^{-1} \times 273 \text{ K} + \frac{180.0 \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.291 \text{ JK}^{-1}\text{mol}^{-1} \times 325 \text{ K}}{\frac{35.0 \text{ g ice}}{18.02 \text{ g ice mol}^{-1}} \times 75.291 \text{ JK}^{-1}\text{mol}^{-1} + \frac{100.0 \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.291 \text{ JK}^{-1}\text{mol}^{-1}} \\
 \\
 T_f = 303 \text{ K}
 \end{aligned}$$

P3.17) A mass of 20.0 g of $\text{H}_2\text{O}(g)$ at 373 K is flowed into 250 g of $\text{H}_2\text{O}(l)$ at 300 K and 1 atm. Calculate the final temperature of the system once equilibrium has been reached. Assume that $C_{P,m}$ for H_2O is constant at its values for 298 K throughout the temperature range of interest.

$$\begin{aligned}
 -n_{steam} \Delta H_{vaporization}^{water} + n_{steam} C_{P,m}^{H_2O} (T_f - T_i^{ice}) + n_{H_2O} C_{P,m}^{H_2O} (T_f - T_i^{H_2O}) &= 0 \\
 T_f = \frac{n_{steam} C_{P,m}^{H_2O} T_i^{steam} + n_{H_2O} C_{P,m}^{H_2O} T_i^{H_2O} + n_{steam} \Delta H_{vaporization}^{water}}{n_{steam} C_{P,m}^{H_2O} + n_{H_2O} C_{P,m}^{H_2O}} = \\
 \frac{\frac{20.0 \text{ g steam}}{18.02 \text{ g steam mol}^{-1}} \times 75.291 \text{ JK}^{-1}\text{mol}^{-1} \times 373 \text{ K} + \frac{250.0 \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.291 \text{ JK}^{-1}\text{mol}^{-1} \times 300 \text{ K}}{\frac{20.0 \text{ g steam}}{18.02 \text{ g steam mol}^{-1}} \times 75.291 \text{ JK}^{-1}\text{mol}^{-1} + \frac{250.0 \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.291 \text{ JK}^{-1}\text{mol}^{-1}} \\
 \\
 T_f = 345 \text{ K}
 \end{aligned}$$

P3.18) Calculate w , q , ΔH , and ΔU for the process in which 1 mol of water undergoes the transition $\text{H}_2\text{O}(l, 373 \text{ K}) \rightarrow \text{H}_2\text{O}(g, 460 \text{ K})$ at 1 bar pressure. The volume of liquid water at 373 K is $1.89 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ and the volume of steam at 373 and 460 K is 3.03 and $3.74 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}$, respectively. For steam, $C_{P,m}$ can be considered constant over the temperature interval of interest at $33.58 \text{ J mol}^{-1} \text{ K}^{-1}$.

Chapter 3/ The Importance of State Functions: Internal Energy and Enthalpy

$$\begin{aligned}
 q &= \Delta H = n\Delta H_{vaporization} + nC_{P,m}^{steam}\Delta T \\
 &= 40656 \text{ J} + 1 \text{ mol} \times 33.58 \text{ J mol}^{-1}\text{K}^{-1} \times (460 \text{ K} - 373 \text{ K}) = 4.35 \times 10^4 \text{ J} \\
 w &= -P_{external}\Delta V = -10^5 \text{ Pa} \times (3.03 \times 10^{-2} \text{ m}^3 - 1.89 \times 10^{-5} \text{ m}^3) - 10^5 \text{ Pa} \times (3.74 \times 10^{-2} \text{ m}^3 - 3.03 \times 10^{-2} \text{ m}^3) \\
 &= -3028 \text{ J} - 710 \text{ J} = -3.74 \times 10^3 \text{ J} \\
 \Delta U &= w + q = 4.35 \times 10^4 \text{ J} - 3738 \text{ J} = 3.98 \times 10^4 \text{ J}
 \end{aligned}$$

P3.19) Because $\left(\frac{\partial H}{\partial P}\right)_T = -C_P \mu_{J-T}$, the change in enthalpy of a gas expanded at constant temperature can be calculated. In order to do so, the functional dependence of μ_{J-T} on P must be known. Treating Ar as a van der Waals gas, calculate ΔH when 1 mol of Ar is expanded from 400 bar to 1.00 bar at 300 K. Assume that μ_{J-T} is independent of pressure and is given by $\mu_{J-T} = \left(\frac{2a}{RT} - b\right)/C_{P,m} = 5/2R$ for Ar. What value would ΔH have if the gas exhibited ideal gas behavior?

$$\begin{aligned}
 \Delta H_m &= - \int_{P_i}^{P_f} C_{P,m} \mu_{J-T} dP \approx -C_{P,m} \mu_{J-T} (P_f - P_i) \\
 &= -C_{P,m} \times \frac{1}{C_{P,m}} \left(\frac{2 \times 0.1355 \text{ m}^6 \text{ Pa mol}^{-2}}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 300 \text{ K}} - 0.03201 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} \right) \times (1.00 \times 10^5 \text{ Pa} - 400 \times 10^5 \text{ Pa}) \\
 &= 3.06 \times 10^3 \text{ J}
 \end{aligned}$$

For an ideal gas, $\Delta H_m = 0$ because μ_{J-T} is zero for an ideal gas.

P3.20) Using the result of Equation (3.8), $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa}$, express β as a function of κ and V_m for an ideal gas, and β as a function of b , κ , and V_m for a van der Waals gas.

For the ideal gas,

$$\left(\frac{\partial P}{\partial T}\right)_P = \frac{R}{V_m} = \frac{\beta}{\kappa}; \quad \beta = \frac{\kappa R}{V_m}$$

For the van der Waals gas,

$$\left(\frac{\partial}{\partial T} \left[\frac{RT}{V_m - b} - \frac{a}{V_m^2} \right] \right)_V = \frac{R}{(V_m - b)}; \quad \beta = \frac{\kappa R}{V_m - b}$$

P3.21) The Joule coefficient is defined as $\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V} \left[P - T \left(\frac{\partial P}{\partial T} \right)_V \right]$. Calculate the Joule coefficient for an ideal gas and for a van der Waals gas.

For an ideal gas

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_{V,m}} \left[P - T \left(\frac{\partial}{\partial T} \frac{nRT}{V} \right)_V \right] = \frac{1}{C_{V,m}} \left[P - \frac{nRT}{V} \right] = 0$$

For a van der Waals gas

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_{V,m}} \left[P - T \left(\frac{\partial}{\partial T} \left[\frac{RT}{V_m - b} - \frac{a}{V_m^2} \right] \right)_V \right] = \frac{1}{C_{V,m}} \left[P - \frac{RT}{(V_m - b)} \right] = -\frac{1}{C_V} \frac{a}{V_m^2}$$

P3.22) Use the relation $\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$ and the cyclic rule to obtain an expression for the internal pressure $\left(\frac{\partial U}{\partial V}\right)_T$, in terms of P , β , T , and κ .

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P = -T \left(\frac{\frac{\partial V}{\partial T}}{\frac{\partial P}{\partial V}} \right)_P - P = T \frac{V\beta}{V\kappa} - P = T \frac{\beta}{\kappa} - P$$

P3.23) Derive the following relation, $\left(\frac{\partial U}{\partial V_m}\right)_T = \frac{3a}{2\sqrt{T}V_m(V_m + b)}$, for the internal pressure of a gas that obeys the Redlich-Kwong equation of state,

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}} \frac{1}{V_m(V_m + b)}.$$

The internal pressure of a gas is given by

$$\left(\frac{\partial V}{\partial T}\right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$$

Using the Redlich-Kwong equation of state,

$$\begin{aligned}\left(\frac{\partial P}{\partial T}\right)_V &= \frac{R}{V_m - b} + \frac{1}{2} \frac{a}{T^{3/2} V_m (V_m + b)} \\ \left(\frac{\partial U}{\partial V}\right)_T &= T \left(\frac{\partial P}{\partial T}\right)_V - P = \frac{RT}{V_m - b} + \frac{1}{2} \frac{a}{\sqrt{T} V_m (V_m + b)} - \left(\frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m (V_m + b)} \right) \\ &= \frac{1}{2} \frac{a}{\sqrt{T} V_m (V_m + b)} + \frac{a}{\sqrt{T} V_m (V_m + b)} = \frac{3a}{2\sqrt{T} V_m (V_m + b)}\end{aligned}$$

P3.24) Derive an expression for the internal pressure of a gas that obeys the Bethelot equation of state, $P = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}$.

The internal pressure of a gas is given by

$$\left(\frac{\partial V}{\partial T}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

Using the Bethelot equation of state

$$\begin{aligned}\left(\frac{\partial P}{\partial T}\right)_V &= \frac{R}{V_m - b} + \frac{a}{T^2 V_m^2} \\ \left(\frac{\partial U}{\partial V}\right)_T &= \frac{RT}{V_m - b} + \frac{a}{TV_m^2} \left(\frac{RT}{V_m - b} - \frac{a}{TV_m^2} \right) = \frac{2a}{TV_m^2}\end{aligned}$$

P3.25) For a gas that obeys the equation of state $V_m = \frac{RT}{P} + B(T)$, derive the result

$$\left(\frac{\partial H}{\partial P}\right)_T = B(T) - T \frac{dB(T)}{dT}.$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P$$

$$\text{For } V_m = \frac{RT}{P} + B(T)$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{dB}{dT}$$

$$\begin{aligned}\left(\frac{\partial H}{\partial P}\right)_T &= \frac{RT}{P} + B(T) - T\left(\frac{R}{P} + \frac{dB}{dT}\right) = \frac{RT}{P} + B(T) - \frac{RT}{P} - T\frac{dB(T)}{dT} \\ &= B(T) - T\frac{dB(T)}{dT}\end{aligned}$$

P3.26) Derive the following expression for calculating the isothermal change in the constant volume heat capacity: $\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$.

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_T$$

The order of differentiation can be reversed because U is a state function.

$$\text{Using the equation } \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\begin{aligned}\left(\frac{\partial C_V}{\partial V}\right)_T &= \left(\frac{\partial}{\partial T}\left(T\left(\frac{\partial P}{\partial T}\right)_V - P\right)\right)_V \\ &= \left(\frac{\partial P}{\partial T}\right)_V + T\left(\frac{\partial^2 P}{\partial T^2}\right)_V - \left(\frac{\partial P}{\partial T}\right)_V = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V\end{aligned}$$

P3.27) Use the result of the Problem P3.26 to show that $\left(\frac{\partial C_V}{\partial V}\right)_T$ for the van der Waals gas is zero.

We use the relationship

$$\left(\frac{\partial C_V}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V$$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V_m - b}$$

$$\left(\frac{\partial^2 P}{\partial T^2} \right)_V = \left(\frac{\partial}{\partial T} \frac{R}{V_m - b} \right)_V = 0$$

$$\text{therefore } \left(\frac{\partial C_V}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V = T \times 0 = 0$$

P3.28) Use the result of Problem P3.26 to derive a formula for $\left(\frac{\partial C_V}{\partial V} \right)_T$ for a gas that

$$\text{obeys the Redlich-Kwong equation of state, } P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}} \frac{1}{V_m (V_m + b)}.$$

We use the relationship

$$\left(\frac{\partial C_V}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V$$

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m (V_m + b)}$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V_m - b} + \frac{a}{2T^{3/2} V_m (V_m + b)}$$

$$\left(\frac{\partial^2 P}{\partial T^2} \right)_V = \frac{-3a}{4T^{5/2} V_m (V_m + b)}$$

$$\left(\frac{\partial C_V}{\partial V} \right)_T = -\frac{3a}{4T^{3/2} V_m (V_m + b)}$$

P3.29) For the equation of state $V_m = (RT/P) + B(T)$, show that

$$\left(\frac{\partial C_{P,m}}{\partial P} \right)_T = -T \frac{d^2 B(T)}{dT^2}.$$

[Hint: Use Equation (3.44) and the property of states functions

with respect to the order of differentiation in mixed second derivatives.]

Using Equation (3.44),

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial H}{\partial P} \right)_T \right)_P = \left(\frac{\partial}{\partial P} \left(\frac{\partial H}{\partial T} \right)_P \right)_T = \left(\frac{\partial C_{P,m}}{\partial P} \right)_T$$

Equation 3.44 states that

$$\left(\frac{\partial H}{\partial P} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_P$$

Therefore,

$$\begin{aligned} \left(\frac{\partial C_{P,m}}{\partial P} \right)_T &= \left(\frac{\partial}{\partial T} \left(V - T \left(\frac{\partial V}{\partial T} \right)_P \right) \right)_P \\ &= \left(\frac{\partial}{\partial T} \left((RT/P) + B(T) - T \left(\frac{\partial[(RT/P) + B(T)]}{\partial T} \right)_P \right) \right)_P \\ &= \left(\frac{\partial}{\partial T} \left((RT/P) + B(T) - T \left(\frac{R}{P} + \frac{dB(T)}{dT} \right)_P \right) \right)_P \\ &= \left(\frac{R}{P} + \frac{dB(T)}{dT} - \frac{R}{P} - \frac{dB(T)}{dT} + T \frac{d^2B(T)}{dT^2} \right)_P \\ &= T \frac{d^2B(T)}{dT^2} \end{aligned}$$

P3.30) Use the relation $C_{P,m} - C_{V,m} = T \left(\frac{\partial V_m}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_P$, the cyclic rule, and the van der

Waals equation of state to derive an equation for $C_{P,m} - C_{V,m}$ in terms of V_m and the gas constants R , a , and b .

We use the cyclic rule to evaluate $\left(\frac{\partial V_m}{\partial T} \right)_P$.

Chapter 3/ The Importance of State Functions: Internal Energy and Enthalpy

$$\left(\frac{\partial V_m}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_{V_m} \left(\frac{\partial P}{\partial V_m} \right)_T = -1$$

$$\left(\frac{\partial V_m}{\partial T} \right)_P = - \left(\frac{\partial P}{\partial T} \right)_{V_m} \left(\frac{\partial V_m}{\partial P} \right)_T$$

$$C_{P,m} - C_{V,m} = T \left(\frac{\partial V_m}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_{V_m} = -T \left[\left(\frac{\partial P}{\partial T} \right)_{V_m} \right]^2 \left(\frac{\partial V_m}{\partial P} \right)_T = -T \frac{\left[\left(\frac{\partial P}{\partial T} \right)_{V_m} \right]^2}{\left(\frac{\partial P}{\partial V_m} \right)_T}$$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\left(\frac{\partial P}{\partial T} \right)_{V_m} = \frac{R}{V_m - b}$$

$$\left(\frac{\partial P}{\partial V_m} \right)_T = \frac{-RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = \frac{-RTV_m^3 + 2a(V_m - b)}{V_m^3(V_m - b)^2}$$

$$C_{P,m} - C_{V,m} = -T \frac{\left(\frac{R}{V_m - b} \right)^2}{\frac{-RT}{(V_m - b)^2} + \frac{2a}{V_m^3}} = -T \frac{R}{-T + \frac{2a(V_m - b)^2}{RV_m^3}} = \frac{R}{1 - \frac{2a(V_m - b)^2}{RTV_m^3}}$$

In the ideal gas limit, $a = 0$, and $C_{P,m} - C_{V,m} = R$.

P3.31) Show that $\left(\frac{\partial U}{\partial V} \right)_T = \frac{\beta T - \kappa P}{\kappa}$.

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$$

Using the cyclic rule

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\beta}{\kappa}$$

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{T\beta}{\kappa} - P = \frac{T\beta - \kappa P}{R}$$

P3.32) Show that the expression $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ can be written in the form

$$\left(\frac{\partial U}{\partial V}\right)_T = T^2 \left(\frac{\partial [P/T]}{\partial T}\right)_V = -\left(\frac{\partial [P/T]}{\partial [1/T]}\right)_V.$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\begin{aligned} \left(\frac{\partial [P/T]}{\partial T}\right)_V &= P\left(\frac{\partial [1/T]}{\partial T}\right)_V + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V \\ &= -\frac{P}{T^2} + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V \end{aligned}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = T\left(\left(\frac{\partial [P/T]}{\partial T}\right)_V + \frac{P}{T^2}\right)$$

$$\begin{aligned} \left(\frac{\partial U}{\partial V}\right)_T &= T^2 \left(\left(\frac{\partial [P/T]}{\partial T}\right)_V + \frac{P}{T^2}\right) - P \\ &= T^2 \left(\frac{\partial [P/T]}{\partial T}\right)_V + P - P = T^2 \left(\frac{\partial [P/T]}{\partial T}\right)_V \end{aligned}$$

We now change the differentiation to the variable $1/T$.

$$\left(\frac{\partial [P/T]}{\partial T}\right)_V = \left(\frac{\partial [P/T]}{\partial [1/T]}\right)_V \left(\frac{\partial [1/T]}{\partial T}\right)_V = -\frac{1}{T^2} \left(\frac{\partial [P/T]}{\partial [1/T]}\right)_V$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T^2 \left(\frac{\partial [P/T]}{\partial T}\right)_V = T^2 \left(-\frac{1}{T^2} \frac{\partial [P/T]}{\partial [1/T]}\right)_V = -\left(\frac{\partial [P/T]}{\partial [1/T]}\right)_V$$

Questions on Concepts

Q4.1) Under what conditions are ΔH and ΔU for a reaction involving gases and/or liquids or solids identical?

$\Delta H = \Delta U + \Delta(PV)$. $\Delta H \approx \Delta U$ for reactions involving only liquids or solids because, to a good approximation, the volume does not change as a result of the reaction. If gases are uninvolved, $\Delta(PV) = \Delta nRT$. Therefore, $\Delta H \approx \Delta U$ if the number of moles of reactants and products that are gases are the same.

Q4.2) If ΔH_f° for the chemical compounds involved in a reaction are available at a given temperature, how can the reaction enthalpy be calculated at another temperature?

The reaction enthalpy can be calculated to high accuracy at another temperature can be calculated only if the heat capacities of all reactants and products are known using

$$\Delta H_T^\circ = \Delta H_{298.15K}^\circ + \int_{298.15K}^T \Delta C_p(T') dT'$$
. If the heat capacities of reactants and products are similar, the reaction enthalpy will not vary greatly over a limited temperature range.

Q4.3) Does the enthalpy of formation of compounds containing a certain element change if the enthalpy of formation of the element under standard state conditions is set equal to 100 kJ mol⁻¹ rather than to zero? If it changes, how will it change for the compound A_nB_m if the formation enthalpy of element A is set equal to 100 kJ mol⁻¹?

Yes, because part of the enthalpy change of the reaction will be attributed to the element. For the reaction $nA + mB \rightarrow A_nB_m$,

$$\begin{aligned}\Delta H_{reaction}^\circ &= \Delta H_f^\circ(A_nB_m) - n\Delta H_f^\circ(A) - m\Delta H_f^\circ(B) \\ \Delta H_f^\circ(A_nB_m) &= \Delta H_{reaction}^\circ + n\Delta H_f^\circ(A) + m\Delta H_f^\circ(B)\end{aligned}$$

Therefore $\Delta H_f^\circ(A_nB_m)$ for the compound will increase by $100n$ kJ mol⁻¹.

Q4.4) Is the enthalpy for breaking the first C-H bond in methane equal to the average C-H bond enthalpy in this molecule? Explain your answer.

No. The average bond enthalpy is the average of the enthalpies of the four steps leading to complete dissociation. The enthalpy of each successive dissociation step will increase.

Q4.5) Why is it valid to add the enthalpies of any sequence of reactions to obtain the enthalpy of the reaction that is the sum of the individual reactions?

Because H is a state function, any path between the reactants and products, regardless of which intermediate products are involved, has the same value for ΔH .

Q4.6) The reactants in the reaction $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$ are initially at 298 K. Why is the reaction enthalpy the same if the reaction is (a) constantly kept at 298 K or (b) if the reaction temperature is not controlled and the heat flow to the surroundings is measured only after the temperature of the products is returned to 298 K?

Q4.7) In calculating $\Delta H_{\text{reaction}}^\circ$ at 285.15 K, only the ΔH_f° of the compounds that take part in the reactions listed in Tables 4.1 and 4.2 (Appendix A, Data Tables) are needed. Is this statement also true if you want to calculate $\Delta H_{\text{reaction}}^\circ$ at 500 K?

No. At any temperature other than 298.15 K, the heat capacities of all elements and compounds that appear in the overall reaction enter into the calculation.

Q4.8) What is the point of having an outer water bath in a bomb calorimeter (see Figure 4.3), especially if its temperature is always equal to that of the inner water bath?

This water bath effectively isolates the calorimeter and the inner water bath from the rest of the universe. Because the temperatures of the water baths are the same, there is no heat flow between them. Because the container of the inner water bath has rigid walls, no work is done on the composite system consisting of the calorimeter and the inner water bath. Therefore, the calorimeter and inner water bath form an isolated composite system.

Q4.9) What is the advantage of a differential scanning calorimeter over a bomb calorimeter in determining the enthalpy of fusion of a series of samples?

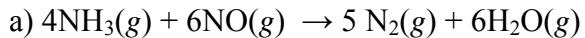
All the samples can be measured in parallel, rather than sequentially. This reduces both the measurement time, and the possibility of errors.

Q4.10) You wish to measure the heat of solution of NaCl in water. Would the calorimetric technique of choice be at constant pressure or constant volume? Why? Constant pressure calorimetry is the technique of choice because none of the reactants or products is gaseous, and it is therefore not necessary to contain the reaction. Constant pressure calorimetry is much easier to carry out than constant volume calorimetry.

Problems

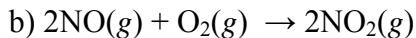
P4.1) Calculate $\Delta H_{\text{reaction}}^\circ$ and $\Delta U_{\text{reaction}}^\circ$ at 298.15 K for the following reactions.

- $4\text{NH}_3(g) + 6\text{NO}(g) \rightarrow 5\text{N}_2(g) + 6\text{H}_2\text{O}(g)$
- $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$
- $\text{TiCl}_4(l) + 2\text{H}_2\text{O}(l) \rightarrow \text{TiO}_2(s) + 4\text{HCl}(g)$
- $2\text{NaOH}(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{Na}_2\text{SO}_4(s) + 2\text{H}_2\text{O}(l)$
- $\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3\text{H}_2(g)$



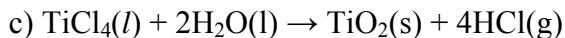
$$\begin{aligned}\Delta H_{\text{reaction}}^{\circ} &= 5\Delta H_f^{\circ}(\text{N}_2, g) + 6\Delta H_f^{\circ}(\text{H}_2\text{O}, g) - 4\Delta H_f^{\circ}(\text{NH}_3, g) - 6\Delta H_f^{\circ}(\text{NO}, g) \\ &= 0 - 6 \times 241.8 \text{ kJ mol}^{-1} + 4 \times 45.9 \text{ kJ mol}^{-1} - 6 \times 91.3 \text{ kJ mol}^{-1} \\ &= -1815.0 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta U_{\text{reaction}}^{\circ} &= \Delta H_{\text{reaction}}^{\circ} - \Delta nRT \\ &= -1815.0 \text{ kJ mol}^{-1} - 8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298.15 \text{ K} = -1817.5 \text{ kJ mol}^{-1}\end{aligned}$$



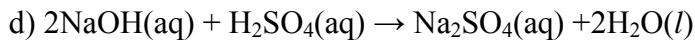
$$\begin{aligned}\Delta H_{\text{reaction}}^{\circ} &= 2\Delta H_f^{\circ}(\text{NO}_2, g) - \Delta H_f^{\circ}(\text{O}_2, g) - 2\Delta H_f^{\circ}(\text{NO}, g) \\ &= 2 \times 33.2 \text{ kJ mol}^{-1} - 0 - 2 \times 91.3 \text{ kJ mol}^{-1} \\ &= -116.2 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta U_{\text{reaction}}^{\circ} &= \Delta H_{\text{reaction}}^{\circ} - \Delta nRT \\ &= -116.2 \text{ kJ mol}^{-1} + 8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298.15 \text{ K} = -113.7 \text{ kJ mol}^{-1}\end{aligned}$$



$$\begin{aligned}\Delta H_{\text{reaction}}^{\circ} &= \Delta H_f^{\circ}(\text{TiO}_2, s) + 4\Delta H_f^{\circ}(\text{HCl}, g) - \Delta H_f^{\circ}(\text{TiCl}_4, l) - 2\Delta H_f^{\circ}(\text{H}_2\text{O}, l) \\ &= -944 - 4 \times 92.3 \text{ kJ mol}^{-1} + 804.2 \text{ kJ mol}^{-1} + 2 \times 285.8 \text{ kJ mol}^{-1} \\ &= 62.6 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta U_{\text{reaction}}^{\circ} &= \Delta H_{\text{reaction}}^{\circ} - \Delta nRT \\ &= 62.6 \text{ kJ mol}^{-1} - 4 \times 8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298.15 \text{ K} = 52.7 \text{ kJ mol}^{-1}\end{aligned}$$

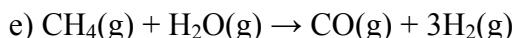


Assume that NaOH(aq) and $\text{H}_2\text{SO}_4(\text{aq})$ are completely dissociated.

The overall reaction is $2\text{OH}^-(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow 2\text{H}_2\text{O}(l)$

$$\begin{aligned}\Delta H_{\text{reaction}}^{\circ} &= 2\Delta H_f^{\circ}(\text{H}_2\text{O}, l) - 2\Delta H_f^{\circ}(\text{H}^+, \text{aq}) - 2\Delta H_f^{\circ}(\text{OH}^-, \text{aq}) \\ &= -2 \times 285.8 \text{ kJ mol}^{-1} - 0 + 2 \times 230.0 \text{ kJ mol}^{-1} \\ &= -111.6 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta U_{\text{reaction}}^{\circ} &= \Delta H_{\text{reaction}}^{\circ} - \Delta nRT \\ &= -111.6 \text{ kJ mol}^{-1} - 0 = -111.6 \text{ kJ mol}^{-1}\end{aligned}$$



$$\begin{aligned}\Delta H_{\text{reaction}}^{\circ} &= \Delta H_f^{\circ}(\text{CO}, g) + 3\Delta H_f^{\circ}(\text{H}_2, g) - \Delta H_f^{\circ}(\text{CH}_4, g) - \Delta H_f^{\circ}(\text{H}_2\text{O}, g) \\ &= -110.5 \text{ kJ mol}^{-1} + 0 + 74.6 \text{ kJ mol}^{-1} + 241.8 \text{ kJ mol}^{-1} \\ &= 205.9 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta U_{\text{reaction}}^{\circ} &= \Delta H_{\text{reaction}}^{\circ} - \Delta nRT \\ &= 205.9 \text{ kJ mol}^{-1} - 2 \times 8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 298.15 \text{ K} = 200.9 \text{ kJ mol}^{-1}\end{aligned}$$

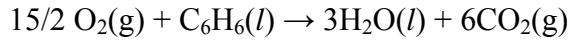


$$\begin{aligned}\Delta H_{\text{reaction}}^{\circ} &= \Delta H_f^{\circ}(\text{CH}_3\text{COOH}, l) - \Delta H_f^{\circ}(\text{CH}_3\text{OH}, g) - \Delta H_f^{\circ}(\text{CO}, g) \\ &= -484.3 \text{ kJ mol}^{-1} + 201.0 \text{ kJ mol}^{-1} + 110.5 \text{ kJ mol}^{-1} \\ &= -172.8 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta U_{\text{reaction}}^{\circ} &= \Delta H_{\text{reaction}}^{\circ} - \Delta nRT \\ &= -172.8 \text{ kJ mol}^{-1} + 2 \times 8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 298.15 \text{ K} = -167.8 \text{ kJ mol}^{-1}\end{aligned}$$

P4.2) Calculate $\Delta H_{\text{reaction}}^{\circ}$ and $\Delta U_{\text{reaction}}^{\circ}$ for the total oxidation of benzene. Also calculate

$$\frac{\Delta H_{\text{reaction}}^{\circ} - \Delta U_{\text{reaction}}^{\circ}}{\Delta H_{\text{reaction}}^{\circ}}.$$



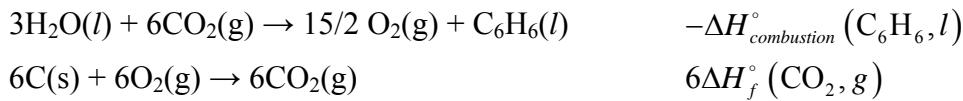
From the data tables,

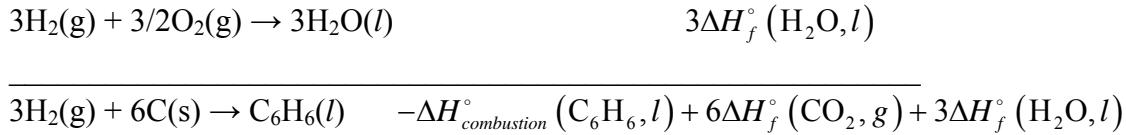
$$\begin{aligned}\Delta H_{\text{combustion}}^{\circ} &= 3\Delta H_f^{\circ}(\text{H}_2\text{O}, l) + 6\Delta H_f^{\circ}(\text{CO}_2, g) - \Delta H_f^{\circ}(\text{C}_6\text{H}_6, l) \\ &= -3 \times 285.8 \text{ kJ mol}^{-1} - 6 \times 393.5 \text{ kJ mol}^{-1} - 49.1 \text{ kJ mol}^{-1} \\ &= 3268 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta U_{\text{reaction}}^{\circ} &= \Delta H_{\text{reaction}}^{\circ} - \Delta nRT = -3268 \text{ kJ mol}^{-1} + 1.5 \times 8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298.15 \text{ K} \\ &= -3264 \text{ kJ mol}^{-1}\end{aligned}$$

$$\frac{\Delta H_{\text{reaction}}^{\circ} - \Delta U_{\text{reaction}}^{\circ}}{\Delta H_{\text{reaction}}^{\circ}} = \frac{-3268 \text{ kJ mol}^{-1} + 3264 \text{ kJ mol}^{-1}}{-3268 \text{ kJ mol}^{-1}} = 0.0122$$

P4.3) Use the tabulated values of the enthalpy of combustion of benzene and the enthalpies of formation of $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ to determine ΔH_f° for benzene.





$$\begin{aligned}\Delta H_f^\circ(\text{C}_6\text{H}_6, l) &= 3268 \text{ kJ mol}^{-1} - 6 \times 393.5 \text{ kJ mol}^{-1} - 3 \times 285.8 \text{ kJ mol}^{-1} \\ &= 49.6 \text{ kJ mol}^{-1}\end{aligned}$$

P4.4) Calculate ΔH for the process in which $\text{N}_2(\text{g})$ initially at 298.15 K at 1 bar is heated to 650 K at 1 bar. Use the temperature dependent heat capacities in the data tables. How large is the relative error if the molar heat capacity is assumed to be constant at its value of 298.15 K over the temperature interval?

$$\begin{aligned}\Delta H^\circ(\text{N}_2, g, 298.15 \text{ K} \rightarrow \text{N}_2, g, 650 \text{ K}) &= \Delta H_f^\circ(\text{N}_2, g, 298.15 \text{ K}) + \int_{298.15}^{650} C_{P,m} \left(\frac{T}{\text{K}} \right) d \frac{T}{\text{K}} \\ &= \left[\int_{298.15}^{650} \left(30.81 - 0.01187 \frac{T}{\text{K}} + 2.3968 \times 10^{-5} \frac{T^2}{\text{K}^2} - 1.0176 \times 10^{-8} \frac{T^3}{\text{K}^3} \right) d \frac{T}{\text{K}} \right] \text{J K}^{-1} \text{mol}^{-1} \\ &= (10841 - 1980 + 1982 - 434.0) \text{ J mol}^{-1} = 10.41 \text{ kJ mol}^{-1}\end{aligned}$$

If it is assumed that the heat capacity is constant at its value at 298 K,

$$\Delta H^\circ \approx \left[\int_{298.15}^{650} (29.13) d \frac{T}{\text{K}} \right] \text{J K}^{-1} \text{mol}^{-1} = 10.25 \text{ kJ mol}^{-1}$$

$$\text{Error} = 100 \times \frac{10.25 \text{ kJ mol}^{-1} - 10.41 \text{ kJ mol}^{-1}}{10.41 \text{ kJ mol}^{-1}} = -1.54\%$$

P4.5) The standard reaction enthalpies at 25°C for the following reactions are given below.

	$\Delta H_{\text{reaction}}^\circ (\text{kJ mol}^{-1})$
$\text{CaC}_2(\text{s}) + 2\text{H}_2\text{O}(l) \rightarrow \text{Ca}(\text{OH})_2(\text{s}) + \text{C}_2\text{H}_2(\text{g})$	-127.9
$\text{Ca}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CaO}(\text{s})$	-635.1
$\text{CaO}(\text{s}) + \text{H}_2\text{O}(l) \rightarrow \text{Ca}(\text{OH})_2(\text{s})$	-65.2

The standard enthalpy of combustion of graphite and $\text{C}_2\text{H}_2(\text{g})$ are $-393.51 \text{ kJ mol}^{-1}$ and $-1299.58 \text{ kJ mol}^{-1}$ respectively. Calculate the standard enthalpy of formation of $\text{CaC}_2(\text{s})$ at 25°C.

	$\Delta H_{\text{reaction}}^\circ (\text{kJ mol}^{-1})$
$\text{Ca}(\text{OH})_2(\text{s}) + \text{C}_2\text{H}_2(\text{g}) \rightarrow \text{CaC}_2(\text{s}) + 2\text{H}_2\text{O}(l)$	+127.9
$\text{CaO}(\text{s}) + \text{H}_2\text{O}(l) \rightarrow \text{Ca}(\text{OH})_2(\text{s})$	-65.2
$2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(l) \rightarrow \text{C}_2\text{H}_2(\text{s}) + 5/2\text{O}_2(\text{s})$	1299.58
$2\text{C}(\text{s}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$	$2 \times (-393.51)$
$\text{Ca}(\text{s}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{CaO}(\text{s})$	-635.1



P4.6) From the following data at 25°C

	$\Delta H_{reaction}^\circ (\text{kJ mol}^{-1})$
$\text{Fe}_2\text{O}_3(s) + 3\text{C(graphite)} \rightarrow 2\text{Fe}(s) + 3\text{CO}(g)$	492.6
$\text{FeO}(s) + \text{C(graphite)} \rightarrow \text{Fe}(s) + \text{CO}(g)$	155.8
$\text{C(graphite)} + \text{O}_2(g) \rightarrow \text{CO}_2(g)$	-393.51
$\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g)$	-282.98

Calculate the standard enthalpy of formation of $\text{FeO}(s)$ and of $\text{Fe}_2\text{O}_3(s)$.

	$\Delta H_{reaction}^\circ (\text{kJ mol}^{-1})$
$\text{Fe}(s) + \text{CO}(g) \rightarrow \text{FeO}(s) + \text{C(graphite)}$	-155.8
$\text{CO}_2(s) \rightarrow \text{CO}(g) + \frac{1}{2}\text{O}_2(g)$	282.98
$\text{C(graphite)} + \text{O}_2(g) \rightarrow \text{CO}_2(g)$	-393.51

$\text{Fe}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{FeO}(s)$	$\Delta H_f^\circ = -266.3 \text{ kJ mol}^{-1}$
	$\Delta H_{reaction}^\circ (\text{kJ mol}^{-1})$
$2\text{Fe}(g) + 3\text{CO}(g) \rightarrow \text{Fe}_2\text{O}_3(s) + 3\text{C(graphite)}$	-492.6
$3\text{C(graphite)} + 3\text{O}_2(g) \rightarrow 3\text{CO}_2(g)$	-3×393.51
$3\text{CO}_2(g) \rightarrow 3\text{CO}(g) + \frac{3}{2}\text{O}_2(g)$	3×282.98
$2\text{Fe}(g) + \frac{3}{2}\text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3(s)$	$\Delta H_f^\circ = -824.2 \text{ kJ mol}^{-1}$

P4.7) Calculate ΔH_f° for $\text{NO}(g)$ at 840 K assuming that the heat capacities of reactants and products are constant over the temperature interval at their values at 298.15 K.

$$\Delta H_f^\circ(\text{NO}, g, 840\text{K}) = \Delta H_f^\circ(\text{NO}, g, 298.15\text{K}) + \int_{298.15}^{650} \Delta C_p \left(\frac{T}{K} \right) d \frac{T}{K}$$

$$\begin{aligned} \Delta C_p &= C_{P,m}(\text{NO}, g) - \frac{1}{2} C_{P,m}(\text{N}_2, g) - \frac{1}{2} C_{P,m}(\text{O}_2, g) \\ &= (29.86 - 0.5 \times 29.13 - 0.5 \times 29.38) \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 0.605 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta H_f^\circ(\text{NO}, g, 840\text{K}) &= \Delta H_f^\circ(\text{NO}, g, 298.15\text{K}) + \left[\int_{298.15}^{650} 0.605 d \frac{T}{K} \right] \text{ J mol}^{-1} \\ &= \Delta H_f^\circ(\text{NO}, g, 298.15\text{K}) + 0.328 \text{ kJ mol}^{-1} = 91.3 \text{ kJ mol}^{-1} + 0.328 \text{ kJ mol}^{-1} = 91.6 \text{ kJ mol}^{-1} \end{aligned}$$

P4.8) Calculate $\Delta H_{reaction}^\circ$ at 650 K for the reaction $4\text{NH}_3(\text{g}) + 6\text{NO}(\text{g}) \rightarrow 5\text{N}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$ using the temperature dependent heat capacities in the data tables.

$$\begin{aligned}\Delta H_{reaction}^\circ(650\text{K}) &= \Delta H_{reaction}^\circ(298.15\text{K}) + \int_{298.15}^{650} \Delta C_p \left(\frac{T}{\text{K}} \right) d\frac{T}{\text{K}} \\ \Delta C_p &= 5C_{P,m}(\text{N}_2, g) + 6C_{P,m}(\text{H}_2\text{O}, g) - 4C_{P,m}(\text{NH}_3, g) - 6C_{P,m}(\text{NO}, g) \\ &= \left[\begin{array}{l} (5 \times 30.81 + 6 \times 33.80 - 4 \times 29.29 - 6 \times 33.58) \\ - (5 \times 0.01187 + 6 \times 0.00795 + 4 \times 0.01103 - 6 \times 0.02593) \frac{T}{\text{K}} \\ + (5 \times 2.3968 + 6 \times 2.8228 - 4 \times 4.2446 - 6 \times 5.3326) \times 10^{-5} \frac{T^2}{\text{K}^2} \\ - (5 \times 1.0176 + 6 \times 1.3115 - 4 \times 2.7706 - 6 \times 2.7744) \times 10^{-8} \frac{T^3}{\text{K}^3} \end{array} \right] \text{J K}^{-1}\text{mol}^{-1} \\ \int_{298.15}^{650} \Delta C_p \left(\frac{T}{\text{K}} \right) d\frac{T}{\text{K}} &= \left[\begin{array}{l} 38.21 + 0.00441 \frac{T}{\text{K}} - 2.0053 \times 10^{-4} \frac{T^2}{\text{K}^2} + 1.4772 \times 10^{-8} \frac{T^3}{\text{K}^3} \end{array} \right] \text{J K}^{-1}\text{mol}^{-1} \\ &= \left[\int_{298.15}^{650} \left(38.21 + 0.00441 \frac{T}{\text{K}} - 2.0053 \times 10^{-4} \frac{T^2}{\text{K}^2} + 1.4772 \times 10^{-8} \frac{T^3}{\text{K}^3} \right) d\frac{T}{\text{K}} \right] \text{J mol}^{-1} \\ &= (13.444 - 0.736 - 16.585 + 0.630) \text{kJ mol}^{-1} = -1.775 \text{ J mol}^{-1} \\ \Delta H_{reaction}^\circ(298.15\text{K}) &= 5\Delta H_f^\circ(\text{N}_2, g) + 6\Delta H_f^\circ(\text{H}_2\text{O}, g) - 4\Delta H_f^\circ(\text{NH}_3, g) - 6\Delta H_f^\circ(\text{NO}, g) \\ \Delta H_{reaction}^\circ(298.15\text{K}) &= -6 \times 241.8 \text{ kJ mol}^{-1} + 4 \times 45.9 \text{ kJ mol}^{-1} - 6 \times 91.3 \text{ kJ mol}^{-1} = -1814 \text{ kJ mol}^{-1} \\ \Delta H_{reaction}^\circ(650\text{K}) &= -1814 \text{ kJ mol}^{-1} - 1.775 \text{ kJ mol}^{-1} = -1812 \text{ kJ mol}^{-1}\end{aligned}$$

P4.9) From the following data at 298.15 K as well as the data tables,

	$\Delta H_{reaction}^\circ(\text{kJ mol}^{-1})$
$\text{Fe}(s) + 2\text{H}_2\text{S}(\text{g}) \rightarrow \text{FeS}_2(\text{s}) + 2\text{H}_2(\text{g})$	-137.0
$\text{H}_2\text{S}(\text{g}) + 3/2 \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g})$	-562.0

calculate the standard enthalpy of formation of $\text{H}_2\text{S}(\text{g})$ and of $\text{FeS}_2(\text{s})$.

	$\Delta H_{reaction}^\circ(\text{kJ mol}^{-1})$
$\text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g}) \rightarrow \text{H}_2\text{S}(\text{g}) + 3/2 \text{O}_2(\text{g})$	562.0
$\text{S}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$	-296.8
$\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$	-285.8
<hr/>	
$\text{H}_2(\text{g}) + \text{S}(\text{s}) \rightarrow \text{H}_2\text{S}(\text{g})$	$\Delta H_f^\circ = -20.6 \text{ kJ mol}^{-1}$
<hr/>	
$\text{Fe}(\text{s}) + 2\text{H}_2\text{S}(\text{g}) \rightarrow \text{FeS}_2(\text{s}) + 2\text{H}_2(\text{g})$	$\Delta H_{reaction}^\circ(\text{kJ mol}^{-1})$
	-137.0

$2\text{H}_2(g) + 2\text{S}(s) \rightarrow 2\text{H}_2\text{S}(g)$	-2×20.6
$\text{Fe}(s) + 2\text{S}(s) \rightarrow \text{FeS}_2(s)$	$\Delta H_f^\circ = -178.2 \text{ kJ mol}^{-1}$

P4.10) Calculate the average C-H bond enthalpy in methane using the data tables. Calculate the percent error in equating C-H bond energy in Table 4.3 with the bond enthalpy.

$$\begin{aligned}\text{CH}_4(\text{g}) &\rightarrow \text{C}(\text{g}) + 4\text{H}(\text{g}) \\ \Delta H_{\text{reaction}}^\circ &= 4\Delta H_f^\circ(\text{H}, \text{g}) + \Delta H_f^\circ(\text{C}, \text{g}) - \Delta H_f^\circ(\text{CH}_4, \text{g}) \\ &= 4 \times 218.0 \text{ kJ mol}^{-1} + 716.7 \text{ kJ mol}^{-1} + 74.6 \text{ kJ mol}^{-1} = 1663 \text{ kJ mol}^{-1} \\ \text{Average Bond Enthalpy} &= \frac{1663 \text{ kJ mol}^{-1}}{4} = 415.8 \text{ kJ mol}^{-1} \\ \text{Relative Error} &= 100 \times \frac{415.8 \text{ kJ mol}^{-1} - 411 \text{ kJ mol}^{-1}}{415.8 \text{ kJ mol}^{-1}} = 1.2\%\end{aligned}$$

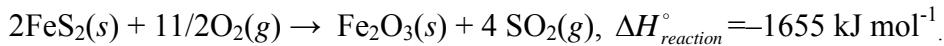
P4.11) Use the average bond energies in Table 4.3 to estimate $\Delta U_{\text{reaction}}^\circ$ for the reaction $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$. Also calculate $\Delta U_{\text{reaction}}$ from the tabulated values of ΔH_f° for reactants and products (Appendix A, Data Tables). Calculate the percent error in estimating $\Delta U_{\text{reaction}}$ from the average bond energies for this reaction.

$$\begin{aligned}\Delta U_{\text{reaction}} &= -(C-C \text{ bond energy} + 6 \text{ C-H bond energy} - H-H \text{ bond energy} - C=C \text{ bond energy} - 4 \text{ C-H bond energy}) \\ \Delta U_{\text{reaction}} &= -(346 \text{ kJ mol}^{-1} + 6 \times 411 \text{ kJ mol}^{-1} - 432 \text{ kJ mol}^{-1} - 602 \text{ kJ mol}^{-1} \\ &\quad - 4 \times 411 \text{ kJ mol}^{-1}) = -134 \text{ kJ mol}^{-1}.\end{aligned}$$

Using the data tables,

$$\begin{aligned}\Delta H_{\text{reaction}}^\circ(298.15 \text{ K}) &= \Delta H_f^\circ(\text{C}_2\text{H}_6, \text{g}) - \Delta H_f^\circ(\text{C}_2\text{H}_4, \text{g}) - \Delta H_f^\circ(\text{H}_2, \text{g}) \\ \Delta H_{\text{reaction}}^\circ(298.15 \text{ K}) &= -84.0 \text{ kJ mol}^{-1} - 52.4 \text{ kJ mol}^{-1} = -136.4 \text{ kJ mol}^{-1} \\ \Delta U_{\text{reaction}}^\circ(298.15 \text{ K}) &= \Delta H_{\text{reaction}}^\circ(298.15 \text{ K}) - \Delta nRT \\ &= -136.4 \text{ kJ mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = -133.9 \text{ kJ mol}^{-1} \\ \text{Relative Error} &= 100 \times \frac{+134 \text{ kJ mol}^{-1} - 133.9 \text{ kJ mol}^{-1}}{-133.9 \text{ kJ mol}^{-1}} \approx 0\%\end{aligned}$$

P4.12) Calculate the standard enthalpy of formation of $\text{FeS}_2(\text{s})$ at 300°C from the data below at 25°C and from the information that for the reaction



Assume that the heat capacities are independent of temperature.

Substance	Fe(s)	FeS ₂ (s)	Fe ₂ O ₃ (s)	S(rhombic)	SO ₂ (g)
ΔH_f° (kJ mol ⁻¹)			-824.2		-296.81
$C_{P,m}/R$	3.02	7.48		2.72	

$$\begin{aligned}\Delta H_{reaction}^\circ &= \Delta H_f^\circ(\text{Fe}_2\text{O}_3, s) + 4 \Delta H_f^\circ(\text{SO}_2, g) - 2 \Delta H_f^\circ(\text{FeS}_2, s) \\ &= -824.2 \text{ kJ mol}^{-1} - 1655 \text{ kJ mol}^{-1} - 1655 \text{ kJ mol}^{-1} - 1655 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}2\text{FeS}_2(\text{s}) + 11/2\text{O}_2(\text{g}) &\rightarrow \text{Fe}_2\text{O}_3(\text{s}) + 4\text{SO}_2(\text{g}) \quad \Delta H_{reaction}^\circ = -1655 \text{ kJ mol}^{-1} \\ -1655 \text{ kJ mol}^{-1} &= \Delta H_f^\circ(\text{Fe}_2\text{O}_3, s) + 4 \Delta H_f^\circ(\text{SO}_2, g) - 2 \Delta H_f^\circ(\text{Fe}_2\text{S}_2, s) \\ \Delta H_f^\circ(\text{Fe}_2\text{S}_2, s, 298 \text{ K}) &= \frac{1655 \text{ kJ mol}^{-1} + \Delta H_f^\circ(\text{Fe}_2\text{O}_3, s) + 4 \Delta H_f^\circ(\text{SO}_2, g)}{2} \\ &= \frac{1655 - 824.2 - 4 \times 296.81 \text{ kJ mol}^{-1}}{2} \\ &= -178.2 \text{ kJ mol}^{-1}\end{aligned}$$

The enthalpy of formation at 300° C is given by

$$\Delta H_f^\circ(\text{FeS}_2(\text{s}), 573 \text{ K}) - \Delta H_f^\circ(\text{FeS}_2(\text{s}), 298 \text{ K}) + \int_{298 \text{ K}}^{573 \text{ K}} \Delta C_p(T) dT$$

Because the heat capacities are assumed to be independent of T,

$$\begin{aligned}\Delta H_f^\circ(\text{FeS}_2(\text{s}), 573 \text{ K}) &= \Delta H_f^\circ(\text{FeS}_2(\text{s}), 298 \text{ K}) \\ &+ [C_{P,m}(\text{FeS}_2, s) - C_{P,m}(\text{Fe}, s) - 2C_{P,m}(\text{S}, s)][573 \text{ K} - 298 \text{ K}] \\ &= -178.2 \text{ kJ mol}^{-1} + 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times (7.48 - 3.02 - 2 \times 2.70) \times [573 \text{ K} - 298 \text{ K}] \\ &= -180.0 \text{ kJ mol}^{-1}\end{aligned}$$

P4.13) At 1000 K, $\Delta H_{reaction}^\circ = -123.77 \text{ kJ mol}^{-1}$ for the reaction

$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$. $C_{P,m} = 3.502R$, $3.466R$, and $4.217R$ for $\text{N}_2(\text{g})$, $\text{H}_2(\text{g})$, and $\text{NH}_3(\text{g})$, respectively. Calculate ΔH_f° of $\text{NH}_3(\text{g})$ at 300 K from this information. Assume that the heat capacities are independent of temperature.

$$\Delta H_{reaction}^\circ(300 \text{ K}) = \Delta H_{reaction}^\circ(1000 \text{ K}) + \int_{1000 \text{ K}}^{300 \text{ K}} \Delta C_p(T) dT$$

For this problem, the heat capacities are assumed to be independent of T.

$$\begin{aligned}
\Delta H_{reaction}^\circ(300 \text{ K}) &= \Delta H_{reaction}^\circ(1000 \text{ K}) + \Delta C_p \Delta T \\
&= -123.77 \text{ kJ mol}^{-1} + [2C_{P,m}(\text{NH}_3, g) - C_{P,m}(\text{N}_2g) - 3C_{P,m}(\text{H}_2, g)][-700 \text{ K}] \\
&= -123.77 \text{ kJ mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times [2 \times 4.217 - 3.502 - 3 \times 3.466][-700 \text{ K}] \\
&= -91.96 \text{ kJ mol}^{-1} \\
\Delta H_f^\circ(\text{NH}_3, g) &= 1/2 \Delta H_{reaction}^\circ(300 \text{ K}) = -45.98 \text{ kJ mol}^{-1}
\end{aligned}$$

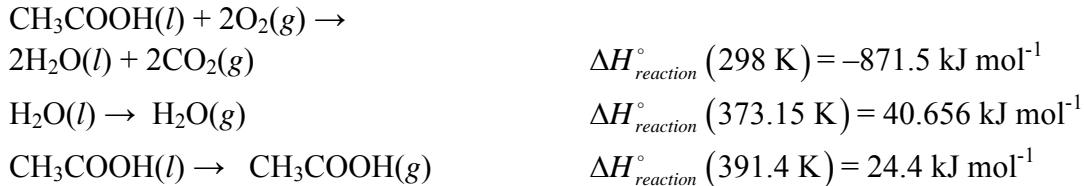
P4.14) At 298 K, $\Delta H_{reaction}^\circ = 131.28 \text{ kJ mol}^{-1}$ for the reaction $\text{C(graphite)} + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + \text{H}_2(g)$. $C_{P,m} = 8.53, 33.58, 29.12$, and $28.82 \text{ J K}^{-1} \text{ mol}^{-1}$ for graphite, $\text{H}_2\text{O}(g)$, $\text{CO}(g)$, and $\text{H}_2(g)$, respectively. Calculate $\Delta H_{reaction}^\circ$ at 125°C from this information. Assume that the heat capacities are independent of temperature.

$$\Delta H_{reaction}^\circ(398 \text{ K}) = \Delta H_{reaction}^\circ(298 \text{ K}) + \int_{298 \text{ K}}^{398 \text{ K}} \Delta C_p(T) dT$$

For this problem, it is assumed that the heat capacities are independent of T .

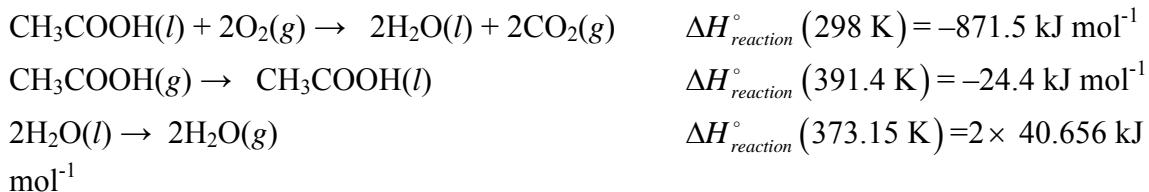
$$\begin{aligned}
\Delta H_{reaction}^\circ(398 \text{ K}) &= \Delta H_{reaction}^\circ(298 \text{ K}) \\
&+ [C_{P,m}(\text{H}_2, g) + C_{P,m}(\text{CO}, g) - C_{P,m}(\text{C, graphite}) - C_{P,m}(\text{H}_2\text{O}, g)] \Delta T \\
&= 131.28 \text{ kJ mol}^{-1} + [28.82 + 29.12 - 8.53 - 33.58] \text{ J mol}^{-1} \text{ K}^{-1} \times 100 \text{ K} \\
&= 132.86 \text{ kJ mol}^{-1}
\end{aligned}$$

P4.15) From the following data, calculate $\Delta H_{reaction}^\circ(391.4 \text{ K})$ for the reaction $\text{CH}_3\text{COOH}(g) + 2\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) + 2\text{CO}_2(g)$. Assume that the heat capacities are independent of temperature.



Substance	$\text{CH}_3\text{COOH}(l)$	$\text{O}_2(g)$	$\text{CO}_2(g)$	$\text{H}_2\text{O}(l)$	$\text{H}_2\text{O}(g)$
$C_{P,m}/R$	14.9	3.53	4.46	9.055	4.038

The desired overall reaction can be related to the individual reactions for which the data are given as follows:



To obtain $\Delta H_{reaction}^\circ(391.4 \text{ K})$, all individual reaction enthalpies must be calculated at 391.4 K.

For the reaction $2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2\text{O}(g)$

$$\begin{aligned} \Delta H_{reaction}^\circ(391.4 \text{ K}) &= \Delta H_{reaction}^\circ(373.15 \text{ K}) + [C_{P,m}(\text{H}_2\text{O}(g)) - C_{P,m}(\text{H}_2\text{O}(l))] \Delta T \\ &= 40.65 \text{ kJ mol}^{-1} + 8.314 \text{ J K}^{-1} \text{ mol}^{-1} [4.038 - 9.055] \times [391.4 \text{ K} - 373.15 \text{ K}] \\ &= 39.89 \text{ kJ mol}^{-1} \end{aligned}$$

For the reaction $\text{CH}_3\text{COOH}(l) + 2\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l) + 2\text{CO}_2(g)$

$$\begin{aligned} \Delta H_{reaction}^\circ(391.4 \text{ K}) &= \Delta H_{reaction}^\circ + \Delta C_P \Delta T \\ &= -871.5 \text{ kJ mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} [2 \times 4.46 + 2 \times 9.055 - 14.9 - 2 \times 3.53] \times [391.4 \text{ K} - 298 \text{ K}] \\ &= -867.6 \text{ kJ mol}^{-1} \end{aligned}$$

The table above can now be rewritten with all enthalpy values given at 391.4 K.

	$\Delta H_{reaction}^\circ(391.4 \text{ K}) (\text{kJ mol}^{-1})$
$\text{CH}_3\text{COOH}(l) + 2\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l) + 2\text{CO}_2(g)$	-867.6 kJ mol ⁻¹
$\text{CH}_3\text{COOH}(g) \rightarrow \text{CH}_3\text{COOH}(l)$	-24.4 kJ mol ⁻¹
$2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2\text{O}(g)$	$2 \times 39.89 \text{ kJ mol}^{-1}$
<hr/>	
$\text{CH}_3\text{COOH}(g) + 2\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) + 2\text{CO}_2(g)$	$\Delta H_{reaction}^\circ = -812.2 \text{ kJ mol}^{-1}$

P4.16) Consider the reaction

$\text{TiO}_2(s) + 2 \text{C(graphite)} + 2 \text{Cl}_2(g) \rightarrow 2 \text{CO}(g) + \text{TiCl}_4(l)$ for which $\Delta H_{reaction}^\circ(298 \text{ K}) = -80.01 \text{ kJ mol}^{-1}$. Given the following data at 25°C,

Substance	$\text{TiO}_2(s)$	$\text{Cl}_2(g)$	C(graphite)	$\text{CO}(g)$	$\text{TiCl}_4(l)$
$\Delta H_f^\circ (\text{kJ mol}^{-1})$	-945			-110.5	
$C_{P,m} (\text{J K}^{-1} \text{ mol}^{-1})$	55.06	33.91	8.53	29.12	145.2

a) Calculate $\Delta H_{reaction}^\circ$ at 135.8°C, the boiling point of TiCl_4 .

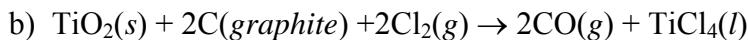
b) Calculate ΔH_f° for $\text{TiCl}_4(l)$ at 25°C.

Assume that the heat capacities are independent of temperature.

$$\text{a) } \Delta H_{\text{reaction}}^{\circ}(409.0 \text{ K}) = \Delta H_{\text{reaction}}^{\circ}(298 \text{ K}) + \int_{298 \text{ K}}^{409.0 \text{ K}} \Delta C_{P,m} dT$$

In this case, the heat capacities are assumed to be independent of T.

$$\begin{aligned}\Delta H_{\text{reaction}}^{\circ}(409.0 \text{ K}) &= \Delta H_{\text{reaction}}^{\circ}(298 \text{ K}) + \Delta C_{P,m} [409.0 \text{ K} - 298 \text{ K}] \\ &= -80.1 \text{ kJ mol}^{-1} + [C_{P,m}(\text{TiCl}_4, l) + 2C_{P,m}(\text{CO}, g) - C_{P,m}(\text{TiO}_2, s) \\ &\quad - 2C_{P,m}(\text{graphite}, s) - 2C_{P,m}(\text{Cl}_2, g)] [409.0 \text{ K} - 298 \text{ K}] \\ &= -80.01 \text{ kJ mol}^{-1} + [145.2 + 2 \times 29.12 - 55.06 - 2 \times 8.53 - 2 \times 33.91] [409.0 \text{ K} - 298 \text{ K}] \\ &= -73.0 \text{ kJ mol}^{-1}\end{aligned}$$



$$\begin{aligned}\Delta H_{\text{reaction}}^{\circ} &= -80.01 \text{ kJ mol}^{-1} = 2\Delta H_f^{\circ}(\text{CO}, g) + \Delta H_f^{\circ}(\text{TiCl}_4, l) - \Delta H_f^{\circ}(\text{TiO}_2, s) \\ \Delta H_f^{\circ}(\text{TiCl}_4, l) &= \Delta H_f^{\circ}(\text{TiO}_2, s) - 2\Delta H_f^{\circ}(\text{CO}, g) - 80.01 \text{ kJ mol}^{-1} \\ &= -945 \text{ kJ mol}^{-1} + 2 \times 110.5 \text{ kJ mol}^{-1} - 80.01 \text{ kJ mol}^{-1} \\ &= -804 \text{ kJ mol}^{-1}\end{aligned}$$

P4.17) From the following data at 25°C

$\frac{1}{2} \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{OH}(g)$	$\Delta H_{\text{reaction}}^{\circ} = 38.95 \text{ kJ mol}^{-1}$
$\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(g)$	$\Delta H_{\text{reaction}}^{\circ} = -241.814 \text{ kJ mol}^{-1}$
$\text{H}_2(g) \rightarrow 2\text{H}(g)$	$\Delta H_{\text{reaction}}^{\circ} = 435.994 \text{ kJ mol}^{-1}$
$\text{O}_2(g) \rightarrow 2\text{O}(g)$	$\Delta H_{\text{reaction}}^{\circ} = 498.34 \text{ kJ mol}^{-1}$

Calculate $\Delta H_{\text{reaction}}^{\circ}$ for

- a) $\text{OH}(g) \rightarrow \text{H}(g) + \text{O}(g)$
- b) $\text{H}_2\text{O}(g) \rightarrow 2\text{H}(g) + \text{O}(g)$
- c) $\text{H}_2\text{O}(g) \rightarrow \text{H}(g) + \text{OH}(g)$

Assuming ideal gas behavior, calculate $\Delta H_{\text{reaction}}^{\circ}$ and $\Delta U_{\text{reaction}}^{\circ}$ for all three reactions.

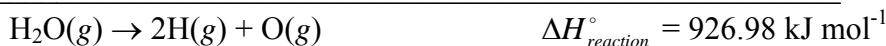
a)

	$\Delta H_{\text{reaction}}^{\circ} (\text{kJ mol}^{-1})$
$\text{OH}(g) \rightarrow \frac{1}{2} \text{H}_2(g) + \frac{1}{2} \text{O}_2(g)$	-38.95
$\frac{1}{2} \text{H}_2(g) \rightarrow \text{H}(g)$	$\frac{1}{2} \times 435.994$
$\frac{1}{2} \text{O}_2(g) \rightarrow \text{O}(g)$	$\frac{1}{2} \times 498.34$



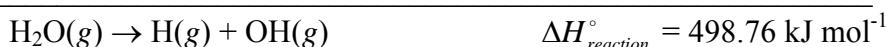
$$\begin{aligned}\Delta U_{\text{reaction}}^{\circ} &= \Delta H_{\text{reaction}}^{\circ} - \Delta nRT \\ &= 428.22 \text{ kJ mol}^{-1} - 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 425.74 \text{ kJ mol}^{-1}\end{aligned}$$

b)	$\Delta H_{\text{reaction}}^{\circ} (\text{kJ mol}^{-1})$
$\text{H}_2\text{O}(g) \rightarrow \text{H}_2(g) + 1/2\text{O}_2(g)$	241.814
$\text{H}_2(g) \rightarrow 2\text{H}(g)$	435.994
$1/2\text{O}_2(g) \rightarrow \text{O}(g)$	$1/2 \times 498.34$



$$\begin{aligned}\Delta U_{\text{reaction}}^{\circ} &= \Delta H_{\text{reaction}}^{\circ} - \Delta nRT \\ &= 926.98 \text{ kJ mol}^{-1} - 2 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 922.02 \text{ kJ mol}^{-1}\end{aligned}$$

c)	$\Delta H_{\text{reaction}}^{\circ} (\text{kJ mol}^{-1})$
$\text{H}_2\text{O}(g) \rightarrow \text{H}_2(g) + 1/2\text{O}_2(g)$	241.814
$1/2\text{H}_2(g) + 1/2\text{O}_2(g) \rightarrow \text{OH}(g)$	38.95
$1/2\text{H}_2(g) \rightarrow \text{H}(g)$	$1/2 \times 435.994$



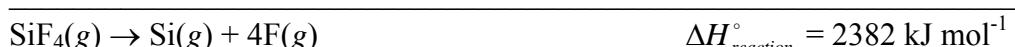
$$\begin{aligned}\Delta U_{\text{reaction}}^{\circ} &= \Delta H_{\text{reaction}}^{\circ} - \Delta nRT \\ &= 498.76 \text{ kJ mol}^{-1} - 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 498.28 \text{ kJ mol}^{-1}\end{aligned}$$

P4.18) Given the data in Table 4.1 and the following information

Substance	$\text{SiF}_4(g)$	$\text{SiCl}_4(g)$	$\text{CF}_4(g)$	$\text{NF}_3(g)$	$\text{OF}_2(g)$	$\text{HF}(g)$
$\Delta H_f^{\circ} (\text{kJ mol}^{-1})$	-1614.9	-657.0	-925	-125	-22	-271

calculate the average single bond enthalpies and energies of the following single bonds: Si-F, Si-Cl, C-F, N-F, O-F, H-F.

The average single bond enthalpy Si-F is calculated as follows:



$$\text{Average Si-F bond enthalpy in } \text{SiF}_4 = \frac{2382 \text{ kJ mol}^{-1}}{4} = 596 \text{ kJ mol}^{-1}$$

$$\Delta U^\circ = \Delta H^\circ - \Delta nRT \\ = 2382 \text{ kJ mol}^{-1} - 4 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 2372 \text{ kJ mol}^{-1}$$

$$\text{Average Si-F bond energy in } \text{SiF}_4 = \frac{2372 \text{ kJ mol}^{-1}}{4} = 593 \text{ kJ mol}^{-1}$$

Average single bond enthalpy in SiCl_4



$$\text{Average single bond enthalpy in } \text{SiCl}_4 = \frac{1592 \text{ kJ mol}^{-1}}{4} = 398 \text{ kJ mol}^{-1}$$

$$\Delta U^\circ = \Delta H^\circ - \Delta nRT \\ = 1592 \text{ kJ mol}^{-1} - 4 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 1582 \text{ kJ mol}^{-1}$$

$$\text{Average Si-Cl bond energy in } \text{SiCl}_4 = \frac{1582 \text{ kJ mol}^{-1}}{4} = 396 \text{ kJ mol}^{-1}$$

Average single bond enthalpy in CF_4



$$\text{Average single bond enthalpy in } \text{CF}_4 = \frac{1959 \text{ kJ mol}^{-1}}{4} = 489 \text{ kJ mol}^{-1}$$

$$\Delta U^\circ = \Delta H^\circ - \Delta nRT \\ = 1959 \text{ kJ mol}^{-1} - 4 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 1949 \text{ kJ mol}^{-1}$$

$$\text{Average C-F bond energy in } \text{CF}_4 = \frac{1949 \text{ kJ mol}^{-1}}{4} = 487 \text{ kJ mol}^{-1}$$

Average single bond enthalpy in NF_3



$$\text{Average single bond enthalpy in NF}_3 = \frac{836 \text{ kJ mol}^{-1}}{3} = 279 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta U^\circ &= \Delta H^\circ - \Delta nRT \\ &= 836 \text{ kJ mol}^{-1} - 3 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 828 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{Average N-F bond energy in NF}_3 = \frac{828 \text{ kJ mol}^{-1}}{3} = 276 \text{ kJ mol}^{-1}$$

Average single bond enthalpy in OF₂

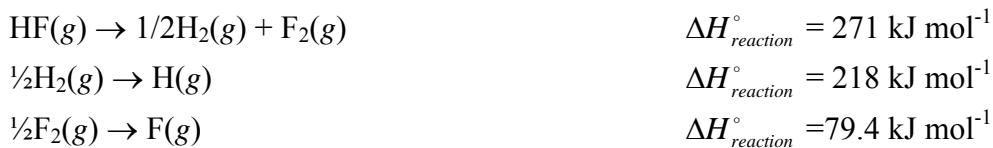


$$\text{Average single bond enthalpy in OF}_2 = \frac{430 \text{ kJ mol}^{-1}}{2} = 215 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta U^\circ &= \Delta H^\circ - \Delta nRT \\ &= 430 \text{ kJ mol}^{-1} - 2 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 425 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{Average O-F bond energy in OF}_2 = \frac{425 \text{ kJ mol}^{-1}}{2} = 213 \text{ kJ mol}^{-1}$$

Average single bond enthalpy in HF



$$\text{Average single bond enthalpy in HF} = 568 \text{ kJ mol}^{-1}$$

$$\Delta U^\circ = \Delta H^\circ - \Delta nRT$$

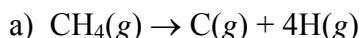
$$= 568 \text{ kJ mol}^{-1} - 1 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 565 \text{ kJ mol}^{-1}$$

Average single bond energy in HF = 565 kJ mol⁻¹

P4.19) Given the data in Table 4.3 and the Data Tables, calculate the average bond enthalpy and energy of

- a) the C–H bond in CH₄
- b) the C–C single bond in C₂H₆
- c) the C=C double bond in C₂H₄

Use your result from part a) to solve the other parts of the problem.



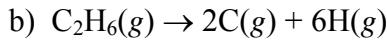
$$\begin{aligned}\Delta H_{\text{reaction}}^{\circ} &= 4\Delta H_f^{\circ}(\text{H}, g) + 4\Delta H_f^{\circ}(\text{C}, g) - 4\Delta H_f^{\circ}(\text{CH}_4, g) \\ &= 4 \times 218.0 \text{ kJ mol}^{-1} + 716.7 \text{ kJ mol}^{-1} + 74.6 \text{ kJ mol}^{-1} \\ &= 1663 \text{ kJ mol}^{-1}\end{aligned}$$

$$\text{Average C-H bond enthalpy in CH}_4 = \frac{1663 \text{ kJ mol}^{-1}}{4} = 416 \text{ kJ mol}^{-1}$$

$$\Delta U^{\circ} = \Delta H^{\circ} - \Delta nRT$$

$$= 1663 \text{ kJ mol}^{-1} - 3 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 1654 \text{ kJ mol}^{-1}$$

$$\text{Average C-H bond energy in CH}_4 = \frac{1654 \text{ kJ mol}^{-1}}{4} = 413 \text{ kJ mol}^{-1}$$



$$\begin{aligned}\Delta H_{\text{reaction}}^{\circ} &= 6\Delta H_f^{\circ}(\text{H}, g) + 2\Delta H_f^{\circ}(\text{C}, g) - \Delta H_f^{\circ}(\text{C}_2\text{H}_6, g) \\ &= 6 \times 218.0 \text{ kJ mol}^{-1} + 2 \times 716.7 \text{ kJ mol}^{-1} + 84.0 \text{ kJ mol}^{-1} \\ &= 2825 \text{ kJ mol}^{-1}\end{aligned}$$

$$\Delta H_{\text{reaction}}^{\circ} = 6 \times \text{C-H bond enthalpy} + \text{C-C bond enthalpy}$$

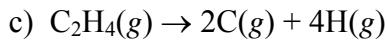
$$\begin{aligned}\text{C-C bond enthalpy} &= 2825 \text{ kJ mol}^{-1} - 6 \times 416 \text{ kJ mol}^{-1} \\ &= 329 \text{ kJ mol}^{-1}\end{aligned}$$

$$\Delta U^{\circ} = \Delta H^{\circ} - \Delta nRT$$

$$= 2825 \text{ kJ mol}^{-1} - 7 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 2808 \text{ kJ mol}^{-1}$$

$$\Delta U^{\circ} = 6 \times \text{C-H bond energy} + \text{C-C bond energy}$$

$$\begin{aligned}\text{C-C bond energy} &= 2808 \text{ kJ mol}^{-1} - 6 \times 413 \text{ kJ mol}^{-1} \\ &\approx 329 \text{ kJ mol}^{-1}\end{aligned}$$



$$\begin{aligned}\Delta H_{reaction}^{\circ} &= 2\Delta H_f^{\circ}(C, g) + 4\Delta H_f^{\circ}(H, g) - \Delta H_f^{\circ}(C_2H_4, g) \\ &= 2 \times 716.7 \text{ kJ mol}^{-1} + 4 \times 218 \text{ kJ mol}^{-1} - 52.4 \text{ kJ mol}^{-1} \\ &= 2253 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta H_{reaction}^{\circ} &= 4 \times \text{C-H bond enthalpy} + \text{C=C bond enthalpy} \\ \text{C=C bond enthalpy} &= 2253 \text{ kJ mol}^{-1} - 4 \times 416 \text{ kJ mol}^{-1} \\ &= 589 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta U^{\circ} &= \Delta H^{\circ} - \Delta nRT \\ &= 2253 \text{ kJ mol}^{-1} - 5 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 2240 \text{ kJ mol}^{-1}\end{aligned}$$

$$\Delta U^{\circ} = 4 \times \text{C-H bond energy} + \text{C=C bond energy}$$

$$\begin{aligned}\text{C-C bond energy} &= 2240 \text{ kJ mol}^{-1} - 4 \times 413 \text{ kJ mol}^{-1} \\ &= 588 \text{ kJ mol}^{-1}\end{aligned}$$

P4.20) A sample of K(s) of mass 2.140g undergoes combustion in a constant volume calorimeter. The calorimeter constant is 1849 J K⁻¹, and the measured temperature rise in the inner water bath containing 1450g of water is 2.62 K. Calculate ΔU_f° and ΔH_f° for K₂O.

$$\begin{aligned}2\text{K}(s) + \frac{1}{2}\text{O}_2(g) &\rightarrow \text{K}_2\text{O}(s) \\ \Delta U_f &= -\frac{M_s}{m_s} \left(\frac{m_{H_2O}}{M_{H_2O}} C_{H_2O,m} \Delta T + C_{calorimeter} \Delta T \right) \\ &= -\frac{39.098 \text{ g mol}^{-1}}{2.240 \text{ g}} \times \frac{2 \text{ mol K}}{1 \text{ mol reaction}} \times \left(\frac{1.450 \times 10^3 \text{ g}}{18.02 \text{ g mol}^{-1}} \times 75.291 \text{ J mol}^{-1} \text{ K}^{-1} \times 2.62 \text{ }^{\circ}\text{C}} \right. \\ &\quad \left. + 1.849 \times 10^3 \text{ J }^{\circ}\text{C}^{-1} \times 2.62 \text{ }^{\circ}\text{C} \right) \\ &= -757 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta H_f^{\circ} &= \Delta U_f^{\circ} + \Delta nRT \\ &= -757 \text{ kJ mol}^{-1} + \frac{1}{2} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} = -756 \text{ kJ mol}^{-1}\end{aligned}$$

P4.21) 1.35g of benzoic acid are reacted with oxygen in a constant volume calorimeter at 298 K to form H₂O(l) and CO₂(g). The mass of the water in the inner bath is 1.240 x 10³ g. The temperature of the calorimeter and its contents rises 3.45 K as a result of this reaction. Calculate the calorimeter constant.

$$\Delta U_{\text{combustion}} = \Delta H_{\text{combustion}} - \Delta nRT$$

For the reaction $\text{C}_6\text{H}_5\text{COOH}(s) + \frac{15}{2}\text{O}_2(g) \rightarrow 7\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$, $\Delta n = -\frac{1}{2}$

$$\Delta U_{\text{combustion}} = -3226.87 \text{ kJ mol}^{-1} - \frac{1}{2} \times 8.3145 \text{ J mol}^{-1}\text{K}^{-1} \times 298.15 \text{ K} = -3228.11 \text{ kJ mol}^{-1}$$

$$C_{\text{calorimeter}} = \frac{-\frac{m_s}{M_s} \Delta U_R - \frac{m_{H_2O}}{M_{H_2O}} C_{H_2O,m} \Delta T}{\Delta T}$$

$$= \frac{\frac{1.350 \text{ g}}{122.13 \text{ g mol}^{-1}} \times 3228.11 \times 10^3 \text{ J mol}^{-1} - \frac{1.240 \times 10^3 \text{ g}}{18.02 \text{ g mol}^{-1}} \times 75.291 \text{ J mol}^{-1} \text{ K}^{-1} \times 3.45^\circ\text{C}}{3.45^\circ\text{C}}$$

$$= 5.16 \times 10^3 \text{ J }^\circ\text{C}^{-1}$$

P4.22) A sample of $\text{Na}_2\text{SO}_4(s)$ is dissolved in 225g of water at 298 K such that the solution is 0.200 molar in Na_2SO_4 . A temperature rise of 0.101°C is observed. The calorimeter constant is 330 J K^{-1} . Calculate the enthalpy of solution of Na_2SO_4 in water at this concentration. Compare your result with that calculated using the data in Table 4.1.

$$0 = \frac{m_s}{M_s} \Delta H_{\text{solution},m} + \frac{m_{H_2O}}{M_{H_2O}} C_{H_2O,m} \Delta T + C_{\text{calorimeter}} \Delta T$$

$$\Delta H_{\text{solution},m} = -\frac{\left(\frac{225 \text{ g}}{18.02 \text{ g mol}^{-1}} \times 75.291 \text{ J K}^{-1} \text{ mol}^{-1} \times 0.151^\circ\text{C} + 330 \text{ J K}^{-1} \times 0.151^\circ\text{C} \right)}{0.225 \text{ L} \times 0.200 \text{ mol L}^{-1}}$$

$$= -2.86 \times 10^3 \text{ J mol}^{-1}$$

$$\Delta H_{\text{solution},m} = 2\Delta H_{\text{solution},m}(\text{Na}^+, aq) + \Delta H_{\text{solution},m}(\text{SO}_4^{2-}, aq) - \Delta H_f(\text{Na}_2\text{SO}_4, s)$$

$$= -2 \times 240.1 \times 10^3 \text{ J mol}^{-1} - 909.3 \times 10^3 \text{ J mol}^{-1} + 1387.1 \times 10^3 \text{ J mol}^{-1}$$

$$= -2.4 \times 10^3 \text{ J mol}^{-1}$$

The relative error is $\frac{-2.86 \text{ kJ mol}^{-1} + 2.4 \text{ kJ mol}^{-1}}{-2.86 \text{ kJ mol}^{-1}} = 16\%$

Questions on Concepts

Q5.1) Classify the following processes as spontaneous or not spontaneous and explain your answer. a) The reversible isothermal expansion of an ideal gas. b) The vaporization of superheated water at 102°C and 1 bar. c) The constant pressure melting of ice at its normal freezing point by the addition of an infinitesimal quantity of heat. d) The adiabatic expansion of a gas into a vacuum.

a) is not spontaneous because the system and surroundings are in equilibrium. b) is spontaneous because the equilibrium phase under the stated conditions is a gas. c) is not spontaneous because the process is reversible. d) is spontaneous because at equilibrium, the density of a gas is uniform throughout its container.

Q5.2) Why are ΔS_{fusion} and $\Delta S_{vaporization}$ always positive?

This is the case because ΔH_{fusion} and $\Delta H_{vaporization}$ are always positive. In each of these transitions, attractive forces must be overcome.

Q5.3) Why is the efficiency of a Carnot heat engine the upper bound to the efficiency of an internal combustion engine?

This the case because the maximum work than can be done on the surroundings in the expansion of a gas is in a reversible process.

Q5.4) The amplitude of a pendulum consisting of a mass on a long wire is initially adjusted to have a very small value. The amplitude is found to decrease slowly with time. Is this process reversible? Would the process be reversible if the amplitude did not decrease with time?

No, because dissipative forces are acting on the system. If the amplitude did not decrease, no dispersive forces act on the system and the oscillation is reversible in the limit of very small amplitudes. If the amplitude did not decrease with time, no dissipative forces act on the system, and because the amplitude is very small, the process is reversible.

Q5.5) A process involving an ideal gas is carried out in which the temperature changes at constant volume. For a fixed value ΔT , the mass of the gas is doubled. The process is repeated with the same initial mass and ΔT is doubled. For which of these processes is ΔS greater? Why?

ΔS is greater if the mass is doubled, because ΔS increases linearly with the amount of material. By contrast, ΔS only increases as the logarithm of the temperature. This increase is much slower than a linear increase.

Q5.6) Under what conditions does the equality $\Delta S = \frac{\Delta H}{T}$ hold?

Because $\Delta S = \frac{dq_{reversible}}{T}$, the equality holds if $dq_{reversible} = \Delta H$. This is the case for a reversible process at constant pressure.

Q5.7) Under what conditions is $\Delta S < 0$ for a spontaneous process?

For a spontaneous process, $\Delta S + \Delta S_{surroundings} < 0$. The inequality $\Delta S < 0$ is satisfied only if $\Delta S_{surroundings} > 0$ and $|\Delta S_{surroundings}| > |\Delta S|$.

Q5.8) Is the equation $\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT + \int_{V_i}^{V_f} \frac{\beta}{\kappa} dV = C_V \ln \frac{T_f}{T_i} + \frac{\beta}{\kappa} (V_f - V_i)$ valid for an ideal gas?

No. Because β and κ are not independent of V for an ideal gas, they can't be taken out of the integral.

Q5.9) Without using equations, explain why ΔS for a liquid or solid is dominated by the temperature dependence of S as both P and T change.

It is useful to think of $S = S(V, T)$. Because V changes very little with P for a liquid or solid, entropy changes are dominated by changes in T rather than P for liquids and solids.

Q5.10) You are told that $\Delta S = 0$ for a process in which the system is coupled to its surroundings. Can you conclude that the process is reversible? Justify your answer.

No. The criterion for reversibility is $\Delta S + \Delta S_{surroundings} = 0$. To decide if this criterion is satisfied, $\Delta S_{surroundings}$ must be known.

Problems

P5.1) Beginning with Equation (5.5), use Equation (5.6) to eliminate V_c and V_d to arrive at the result $w_{cycle} = nR(T_{hot} - T_{cold}) \ln \frac{V_b}{V_a}$.

$$w_{ab} = -nRT_{hot} \ln \frac{V_b}{V_a}$$

$$w_{bc} = nC_{V,m} (T_{cold} - T_{hot})$$

$$w_{cd} = -nRT_{cold} \ln \frac{V_d}{V_c}$$

$$w_{da} = nC_{V,m} (T_{hot} - T_{cold}) = -w_{bc}$$

$$w_{total} = -nRT_{hot} \ln \frac{V_b}{V_a} - nRT_{cold} \ln \frac{V_d}{V_c}$$

$$T_{hot} V_c^{\gamma-1} = T_{cold} V_b^{\gamma-1} \text{ and } T_{cold} V_a^{\gamma-1} = T_{hot} V_d^{\gamma-1}$$

Solving the last two equations for T_{hot} and equating the results,

$$T_{hot} = T_{cold} \frac{V_b^{\gamma-1}}{V_c^{\gamma-1}} = T_{cold} \frac{V_a^{\gamma-1}}{V_d^{\gamma-1}}. \text{ Therefore, } \frac{V_b}{V_c} = \frac{V_a}{V_d} \text{ or } \frac{V_c}{V_d} = \frac{V_b}{V_a} \text{ and}$$

$$w_{total} = -nRT_{hot} \ln \frac{V_b}{V_a} - nRT_{cold} \ln \frac{V_d}{V_c} = -nR(T_{hot} - T_{cold}) \ln \frac{V_b}{V_a}$$

P5.2) Consider the reversible Carnot cycle shown in Figure 5.2 with 1 mol of an ideal gas with $C_V = 3/2R$ as the working substance. The initial isothermal expansion occurs at the hot reservoir temperature of $T_{hot} = 600^\circ\text{C}$ from an initial volume of 3.50 L (V_a) to a volume of 10.0 L (V_b). The system then undergoes an adiabatic expansion until the temperature falls to $T_{cold} = 150^\circ\text{C}$. The system then undergoes an isothermal compression and a subsequent adiabatic compression until the initial state described by $T_a = 600^\circ\text{C}$ and $V_a = 3.50 \text{ L}$ is reached.

- a) Calculate V_c and V_d .
- b) Calculate w for each step in the cycle and for the total cycle.
- c) Calculate ε and the amount of heat that is extracted from the hot reservoir to do 1.00 kJ of work in the surroundings.

a) We first calculate V_c and V_d .

$$\frac{T_c}{T_b} = \left(\frac{V_c}{V_b} \right)^{1-\gamma}; \frac{V_c}{V_b} = \left(\frac{T_c}{T_b} \right)^{\frac{1}{1-\gamma}}$$

$$\frac{V_c}{V_b} = \left(\frac{423 \text{ K}}{873 \text{ K}} \right)^{\frac{1}{1-\frac{5}{3}}} = \left(\frac{423 \text{ K}}{873 \text{ K}} \right)^{\frac{3}{2}} = 2.96; \quad V_c = 29.649 \text{ L} \rightarrow 29.6 \text{ L}$$

$$\frac{T_d}{T_a} = \left(\frac{V_d}{V_a} \right)^{1-\gamma}; \frac{V_d}{V_a} = \left(\frac{T_d}{T_a} \right)^{\frac{1}{1-\gamma}}$$

$$\frac{V_d}{V_a} = \left(\frac{423 \text{ K}}{873 \text{ K}} \right)^{\frac{1}{1-\frac{5}{3}}} = \left(\frac{423 \text{ K}}{873 \text{ K}} \right)^{\frac{3}{2}} = 2.96; \quad V_d = 10.377 \text{ L} \rightarrow 10.4 \text{ L}$$

b) We next calculate w for each step in the cycle, and for the total cycle.

$$w_{ab} = -nRT_a \ln \frac{V_b}{V_a} = -1 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 873 \text{ K} \times \ln \frac{10.0 \text{ L}}{3.50 \text{ L}} = -7.62 \times 10^3 \text{ J}$$

$$w_{bc} = nC_{V,m}(T_c - T_b) = 1 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times (423 \text{ K} - 873 \text{ K}) = -5.61 \times 10^3 \text{ J}$$

$$w_{cd} = -nRT_c \ln \frac{V_d}{V_c} = -1 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 423 \text{ K} \times \ln \frac{10.377 \text{ L}}{29.649 \text{ L}} = +3.692 \times 10^3 \text{ J} \rightarrow +3.69 \times 10^3 \text{ J}$$

$$w_{da} = nC_{V,m}(T_a - T_d) = 1 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times (873 \text{ K} - 423 \text{ K}) = +5.61 \times 10^3 \text{ J}$$

$$w_{total} = -7.62 \times 10^3 \text{ J} - 5.61 \times 10^3 \text{ J} + 3.69 \times 10^3 \text{ J} + 5.61 \times 10^3 \text{ J} = -3.93 \times 10^3 \text{ J}$$

$$\varepsilon = 1 - \frac{T_{cold}}{T_{hot}} = 1 - \frac{423 \text{ K}}{873 \text{ K}} = 0.515 \quad q = \frac{w}{\varepsilon} = 1.94$$

Therefore, 1.94 kJ of heat must be extracted from the surroundings to do 1.00 kJ of work in the surroundings.

P5.3) Using your results from Problem P5.2, calculate q , ΔU , and ΔH for each step in the cycle and for the total cycle described in Problem P5.2.

$$a \rightarrow b \quad \Delta U = \Delta H = 0 \text{ because } \Delta T = 0. \quad q = -w = 7.62 \times 10^3 \text{ J}$$

$$b \rightarrow c \quad \Delta U = w = -5.61 \times 10^3 \text{ J} \text{ because } q = 0 \quad \Delta H = \Delta U + nR\Delta T = -9.35 \times 10^3 \text{ J}$$

$$c \rightarrow d \quad \Delta U = \Delta H = 0 \text{ because } \Delta T = 0. \quad q = -w = -3.69 \times 10^3 \text{ J}$$

$$d \rightarrow a \quad \Delta U = w = 5.61 \times 10^3 \text{ J} \text{ because } q = 0 \quad \Delta H = \Delta U + nR\Delta T = 9.35 \times 10^3 \text{ J}$$

$$q_{total} = 7.62 \times 10^3 \text{ J} - 3.69 \times 10^3 \text{ J} = 3.93 \times 10^3 \text{ J} = -w_{total}$$

$$\Delta U_{total} = \Delta H_{total} = 0$$

P5.4) Using your results from Problems P5.2 and P5.3, calculate ΔS , $\Delta S_{surroundings}$, and ΔS_{total} for each step in the cycle and for the total cycle described in Problem P5.2.

$$a \rightarrow b \quad \Delta S = -\Delta S_{surroundings} = \frac{q_{reversible}}{T} = \frac{7.62 \times 10^3 \text{ J}}{873 \text{ K}} = 8.73 \text{ J K}^{-1} \quad \Delta S_{total} = 0$$

$$b \rightarrow c \quad \Delta S = -\Delta S_{surroundings} = 0 \text{ because } q_{reversible} = 0 \quad \Delta S_{total} = 0$$

$$c \rightarrow d \quad \Delta S = -\Delta S_{surroundings} = \frac{q_{reversible}}{T} = \frac{-3.692 \times 10^3 \text{ J}}{423 \text{ K}} = -8.73 \text{ J K}^{-1} \quad \Delta S_{total} = 0$$

$$d \rightarrow a \quad \Delta S = -\Delta S_{surroundings} = 0 \text{ because } q_{reversible} = 0. \quad \Delta S_{total} = 0.$$

For the cycle, $\Delta S = \Delta S_{surroundings} = \Delta S_{total} = 0$.

P5.5) Calculate ΔS if the temperature of 1 mol of an ideal gas with $C_V = 3/2R$ is increased from 150 to 350 K under conditions of (a) constant pressure and (b) constant volume.

a) at constant pressure

$$\Delta S = nC_{P,m} \ln \frac{T_f}{T_i} = 1 \text{ mol} \times \left(\frac{3}{2} + 1 \right) \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \ln \frac{350 \text{ K}}{150 \text{ K}} = 17.6 \text{ J K}^{-1}$$

b) at constant volume

$$\Delta S = nC_{V,m} \ln \frac{T_f}{T_i} = 1 \text{ mol} \times \frac{3}{2} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \ln \frac{350 \text{ K}}{150 \text{ K}} = 10.6 \text{ J K}^{-1}$$

P5.6) One mole of N₂ at 20.5°C and 6.00 bar undergoes a transformation to the state

described by 145°C and 2.75 bar. Calculate ΔS if

$$\frac{C_{P,m}}{\text{J mol}^{-1}\text{K}^{-1}} = 30.81 - 11.87 \times 10^{-3} \frac{T}{\text{K}} + 2.3968 \times 10^{-5} \frac{T^2}{\text{K}^2} - 1.0176 \times 10^{-8} \frac{T^3}{\text{K}^3}.$$

$$\begin{aligned} \Delta S &= -nR \ln \frac{P_f}{P_i} + n \int_{T_i}^{T_f} \frac{C_{P,m}}{T} dT \\ &= -1 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \ln \frac{2.75 \text{ bar}}{6.00 \text{ bar}} \\ &\quad + \int_{293.65}^{418.15} \frac{\left(30.81 - 11.87 \times 10^{-3} \frac{T}{\text{K}} + 2.3968 \times 10^{-5} \left(\frac{T}{\text{K}} \right)^2 - 1.0176 \times 10^{-8} \left(\frac{T}{\text{K}} \right)^3 \right)}{T} d \frac{T}{\text{K}} \text{ JK}^{-1} \\ &= 6.48 \text{ J K}^{-1} + \left[30.81 \ln \frac{T}{\text{K}} - 0.01187 \frac{T}{\text{K}} + 1.1984 \times 10^{-5} \frac{T^2}{\text{K}^2} - 0.3392 \times 10^{-8} \left(\frac{T}{\text{K}} \right)^3 \right]_{293.5}^{418} \text{ JK}^{-1} \\ &= 6.48 \text{ JK}^{-1} + 10.89 \text{ JK}^{-1} - 1.48 \text{ JK}^{-1} + 1.06 \text{ JK}^{-1} - 0.16 \text{ JK}^{-1} = 16.8 \text{ JK}^{-1} \end{aligned}$$

P5.7) One mole of an ideal gas with $C_V = 3/2R$ undergoes the transformations described in the following list from an initial state described by $T = 300 \text{ K}$ and $P = 1.00 \text{ bar}$.

Calculate q , w , ΔU , ΔH , and ΔS for each process.

- The gas is heated to 450 K at a constant external pressure of 1.00 bar.
- The gas is heated to 450 K at a constant volume corresponding to the initial volume.
- The gas undergoes a reversible isothermal expansion at 300 K until the pressure is half of its initial value.

- The gas is heated to 450 K at a constant pressure of 1.00 bar.

$$V_i = \frac{nRT_i}{P_i} = \frac{1 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 300 \text{ K}}{10^5 \text{ Pa}} = 2.49 \times 10^{-2} \text{ m}^3$$

$$V_f = \frac{T_f}{T_i} V_i = \frac{450 \text{ K}}{300 \text{ K}} \times 2.49 \times 10^{-2} \text{ m}^3 = 3.74 \times 10^{-2} \text{ m}^3$$

$$w = -P_{\text{external}} \Delta V = -10^5 \text{ Pa} \times (3.74 \times 10^{-2} \text{ m}^3 - 2.49 \times 10^{-2} \text{ m}^3) = -1.25 \times 10^3 \text{ J}$$

$$\Delta U = nC_{V,m} \Delta T = 1 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times 150 \text{ K} = 1.87 \times 10^3 \text{ J}$$

$$q = \Delta H = \Delta U - w = 1.87 \times 10^3 \text{ J} + 1.25 \times 10^3 \text{ J} = 3.12 \times 10^3 \text{ J}$$

$$\Delta S = nC_{P,m} \ln \frac{T_f}{T_i} = 1 \text{ mol} \times \left(\frac{3}{2} + 1 \right) \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \ln \frac{450 \text{ K}}{300 \text{ K}} = 8.43 \text{ J K}^{-1}$$

b) The gas is heated to 450 K at a constant volume corresponding to the initial volume.

$w = 0$ because $\Delta V = 0$.

$$\Delta U = q = nC_{V,m} \Delta T = 1 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times 150 \text{ K} = 1.87 \times 10^3 \text{ J}$$

$$\Delta H = nC_{P,m} \Delta T = 1 \text{ mol} \times \frac{5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times 150 \text{ K} = 3.12 \times 10^3 \text{ J}$$

$$\Delta S = nC_{V,m} \ln \frac{T_f}{T_i} = 1 \text{ mol} \times \left(\frac{3}{2} \right) \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \ln \frac{450 \text{ K}}{300 \text{ K}} = 5.06 \text{ J K}^{-1}$$

c) The gas undergoes a reversible isothermal expansion at 300 K until the pressure is half of its initial value.

$\Delta U = \Delta H = 0$ because $\Delta T = 0$.

$$w_{\text{reversible}} = -q = -nRT \ln \frac{V_f}{V_i} = -1 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 300 \text{ K} \times \ln 2 = -1.73 \times 10^3 \text{ J}$$

$$\Delta S = \frac{q_{\text{reversible}}}{T} = \frac{1.73 \times 10^3 \text{ J}}{300 \text{ K}} = 5.76 \text{ J K}^{-1}$$

P5.8) Calculate $\Delta S_{\text{surroundings}}$ and ΔS_{total} for each of the processes described in Problem P5.7. Which of the processes is a spontaneous process? The state of the surroundings for each part is as follows:

a. 450 K, 1 bar b. 450 K, 1 bar c. 300 K, 0.500 bar

a) The gas is heated to 450 K at a constant pressure of 1.00 bar.

$$\Delta S_{\text{surroundings}} = \frac{-q}{T_{\text{surroundings}}} = \frac{-3.12 \times 10^3 \text{ J}}{450 \text{ K}} = -6.93 \text{ J K}^{-1}$$

$$\Delta S_{\text{total}} = \Delta S + \Delta S_{\text{surroundings}} = 8.43 \text{ J K}^{-1} - 6.93 \text{ J K}^{-1} = 1.50 \text{ J K}^{-1}$$

The process is spontaneous.

b) The gas is heated to 450 K at a constant volume corresponding to the initial volume.

$$\Delta S_{surroundings} = \frac{-q}{T_{surroundings}} = \frac{-1.87 \times 10^3 \text{ J}}{450 \text{ K}} = -4.16 \text{ J K}^{-1}$$

$$\Delta S_{total} = \Delta S + \Delta S_{surroundings} = 5.06 \text{ J K}^{-1} - 4.16 \text{ J K}^{-1} = 0.90 \text{ J K}^{-1}$$

The process is spontaneous.

c) The gas undergoes a reversible isothermal expansion at 300 K until the pressure is half of its initial value.

$$\Delta S_{surroundings} = \frac{q}{T} = \frac{-1.73 \times 10^3 \text{ J}}{300 \text{ K}} = -5.76 \text{ J K}^{-1}$$

$$\Delta S_{total} = \Delta S + \Delta S_{surroundings} = 5.76 \text{ J K}^{-1} - 5.76 \text{ J K}^{-1} = 0$$

There is no natural direction of change in this process because it is reversible.

P5.9) At the transition temperature of 95.4°C, the enthalpy of transition from rhombic to monoclinic sulfur is 0.38 kJ mol⁻¹.

a. Calculate the entropy of transition under these conditions.

b. At its melting point, 119°C, the enthalpy of fusion of monoclinic sulfur is 1.23 kJ mol⁻¹. Calculate the entropy of fusion.

c. The values given in parts (a) and (b) are for 1 mol of sulfur; however, in crystalline and liquid sulfur, the molecule is present as S₈. Convert the values of the enthalpy and entropy of fusion in parts (a) and (b) to those appropriate for S₈.

$$a) \Delta S_{transition} = \frac{\Delta H_{transition}}{T_{transition}} = \frac{0.38 \text{ kJ mol}^{-1}}{(273.15+95.4) \text{ K}} = 1.03 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$b) \Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{fusion}} = \frac{1.23 \text{ kJ mol}^{-1}}{(273.15+119) \text{ K}} = 3.14 \text{ J K}^{-1} \text{ mol}^{-1}$$

c) Each of the ΔS in parts (a) and (b) should be multiplied by 8.

$$\Delta S_{transition} = 8.24 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{fusion} = 25.12 \text{ J K}^{-1} \text{ mol}^{-1}$$

P5.10)

a. Calculate ΔS if 1 mol of liquid water is heated from 0° to 100°C under constant pressure if C_{P,m} = 75.291 J K⁻¹ mol⁻¹.

b. The melting point of water at the pressure of interest is 0°C and the enthalpy of fusion is 6.0095 kJ mol⁻¹. The boiling point is 100°C and the enthalpy of vaporization is 40.6563 kJ mol⁻¹. Calculate ΔS for the transformation H₂O(s, 0°C) → H₂O(g, 100°C).

a) The heat input is the same for a reversible and an irreversible process.

$$dq = dq_{reversible} = nC_{P,m}dT$$

$$\begin{aligned}\Delta S &= n \int \frac{C_{P,m}}{T} dT = nC_{P,m} \ln \frac{T_f}{T_i} \\ &= 1 \text{ mol} \times 753 \text{ J mol}^{-1} \text{ K}^{-1} \ln \frac{373.15 \text{ K}}{273.15 \text{ K}} \\ &= 23.49 \text{ J K}^{-1}\end{aligned}$$

b)

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{fusion}} = \frac{6009 \text{ J}}{273.15 \text{ K}} = 22.00 \text{ J K}^{-1}$$

$$\Delta S_{vaporization} = \frac{\Delta H_{vaporization}}{T_{vaporization}} = \frac{40656 \text{ J}}{373.15 \text{ K}} = 108.95 \text{ J K}^{-1}$$

$$\begin{aligned}\Delta S_{total} &= \Delta S_{fusion} + \Delta S_{vaporization} + \Delta S_{heating} = (22.00 + 108.95 + 23.49) \text{ J K}^{-1} \\ &= 154.4 \text{ J K}^{-1}\end{aligned}$$

P5.11) One mole of an ideal gas with $C_{V,m} = 5/2R$ undergoes the transformations described in the following list from an initial state described by $T = 250 \text{ K}$ and $P = 1.00 \text{ bar}$. Calculate q , w , ΔU , ΔH , and ΔS for each process.

- a. The gas undergoes a reversible adiabatic expansion until the final pressure is half its initial value.
 - b. The gas undergoes an adiabatic expansion against a constant external pressure of 0.500 bar until the final pressure is half its initial value.
 - c. The gas undergoes an expansion against a constant external pressure of zero bar until the final pressure is equal to half of its initial value.
- a) The gas undergoes a reversible adiabatic expansion until the final pressure is half its initial value.
- $q = 0$ because the process is adiabatic.

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i} \right)^{1-\gamma} = \left(\frac{T_f}{T_i} \right)^{1-\gamma} \left(\frac{P_i}{P_f} \right)^{1-\gamma}; = \left(\frac{T_f}{T_i} \right)^\gamma = \left(\frac{P_i}{P_f} \right)^{1-\gamma}; \frac{T_f}{T_i} = \left(\frac{P_i}{P_f} \right)^{\frac{1-\gamma}{\gamma}}$$

$$\frac{T_f}{T_i} = \left(\frac{1.00 \text{ bar}}{0.500 \text{ bar}} \right)^{\frac{1-\gamma}{\gamma}} = (2.00)^{\frac{2}{7}} = 0.820$$

$$T_f = 0.820 \times 250 \text{ K} = 205 \text{ K}$$

$$\Delta U = w = nC_{v,m}\Delta T = 1 \text{ mol} \times \frac{5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times (205 \text{ K} - 250 \text{ K}) = -935 \text{ J}$$

$$\Delta H = nC_{p,m}\Delta T = 1 \text{ mol} \times \frac{7 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times (205 \text{ K} - 250 \text{ K}) = -1.31 \times 10^3 \text{ J}$$

$\Delta S = 0$ because $q_{reversible} = 0$.

b) The gas undergoes an adiabatic expansion against a constant external pressure of 0.500 bar until the final pressure is half its initial value.

$q = 0$ because the process is adiabatic.

$$nC_{v,m}(T_f - T_i) = -nRP_{external} \left(\frac{T_f}{P_f} - \frac{T_i}{P_i} \right)$$

$$T_f \left(nC_{v,m} + \frac{nRP_{external}}{P_f} \right) = T_i \left(nC_{v,m} + \frac{nRP_{external}}{P_i} \right)$$

$$T_f = T_i \left(\frac{C_{v,m} + \frac{RP_{external}}{P_i}}{C_{v,m} + \frac{RP_{external}}{P_f}} \right) = 250K \left(\frac{2.5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} + \frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 0.500 \text{ bar}}{1.00 \text{ bar}}}{2.5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} + \frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 0.500 \text{ bar}}{0.500 \text{ bar}}} \right)$$

$$T_f = 214 \text{ K}$$

$$\Delta U = w = nC_{v,m}\Delta T = 1 \text{ mol} \times \frac{5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times (214 \text{ K} - 250 \text{ K}) = -748 \text{ J}$$

$$\Delta H = nC_{p,m}\Delta T = 1 \text{ mol} \times \frac{7 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times (214 \text{ K} - 250 \text{ K}) = -1.05 \times 10^3 \text{ J}$$

$$\Delta S = -nR \ln \frac{P_f}{P_i} + nC_{p,m} \ln \frac{T_f}{T_i}$$

$$= -1 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \ln \frac{0.500 \text{ bar}}{1.00 \text{ bar}} + 1 \text{ mol} \times \frac{7 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times \ln \frac{214 \text{ K}}{250 \text{ K}}$$

$$= 5.76 \text{ J K}^{-1} - 4.52 \text{ J K}^{-1} = 1.24 \text{ J K}^{-1}$$

c) The gas undergoes an expansion against a constant external pressure of zero bar until the final pressure is equal to half of its initial value.

ΔT and $w = 0$. Therefore $\Delta U = \Delta H = 0$ and $q = \Delta U - w = 0$.

$$\Delta S = -nR \ln \frac{P_f}{P_i} = -8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \ln \frac{0.500 \text{ bar}}{1.00 \text{ bar}} = 5.76 \text{ J K}^{-1}$$

P5.12) The standard entropy of $\text{Pb}(s)$ at 298.15 K is $64.80 \text{ J K}^{-1} \text{ mol}^{-1}$. Assume that the heat capacity of $\text{Pb}(s)$ is given by $\frac{C_{P,m}(\text{Pb}, s)}{\text{J mol}^{-1}\text{K}^{-1}} = 22.13 + 0.01172 \frac{T}{\text{K}} + 1.00 \times 10^{-5} \frac{T^2}{\text{K}^2}$. The melting point is 327.4°C and the heat of fusion under these conditions is 4770 J mol^{-1} .

Assume that the heat capacity of $\text{Pb}(l)$ is given by $\frac{C_{P,m}(\text{Pb}, l)}{\text{J K}^{-1}\text{mol}^{-1}} = 32.51 - 0.00301 \frac{T}{\text{K}}$.

a. Calculate the standard entropy of $\text{Pb}(l)$ at 500°C.

b. Calculate ΔH for the transformation $\text{Pb}(s, 25^\circ\text{C}) \rightarrow \text{Pb}(l, 500^\circ\text{C})$.

$$\begin{aligned} \text{a) } S_m^\circ(\text{Pb}, l, 773 \text{ K}) &= S_m^\circ(\text{Pb}, s, 298.15 \text{ K}) \\ &+ \int_{298.15}^{600.55} \frac{C_{P,m}}{[T / \text{K}]} d[T / \text{K}] + \frac{\Delta H_{fusion}}{T_{fusion}} + \int_{600.55}^{773.15} \frac{C_{P,m}}{[T / \text{K}]} d[T / \text{K}] \\ &= 64.80 \text{ J mol}^{-1} \text{ K}^{-1} \\ &+ \int_{298.15}^{600.55} \frac{22.13 + 0.01172 [T / \text{K}] + 1.00 \times 10^{-5} [T / \text{K}]^2}{[T / \text{K}]} d[T / \text{K}] \\ &+ \frac{4770 \text{ J mol}^{-1}}{600.55 \text{ K}} \\ &+ \int_{600.55}^{773.15} \frac{32.51 - 0.00301 [T / \text{K}]}{[T / \text{K}]} d[T / \text{K}] \\ &= 64.80 \text{ J mol}^{-1} \text{ K}^{-1} + 20.40 \text{ J mol}^{-1} \text{ K}^{-1} + 7.94 \text{ J mol}^{-1} \text{ K}^{-1} + 7.69 \text{ J mol}^{-1} \text{ K}^{-1} \\ &= 100.8 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

$$\begin{aligned} \text{b) } \Delta H_{total} &= \int_{298.15}^{600.55} C_{P,m}^{solid} d[T / \text{K}] + \Delta H_{fusion} + \int_{600.55}^{773.15} C_{P,m}^{liquid} d[T / \text{K}] \\ &= 8918 \text{ J mol}^{-1} + 4770 \text{ J mol}^{-1} + 5254 \text{ J mol}^{-1} \\ &= 18.94 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

P5.13) Between 0°C and 100°C, the heat capacity of Hg(l) is given by

$\frac{C_{P,m}(\text{Hg}, l)}{\text{J K}^{-1} \text{mol}^{-1}} = 30.093 - 4.944 \times 10^{-3} \frac{T}{\text{K}}$. Calculate ΔH and ΔS if 1 mol of Hg(l) is raised in temperature from 0° to 100°C at constant P .

$$\begin{aligned}\Delta H_m &= \int_{T_i}^{T_f} C_{P,m} d[T / K] \\ &= 30.093(T_f - T_i) - 2.472 \times 10^{-3} (T_f^2 - T_i^2) \text{ J mol}^{-1} \\ &= 2.84 \times 10^3 \text{ J mol}^{-1} \\ \Delta S_m &= \int_{T_i}^{T_f} \frac{C_{P,m}}{[T / K]} d[T / K] = 30.093 \ln \frac{T_f}{T_i} \\ &\quad - 4.944 \times 10^{-3} (T_f - T_i) = 8.90 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

P5.14) One mole of a van der Waals gas at 27°C is expanded isothermally and reversibly from an initial volume of 0.020 m³ to a final volume of 0.060 m³. For the van der Waals gas, $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V_m^2}$. Assume that $a = 0.556 \text{ Pa m}^6 \text{ mol}^{-2}$, and that $b = 64 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. Calculate q , w , ΔU , ΔH , and ΔS for the process.

$$\Delta U = \int_{V_i}^{V_f} \left(\frac{\partial U}{\partial V} \right)_T dV$$

for a van der Waals gas

$$\Delta U = a \left(\frac{1}{V_{m,i}} - \frac{1}{V_{m,f}} \right)$$

as shown in Example Problem 3.5

$$\Delta U = 0.556 \text{ Pa m}^6 \text{ mol}^{-2} \left(\frac{1}{0.020 \text{ m}^3} - \frac{1}{0.060 \text{ m}^3} \right) \times 1 \text{ mol} = 18.5 \text{ J}$$

$$\begin{aligned} w &= - \int_{V_i}^{V_f} P dV = -RT \int_{V_i}^{V_f} \frac{dV}{V_m - b} + a \int_{V_i}^{V_f} \frac{dV}{V^2} \\ &= -RT \ln \frac{(V_f - b)}{(V_i - b)} - a \left(\frac{1}{V_f} - \frac{1}{V_i} \right) \\ &= 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300.15 \text{ K} \ln \frac{0.059936}{0.019936} \\ &\quad - 0.556 \text{ Pa m}^6 \text{ mol}^{-2} \left(\frac{1}{0.060 \text{ m}^3} - \frac{1}{0.020 \text{ m}^3} \right) = -2.73 \times 10^3 \text{ J} \end{aligned}$$

$$P_i = \frac{RT}{V_i - b} - \frac{a}{V_i^2} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300.15 \text{ K}}{0.019936 \text{ m}^3} - \frac{0.556 \text{ Pa m}^6 \text{ mol}}{\left(0.020 \text{ m}^3\right)^2} = 1.237 \times 10^5 \text{ Pa}$$

$$P_f = \frac{RT}{V_f - b} - \frac{a}{V_f^2} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300.15 \text{ K}}{0.059936 \text{ m}^3} - \frac{0.566 \text{ Pa m}^6 \text{ mol}^{-2}}{\left(0.060 \text{ m}^3\right)^2} = 4.146 \times 10^4 \text{ Pa}$$

$$\begin{aligned} \Delta H &= \Delta U + \Delta(PV) = \Delta U + P_f V_f - P_i V_i \\ &= 18.5 \text{ J} + (4.146 \times 10^4 \text{ Pa} \times 0.060 \text{ m}^3 - 1.237 \times 10^5 \text{ Pa} \times 0.020 \text{ m}^3) = 32.1 \text{ J} \end{aligned}$$

$$q = \Delta U - w \approx 2.73 \times 10^3 \text{ J}$$

$$\Delta S = \frac{q_{reversible}}{T} = \frac{2.73 \times 10^3 \text{ J}}{300.13 \text{ K}} = 9.10 \text{ J K}^{-1}$$

P5.15) The heat capacity of α -quartz is given by

$\frac{C_{P,m}(\alpha\text{-quartz}, s)}{\text{J K}^{-1} \text{mol}^{-1}} = 46.94 + 34.31 \times 10^{-3} \frac{T}{\text{K}} - 11.30 \times 10^{-5} \frac{T^2}{\text{K}^2}$. The coefficient of thermal expansion is given by $\beta = 0.3530 \times 10^{-4} \text{ K}^{-1}$ and $V_m = 22.6 \text{ cm}^3 \text{ mol}^{-1}$. Calculate ΔS_m for the transformation α -quartz (25°C, 1 atm) \rightarrow α -quartz (225°C, 1000 atm).

From equations 5.23 and 5.24

$$\begin{aligned}
\Delta S &= \int_{T_i}^{T_f} C_p \frac{dT}{T} - V \beta (P_f - P_i) \\
&= \left[46.94 \ln \frac{498 \text{ K}}{298 \text{ K}} + 34.31 \times 10^{-3} \times (498 - 298) - 5.65 \times 10^{-5} \times (498^2 - 298^2) \right] \text{ J K}^{-1} \text{ mol}^{-1} \\
&\quad - 22.6 \text{ cm}^3 \text{ mol}^{-1} \times \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \times 0.3530 \times 10^{-4} \text{ K}^{-1} \times 999 \text{ atm} \times \frac{1.0125 \times 10^5 \text{ Pa}}{\text{atm}} \\
&= 22.11 \text{ J K}^{-1} \text{ mol}^{-1} - 0.0807 \text{ J K}^{-1} \text{ mol}^{-1} = 21.88 \text{ J K}^{-1} \text{ mol}^{-1}
\end{aligned}$$

P5.16) Calculate $\Delta S_{surroundings}$ and ΔS_{total} for the processes described in parts (a) and (b) of Problem P5.11. Which of the processes is a spontaneous process? The state of the surroundings for each part is as follows:

- a. 250 K, 0.500 bar b. 300 K, 0.500 bar

$\Delta S_{surroundings} = 0$ for a) and b) because $q = 0$.

- a) $\Delta S_{total} = \Delta S + \Delta S_{surroundings} = 0 + 0 = 0$. The process is not spontaneous.
b) $\Delta S_{total} = \Delta S + \Delta S_{surroundings} = 1.24 \text{ J K}^{-1} + 0 = 1.24 \text{ J K}^{-1}$. The process is spontaneous.

P5.17) Calculate ΔS , ΔS_{total} , and $\Delta S_{surroundings}$ when the volume of 85.0 g of CO initially at 298 K and 1.00 bar increases by a factor of three in (a) an adiabatic reversible expansion, (b) an expansion against $P_{external} = 0$, and (c) an isothermal reversible expansion. Take $C_{p,m}$ to be constant at the value $29.14 \text{ J mol}^{-1} \text{ K}^{-1}$ and assume ideal gas behavior. State whether each process is spontaneous.

- a) an adiabatic reversible expansion

$\Delta S_{surroundings} = 0$ because $q = 0$. $\Delta S = 0$ because the process is reversible.

$\Delta S_{total} = \Delta S + \Delta S_{surroundings} = 0$. The process is not spontaneous.

- b) an expansion against $P_{external} = 0$
 ΔT and $w = 0$. Therefore $\Delta U = q = 0$.

$$\begin{aligned}
\Delta S &= nR \ln \frac{V_f}{V_i} = \frac{85.0 \text{ g}}{28.01 \text{ g mol}^{-1}} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln 3 \\
&= 3.03 \text{ mol} \times 9.13 \text{ J mol}^{-1} \text{ K}^{-1} = 27.7 \text{ J K}^{-1}
\end{aligned}$$

$\Delta S_{total} = \Delta S + \Delta S_{surroundings} = 27.7 \text{ J K}^{-1} + 0 = 27.17 \text{ J K}^{-1}$. The process is spontaneous.

- c) an isothermal reversible expansion
 $\Delta T = 0$. Therefore $\Delta U = 0$.

$$w = -q = -nRT \ln \frac{V_f}{V_i} = -3.03 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln 3 = -8.25 \times 10^3 \text{ J}$$

$$\Delta S = \frac{q_{reversible}}{T} = \frac{8.25 \times 10^3 \text{ J}}{298 \text{ K}} = 27.7 \text{ J K}^{-1}$$

$$\Delta S_{surroundings} = \frac{-q}{T} = \frac{-8.25 \times 10^3 \text{ J}}{298 \text{ K}} = -27.7 \text{ J K}^{-1}$$

$\Delta S_{total} = \Delta S + \Delta S_{surroundings} = 27.7 \text{ J K}^{-1} - 27.7 \text{ J K}^{-1} = 0$. The system and surroundings are at equilibrium.

P5.18) One mole of an ideal gas with $C_{V,m} = 3/2R$ is transformed from an initial state $T = 600 \text{ K}$ and $P = 1.00 \text{ bar}$ to a final state $T = 250 \text{ K}$ and $P = 4.50 \text{ bar}$. Calculate ΔU , ΔH , and ΔS for this process.

$$\Delta U = nC_{V,m}\Delta T = 1 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{2} \times (250 \text{ K} - 600 \text{ K}) = -4.36 \times 10^3 \text{ J}$$

$$\Delta H = nC_{P,m}\Delta T = 1 \text{ mol} \times \frac{5 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{2} \times (250 \text{ K} - 600 \text{ K}) = -7.27 \times 10^3 \text{ J}$$

$$\begin{aligned} \Delta S &= -nR \ln \frac{P_f}{P_i} + nC_{P,m} \ln \frac{T_f}{T_i} \\ &= -1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \frac{4.500 \text{ bar}}{1.00 \text{ bar}} + 1 \text{ mol} \times \frac{5 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{2} \times \ln \frac{250 \text{ K}}{600 \text{ K}} \\ &= -12.5 \text{ J K}^{-1} - 18.2 \text{ J K}^{-1} = -30.7 \text{ J K}^{-1} \end{aligned}$$

P5.19) An ideal gas sample containing 2.50 mol for which $C_{V,m} = 3/2R$ undergoes the following reversible cyclical process from an initial state characterized by $T = 450 \text{ K}$ and $P = 1.00 \text{ bar}$:

- It is expanded reversibly and adiabatically until the volume doubles.
- It is reversibly heated at constant volume until T increases to 450 K.
- The pressure is increased in an isothermal reversible compression until $P = 1.00 \text{ bar}$.

Calculate q , w , ΔU , ΔH , ΔS , $\Delta S_{surroundings}$, and ΔS_{total} for each step in the cycle, and for the total cycle. The temperature of the surroundings is 300 K.

a) The temperature at the end of the adiabatic reversible expansion is calculated.

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i} \right)^{1-\gamma} = (2)^{1-\frac{5}{3}} = (2)^{\frac{2}{3}} = 0.630$$

$$T_f = 0.630 \times 450 \text{ K} = 283 \text{ K}$$

The initial and final volume and the final pressure are calculated.

$$V_i = \frac{nRT_i}{P_i} = \frac{2.50 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 450\text{ K}}{10^5 \text{ Pa}} = 9.25 \times 10^{-2} \text{ m}^3$$

$$V_f = 2V_i = 0.185 \text{ m}^3$$

$$P_f = P_i \frac{V_i}{V_f} \frac{T_f}{T_i} = 1.00 \text{ bar} \times \frac{1}{2} \times \frac{283 \text{ K}}{450 \text{ K}} = 0.314 \text{ bar}$$

$q = 0$ because the expansion is adiabatic.

$$\Delta U = w = nC_{V,m}\Delta T = 2.50 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times (283 \text{ K} - 450 \text{ K}) = -5.21 \times 10^3 \text{ J}$$

$$\Delta H = nC_{P,m}\Delta T = 2.50 \text{ mol} \times \frac{5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times (283 \text{ K} - 450 \text{ K}) = -8.68 \times 10^3 \text{ J}$$

$\Delta S = 0$ because $q_{\text{reversible}} = 0$. $\Delta S_{\text{surroundings}} = 0$ because $q = 0$. $\Delta S_{\text{total}} = 0$.

b) $w = 0$ because $\Delta V = 0$.

$$\Delta U = q = nC_{V,m}\Delta T = 2.50 \text{ mol} \times \frac{3 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times (450 \text{ K} - 283 \text{ K}) = 5.21 \times 10^3 \text{ J}$$

$$\Delta H = nC_{P,m}\Delta T = 2.50 \text{ mol} \times \frac{5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times (450 \text{ K} - 283 \text{ K}) = 8.68 \times 10^3 \text{ J}$$

The pressure at the end of the process is calculated in order to calculate ΔS .

$$P_f = P_i \frac{T_f}{T_i} = 0.314 \text{ bar} \times \frac{450 \text{ K}}{283 \text{ K}} = 0.500 \text{ bar}$$

$$\begin{aligned} \Delta S &= -nR \ln \frac{P_f}{P_i} + nC_{P,m} \ln \frac{T_f}{T_i} \\ &= -2.50 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \ln \frac{0.500 \text{ bar}}{0.314 \text{ bar}} + 2.50 \text{ mol} \times \frac{5 \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}}{2} \times \ln \frac{450 \text{ K}}{283 \text{ K}} \\ &= -9.63 \text{ J K}^{-1} + 24.10 \text{ J K}^{-1} = 14.5 \text{ J K}^{-1} \end{aligned}$$

$$\Delta S_{\text{surroundings}} = \frac{-q}{T_{\text{surroundings}}} = \frac{-5.21 \times 10^3 \text{ J}}{300 \text{ K}} = -17.4 \text{ J K}^{-1}$$

$$\Delta S_{\text{total}} = \Delta S + \Delta S_{\text{surroundings}} = 14.5 \text{ J K}^{-1} - 17.4 \text{ J K}^{-1} = -2.90 \text{ J K}^{-1}$$

c) $\Delta H = \Delta U = 0$ because $\Delta T = 0$.

$$\begin{aligned} w &= -q = -nRT \ln \frac{V_f}{V_i} = -nRT \ln \frac{P_i}{P_f} \\ &= -2.50 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 450 \text{ K} \times \ln \frac{1}{2} = 6.48 \times 10^3 \text{ J} \end{aligned}$$

$$\Delta S = -nR \ln \frac{P_f}{P_i} = -2.50 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \ln \frac{1.00 \text{ bar}}{0.500 \text{ bar}} = -14.5 \text{ J K}^{-1}$$

$$\Delta S_{surroundings} = \frac{-q}{T_{surroundings}} = \frac{6.48 \times 10^3 \text{ J}}{300 \text{ K}} = 21.6 \text{ J K}^{-1}$$

$$\Delta S_{total} = \Delta S_{surroundings} + \Delta S = 7.1 \text{ J K}^{-1}$$

For the entire cycle,

$$w_{total} = -5.21 \times 10^3 \text{ J} + 0 + 6.48 \times 10^3 \text{ J} = 1.27 \times 10^3 \text{ J}$$

$$q_{total} = 0 + 5.21 \times 10^3 \text{ J} - 6.48 \times 10^3 \text{ J} = -1.27 \times 10^3 \text{ J}$$

$$\Delta U_{total} = -5.21 \times 10^3 \text{ J} + 5.21 \times 10^3 \text{ J} + 0 = 0$$

$$\Delta H_{total} = -8.68 \times 10^3 \text{ J} + 8.68 \times 10^3 \text{ J} + 0 = 0$$

$$\Delta S_{total} = 0 + 14.5 \text{ J K}^{-1} - 14.5 \text{ J K}^{-1} = 0$$

$$\Delta S_{surroundings} = \Delta S_{total} = 0 - 17.4 \text{ J K}^{-1} + 21.6 \text{ J K}^{-1} = 4.20 \text{ J K}^{-1}$$

P5.20) One mole of $\text{H}_2\text{O}(l)$ is compressed from a state described by

$P = 1.00 \text{ bar}$ and $T = 298 \text{ K}$ to a state described by $P = 800 \text{ bar}$ and $T = 450 \text{ K}$. In addition, $\beta = 2.07 \times 10^{-4} \text{ K}^{-1}$ and the density can be assumed to be constant at the value 997 kg m^{-3} . Calculate ΔS for this transformation, assuming that $\kappa = 0$.

From equation 5.24,

$$\begin{aligned} \Delta S &= \int_{T_i}^{T_f} \frac{C_p}{T} dT - \int_{P_i}^{P_f} V \beta dP \approx n C_{P,m} \ln \frac{T_f}{T_i} - n V_{m,i} \beta (P_f - P_i) \\ &= 1 \text{ mol} \times 75.3 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \frac{450 \text{ K}}{298 \text{ K}} \\ &\quad - 1 \text{ mol} \times \frac{18.02 \times 10^{-3} \text{ kg mol}^{-1}}{997 \text{ kg m}^{-3}} \times 2.07 \times 10^{-4} \text{ K}^{-1} \times 799 \text{ bar} \times 10^5 \text{ Pa bar}^{-1} \\ &= 31.0 \text{ J K}^{-1} - 0.299 \text{ J K}^{-1} = 30.7 \text{ J K}^{-1} \end{aligned}$$

P5.21) A 25.0 g mass of ice at 273 K is added to 150.0 g of $\text{H}_2\text{O}(l)$ at 360 K at constant

pressure. Is the final state of the system ice or liquid water? Calculate ΔS for the process.

Is the process spontaneous?

Assume initially that the final state is water. If this is not the case, the calculated temperature will be below 273 K. Calculate ΔS for the ice and water separately, and add them to get the overall ΔS for the process.

$$\begin{aligned}
n_{ice} \Delta H_{fusion}^{ice} + n_{ice} C_{P,m}^{H_2O} (T_f - T_i^{ice}) + n_{H_2O} C_{P,m}^{H_2O} (T_f - T_i^{H_2O}) &= 0 \\
T_f = \frac{n_{ice} C_{P,m}^{H_2O} T_i^{ice} + n_{H_2O} C_{P,m}^{H_2O} T_i^{H_2O} - n_{ice} \Delta H_{fusion}^{ice}}{n_{ice} C_{P,m}^{H_2O} + n_{H_2O} C_{P,m}^{H_2O}} = \\
&\frac{\frac{25.0 \text{ g ice}}{18.02 \text{ g ice mol}^{-1}} \times 75.3 \text{ JK}^{-1}\text{mol}^{-1} \times 273 \text{ K} + \frac{150 \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.3 \text{ JK}^{-1}\text{mol}^{-1} \times 360 \text{ K}}{\frac{25.0 \text{ g ice}}{18.02 \text{ g ice mol}^{-1}} \times 75.3 \text{ JK}^{-1}\text{mol}^{-1} + \frac{150 \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.3 \text{ JK}^{-1}\text{mol}^{-1}} \\
&- \frac{\frac{25.0 \text{ g ice}}{18.02 \text{ g ice mol}^{-1}} \times 6010 \text{ J mol}^{-1}}{\frac{25.0 \text{ g ice}}{18.02 \text{ g ice mol}^{-1}} \times 75.3 \text{ JK}^{-1}\text{mol}^{-1} + \frac{150 \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.3 \text{ JK}^{-1}\text{mol}^{-1}}
\end{aligned}$$

$$T_f = 336.2 \text{ K} \rightarrow 336 \text{ K}$$

ΔS is calculated for the ice. It consists of melting the ice at 273 K and heating the resulting water to 336 K.

$$\begin{aligned}
\Delta S &= n \frac{\Delta H_{fusion}}{T_{fusion}} + n C_{P,m} \ln \frac{T_f}{T_{fusion}} \\
&= \frac{25.0 \text{ g ice}}{18.02 \text{ g ice mol}^{-1}} \times \frac{6010 \text{ J mol}^{-1}}{273 \text{ K}} + \frac{25.0 \text{ g ice}}{18.02 \text{ g ice mol}^{-1}} \times 75.3 \text{ JK}^{-1}\text{mol}^{-1} \ln \frac{336.2 \text{ K}}{273 \text{ K}} \\
&= 30.5 \text{ JK}^{-1} + 21.8 \text{ JK}^{-1} = 52.3 \text{ JK}^{-1}
\end{aligned}$$

ΔS is calculated for the water. It consists of cooling the water from 360 K to 336 K.

$$\Delta S = n C_{P,m} \ln \frac{T_f}{T_{fusion}} = \frac{150.0 \text{ g}}{18.02 \text{ g mol}^{-1}} \times 75.3 \text{ JK}^{-1}\text{mol}^{-1} \times \ln \frac{336.2 \text{ K}}{360 \text{ K}} = -42.9 \text{ JK}^{-1}$$

$\Delta S_{total} = 0 + 52.3 \text{ JK}^{-1} - 42.9 \text{ JK}^{-1} = 9.4 \text{ JK}^{-1}$. The process is spontaneous.

P5.22) 15.0 grams of steam at 373 K is added to 250.0 g of $\text{H}_2\text{O}(l)$ at 298 K at a constant pressure of 1 bar. Is the final state of the system steam or liquid water? Calculate ΔS for the process.

Assume that the final state is liquid water. If this is not the case, the calculated temperature will be greater than 373 K.

$$\begin{aligned}
& -n_{steam} \Delta H_{vaporization}^{H_2O} + n_{steam} C_{P,m}^{H_2O} (T_f - T_i^{steam}) + n_{H_2O} C_{P,m}^{H_2O} (T_f - T_i^{H_2O}) = 0 \\
& T_f = \frac{n_{steam} C_{P,m}^{H_2O} T_i^{steam} + n_{H_2O} C_{P,m}^{H_2O} T_i^{H_2O} + n_{steam} \Delta H_{vaporization}^{H_2O}}{n_{steam} C_{P,m}^{H_2O} + n_{H_2O} C_{P,m}^{H_2O}} = \\
& \frac{\frac{15.0 \text{ g steam}}{18.02 \text{ g mol}^{-1}} \times 75.291 \text{ J K}^{-1} \text{ mol}^{-1} \times 373 \text{ K} + \frac{250 \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.291 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{\frac{15.0 \text{ g steam}}{18.02 \text{ g mol}^{-1}} \times 75.291 \text{ J K}^{-1} \text{ mol}^{-1} + \frac{250 \text{ g H}_2\text{O}}{18.02 \text{ g H}_2\text{O mol}^{-1}} \times 75.291 \text{ J K}^{-1} \text{ mol}^{-1}} \\
& T_f = 333 \text{ K}
\end{aligned}$$

ΔS is calculated for the steam. It consists of condensing the steam at 373 K and cooling the resulting water to 333 K.

$$\begin{aligned}
\Delta S &= -n \frac{\Delta H_{vaporization}}{T_{vaporization}} + n C_{P,m} \ln \frac{T_f}{T_{vaporization}} \\
&= -\frac{15.0 \text{ g steam}}{18.02 \text{ g mol}^{-1}} \times \frac{40650 \text{ J mol}^{-1}}{373 \text{ K}} + \frac{15.0 \text{ g ice}}{18.02 \text{ g ice mol}^{-1}} \times 75.291 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \frac{333 \text{ K}}{373 \text{ K}} \\
&= -90.7 \text{ J K}^{-1} - 7.11 \text{ J K}^{-1} = -97.8 \text{ J K}^{-1}
\end{aligned}$$

ΔS is calculated for the water. It consists of heating the water from 298 K to 333 K.

$$\Delta S = n C_{P,m} \ln \frac{T_f}{T_{fusion}} = \frac{250.0 \text{ g}}{18.02 \text{ g mol}^{-1}} \times 75.291 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \frac{333 \text{ K}}{298 \text{ K}} = 116 \text{ J K}^{-1}$$

$\Delta S_{total} = 0 + 116 \text{ J K}^{-1} - 97.8 \text{ J K}^{-1} = 18.2 \text{ J K}^{-1}$. The process is spontaneous.

P5.23) The maximum theoretical efficiency of an internal combustion engine is achieved in a reversible Carnot cycle. Assume that the engine is operating in the Otto cycle and that $C_{V,m} = 5/2R$ for the fuel-air mixture initially at 298 K (the temperature of the cold reservoir). The mixture is compressed by a factor of 8.0 in the adiabatic compression step. What is the maximum theoretical efficiency of this engine? How much would the efficiency increase if the compression ratio could be increased to 30? Do you see a problem in doing so?

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i} \right)^{1-\gamma} = \left(\frac{1}{8} \right)^{1-\frac{7}{5}} = \left(\frac{1}{8} \right)^{-0.4} = 2.30$$

$$T_f = 2.30 \times 298 \text{ K} = 684 \text{ K}$$

$$\varepsilon = 1 - \frac{T_{cold}}{T_{hot}} = 1 - \frac{298}{684} = 0.564$$

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i} \right)^{1-\gamma} = \left(\frac{1}{30} \right)^{1-\frac{7}{5}} = \left(\frac{1}{30} \right)^{-0.4} = 3.89$$

$$T_f = 3.89 \times 298 \text{ K} = 1162 \text{ K}$$

$$\varepsilon = 1 - \frac{T_{cold}}{T_{hot}} = 1 - \frac{298 \text{ K}}{1162 \text{ K}} = 0.744$$

It would be difficult to avoid ignition of the fuel-air mixture before the compression was complete.

P5.24) One mole of $\text{H}_2\text{O}(l)$ is supercooled to -2.25°C at 1 bar pressure. The freezing temperature of water at this pressure is 0.00°C . The transformation $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s)$ is suddenly observed to occur. By calculating ΔS , $\Delta S_{surroundings}$ and ΔS_{total} , verify that this transformation is spontaneous at -2.25°C . The heat capacities are given by $C_p(\text{H}_2\text{O}(l)) = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $C_p(\text{H}_2\text{O}(s)) = 37.7 \text{ J K}^{-1} \text{ mol}^{-1}$, and $\Delta H_{fusion} = 6.008 \text{ kJ mol}^{-1}$ at 0.00°C . Assume that the surroundings are at -2.25°C . [Hint: Consider the two pathways at 1 bar: (a) $\text{H}_2\text{O}(l, -2.25^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, -2.25^\circ\text{C})$ and (b) $\text{H}_2\text{O}(l, -2.25^\circ\text{C}) \rightarrow \text{H}_2\text{O}(l, 0.00^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, 0.00^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, -2.25^\circ\text{C})$. Because S is a state function, ΔS must be the same for both pathways.]

For pathway b) $\text{H}_2\text{O}(l, -2.25^\circ\text{C}) \rightarrow \text{H}_2\text{O}(l, 0.00^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, 0.00^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, -2.25^\circ\text{C})$

$$\begin{aligned}\Delta S &= nC_{p,m}(l)\ln\frac{273.15 \text{ K}}{270.90 \text{ K}} - n\frac{\Delta H_{fusion}}{273.15 \text{ K}} + nC_{p,m}(s)\ln\frac{270.90 \text{ K}}{273.15 \text{ K}} \\ &= 1 \text{ mol} \times 75.3 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln\frac{273.15 \text{ K}}{270.90 \text{ K}} - 1 \text{ mol} \times \frac{6008 \text{ J mol}^{-1}}{273.15 \text{ K}} \\ &\quad + 1 \text{ mol} \times 37.7 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln\frac{270.90 \text{ K}}{273.15 \text{ K}} \\ &= 0.608 \text{ J K}^{-1} - 22.0 \text{ J K}^{-1} - 0.312 \text{ J K}^{-1} = -21.7 \text{ J K}^{-1}\end{aligned}$$

To calculate $\Delta S_{surroundings}$, we first calculate $\Delta H_P = q$.

$$\Delta H(-2.25^\circ\text{C}) = \Delta H(0.00^\circ\text{C}) + (C_p(\text{solid}) - C_p(\text{liquid}))\Delta T$$

$$\begin{aligned}\Delta H(-2.25^\circ\text{C}) &= -6008 \text{ J mol}^{-1} + (37.7 \text{ J mol}^{-1} \text{ K}^{-1} - 73.15 \text{ J mol}^{-1} \text{ K}^{-1}) \times (-2.25 \text{ K}) \\ &= -5928 \text{ J mol}^{-1} = q\end{aligned}$$

$$\Delta S_{surroundings} = \frac{-q}{T_{surroundings}} = \frac{5928 \text{ J mol}^{-1}}{270.90 \text{ K}} = 21.9 \text{ J K}^{-1}$$

$\Delta S_{total} = 21.9 \text{ J K}^{-1} - 21.7 \text{ J K}^{-1} = 0.2 \text{ J K}^{-1} > 0$. The process is spontaneous.

P5.25) An air conditioner is a refrigerator with the inside of the house acting as the cold reservoir and the outside atmosphere acting as the hot reservoir. Assume that an air conditioner consumes $1.50 \times 10^3 \text{ W}$ of electrical power, and that it can be idealized as a

reversible Carnot refrigerator. If the coefficient of performance of this device is 2.50, how much heat can be extracted from the house in a 24-hour period?

$$\eta_r = \frac{q_{cold}}{w} = 2.50; \quad q_{cold} = 2.50w$$

$$q_{cold} = 2.50 \times 1.50 \times 10^3 \text{ J s}^{-1} \times \frac{3600 \text{ s}}{\text{hr}} \times 24 \text{ hr} = 3.24 \times 10^8 \text{ J}$$

P5.26) The interior of a refrigerator is typically held at 277 K and the interior of a freezer is typically held at 255 K. If the room temperature is 294 K, by what factor is it more expensive to extract the same amount of heat from the freezer than from the refrigerator? Assume that the theoretical limit for the performance of a reversible refrigerator is valid.

From equation 5.44

$$\eta_r = \frac{T_{cold}}{T_{hot} - T_{cold}}$$

$$\text{for the freezer } \eta_r = \frac{255 \text{ K}}{294 \text{ K} - 255 \text{ K}} = 6.5$$

$$\text{for the refrigerator } \eta_r = \frac{277 \text{ K}}{294 \text{ K} - 277 \text{ K}} = 16.3$$

The freezer is more expansive to operate than the refrigerator by the ratio $16.3/6.5 = 2.5$.

P5.27) The Chalk Point, Maryland, generating station supplies electrical power to the Washington, D.C., area. Units 1 and 2 have a gross generating capacity of 710 MW (megawatt). The steam pressure is $25 \times 10^6 \text{ Pa}$, and the superheater outlet temperature (T_h) is 540°C. The condensate temperature (T_c) is 30°C.

- a. What is the efficiency of a reversible Carnot engine operating under these conditions?
- b. If the efficiency of the boiler is 91.2%, the overall efficiency of the turbine, which includes the Carnot efficiency and its mechanical efficiency, is 46.7%, and the efficiency of the generator is 98.4%, what is the efficiency of the total generating unit? (Another 5% needs to be subtracted off for other plant losses.)
- c. One of the coal burning units produces 355 MW. How many metric tons (1 metric ton = $1 \times 10^6 \text{ g}$) of coal per hour are required to operate this unit at its peak output if the enthalpy of combustion of coal is $29.0 \times 10^3 \text{ kJ kg}^{-1}$?

$$\text{a) } \varepsilon = \frac{T_{hot} - T_{cold}}{T_{hot}} = 1 - \frac{303 \text{ K}}{813 \text{ K}} = 0.627$$

b) The efficiency of the generating plant is the product of the individual efficiencies.

$$\varepsilon = 0.912 \times 0.467 \times 0.984 \times 0.95 = 0.398$$

c) The energy output per hour is given by $355 \text{ MW} \times \frac{3600 \text{ s}}{\text{hr}} = 1.278 \times 10^{12} \text{ J hr}^{-1}$

The heat required to output this energy is

$$q = \frac{E_{output}}{\varepsilon} = \frac{1.278 \times 10^{12} \text{ J hr}^{-1}}{0.398} = 3.211 \times 10^{12} \text{ J hr}^{-1}$$

The number of tons of coal needed is $\frac{3.211 \times 10^{12} \text{ J hr}^{-1}}{29.0 \times 10^9 \text{ J ton}^{-1}} = 110.7 \text{ ton hr}^{-1}$.

P5.28) The mean solar flux at the Earth's surface is $\sim 4.00 \text{ J cm}^{-2} \text{ min}^{-1}$. In a nonfocusing solar collector, the temperature can reach a value of 90.0°C . A heat engine is operated using the collector as the hot reservoir and a cold reservoir at 298 K . Calculate the area of the collector needed to produce one horsepower (1 hp = 746 watts). Assume that the engine operates at the maximum Carnot efficiency.

$$\varepsilon = 1 - \frac{T_{hot}}{T_{cold}} = 1 - \frac{298 \text{ K}}{363 \text{ K}} = 0.179$$

The area required for the solar panel is $\frac{2.5 \times 10^5 \text{ J min}^{-1}}{4.00 \text{ J} (\text{cm}^2)^{-1} \text{ min}^{-1}} = 6.25 \text{ m}^2$

P5.29) A refrigerator is operated by a 0.25-hp (1 hp = 746 watts) motor. If the interior is to be maintained at -20°C and the room temperature is 35°C , what is the maximum heat leak (in watts) that can be tolerated? Assume that the coefficient of performance is 75% of the maximum theoretical value.

The coefficient of performance is

$$\eta_r = 6.75 \times \frac{T_{cold}}{T_{hot} - T_{cold}} = 3.45$$

The maximum heat that can be removed from the cold reservoir is given by

Input power \times coefficient of performance

$$= 0.25 \text{ hp} \times \frac{746 \text{ W}}{\text{hp}} \times 3.45 = 640 \text{ W} = 640 \text{ J s}^{-1}$$

If the heat leak is greater than this value, the temperature in the refrigerator will rise.

P5.30) An electrical motor is used to operate a Carnot refrigerator with an interior temperature of 0°C. Liquid water at 0°C is placed into the refrigerator and transformed to ice at 0°C. If the room temperature is 20°C, what mass of ice can be produced in one minute by a 0.25-hp motor that is running continuously? Assume that the refrigerator is perfectly insulated and operates at the maximum theoretical efficiency.

We need to find the amount of heat per unit time that can be removed from the interior of the refrigerator.

$$\begin{aligned} \frac{q}{t} &= \eta_r \left(\frac{-w}{t} \right) = \frac{T_{cold}}{T_{hot} - T_{cold}} \left(\frac{-w}{t} \right) \\ &= \frac{273 \text{ K}}{293 \text{ K} - 273 \text{ K}} \times 0.25 \text{ hp} \times \frac{746 \text{ W}}{\text{hp}} = 2546 \text{ W} = 2546 \text{ J s}^{-1} \end{aligned}$$

The number of grams of ice that can be frozen in one minute by this amount of heat extraction is

$$m_{ice} = \frac{q/t}{\Delta H_{fusion}} \times t = \frac{2546 \text{ J s}^{-1}}{6008 \text{ J mol}^{-1}} \times \frac{18.02 \text{ g}}{\text{mol}} \times \frac{60 \text{ s}}{\text{min}} = 4.5 \times 10^2 \text{ g}$$

P5.31) Calculate ΔS° for the reaction $\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g)$ at 650 K. Omit terms in the temperature-dependent heat capacities higher than $\frac{T^2}{\text{K}^2}$.

From Table 2.4,

$$\begin{aligned} C_p^\circ(\text{H}_2, g) &= 22.66 + 4.38 \times 10^{-2} \frac{T}{\text{K}} - 1.0835 \times 10^{-4} \frac{T^2}{\text{K}^2} \text{ J K}^{-1}\text{mol}^{-1} \\ C_p^\circ(\text{Cl}_2, g) &= 22.85 + 6.543 \times 10^{-2} \frac{T}{\text{K}} - 1.2517 \times 10^{-4} \frac{T^2}{\text{K}^2} \text{ J K}^{-1}\text{mol}^{-1} \\ C_p^\circ(\text{HCl}, g) &= 29.81 - 4.12 \times 10^{-3} \frac{T}{\text{K}} + 6.2231 \times 10^{-6} \frac{T^2}{\text{K}^2} \text{ J K}^{-1}\text{mol}^{-1} \\ \Delta C_p^\circ &= 2 \left(29.81 - 4.12 \times 10^{-3} \frac{T}{\text{K}} + 6.2231 \times 10^{-6} \frac{T^2}{\text{K}^2} \text{ J K}^{-1}\text{mol}^{-1} \right) \\ &\quad - \left(22.66 + 4.38 \times 10^{-2} \frac{T}{\text{K}} - 1.0835 \times 10^{-4} \frac{T^2}{\text{K}^2} \text{ J K}^{-1}\text{mol}^{-1} \right) \\ &\quad - \left(22.85 + 6.543 \times 10^{-2} \frac{T}{\text{K}} - 1.2517 \times 10^{-4} \frac{T^2}{\text{K}^2} \text{ J K}^{-1}\text{mol}^{-1} \right) \\ \Delta C_p^\circ &= 14.11 - 0.117 \frac{T}{\text{K}} + 2.460 \times 10^{-4} \frac{T^2}{\text{K}^2} \text{ J K}^{-1}\text{mol}^{-1} \end{aligned}$$

$$\begin{aligned}
\Delta S^\circ &= 2S_{298.15}^\circ(\text{HCl}, g) - S_{298.15}^\circ(\text{Cl}_2, g) - S_{298.15}^\circ(\text{H}_2, g) \\
&= 2 \times 186.9 \text{ J K}^{-1}\text{mol}^{-1} - 223.1 \text{ J K}^{-1}\text{mol}^{-1} - 130.7 \text{ J K}^{-1}\text{mol}^{-1} \\
&= 22.0 \text{ J K}^{-1}\text{mol}^{-1} \\
\Delta S_T^\circ &= \Delta S_{298.15}^\circ + \int_{298.15}^T \frac{\Delta C_p^\circ}{T'} dT' \\
&= 20.0 \text{ J K}^{-1}\text{mol}^{-1} + \int_{298.15}^{650} \frac{\left(14.11 - 0.117 \frac{T}{\text{K}} + 2.460 \times 10^{-4} \frac{T^2}{\text{K}^2} \text{ J K}^{-1}\text{mol}^{-1}\right)}{\frac{T}{\text{K}}} d \frac{T}{\text{K}} \text{ J K}^{-1}\text{mol}^{-1} \\
&= 20.0 \text{ J K}^{-1}\text{mol}^{-1} + 10.99 \text{ J K}^{-1}\text{mol}^{-1} - 41.33 \text{ J K}^{-1}\text{mol}^{-1} + 41.03 \text{ J K}^{-1}\text{mol}^{-1} \\
&= 20.0 \text{ J K}^{-1}\text{mol}^{-1} + 10.69 \text{ J K}^{-1}\text{mol}^{-1} = 30.69 \text{ J K}^{-1}\text{mol}^{-1}
\end{aligned}$$

Questions on Concepts

Q6.1) Under what conditions is $dA \leq 0$ a condition that defines the spontaneity of a process?

This is the case at constant T and V if no nonexpansion work is possible.

Q6.2) Under what conditions is $dG \leq 0$ a condition that defines the spontaneity of a process?

This is the case at constant T and P if no nonexpansion work is possible.

Q6.3) Which thermodynamic state function gives a measure of the maximum electric work that can be carried out in a fuel cell?

ΔG because $dG \leq dw_{nonexpansion}$

Q6.4) By invoking the pressure dependence of the chemical potential, show that if a valve separating a vessel of pure A from a vessel containing a mixture of A and B is opened, mixing will occur. Both A and B are ideal gases, and the initial pressure in both vessels is 1 bar.

The chemical potential of A in the mixture than in the pure gas because

$\mu_A(T, P) = \mu_A^\circ(T) + RT \ln \frac{P_A}{P^\circ}$, and $P_A < P^\circ$. Because mass flows from regions of high chemical potential to regions of low chemical potential, pure A will flow into the mixture, and the contents of both vessels will be mixed.

Q6.5) Under what condition is $K_P = K_x$?

This is the case for a reaction involving gases if $\Delta n = 0$.

Q6.6) It is found that K_P is independent of T for a particular chemical reaction. What does this tell you about the reaction?

This is true if $\Delta H_{reaction} = 0$.

Q6.7) The reaction $A + B \rightarrow C + D$ is at equilibrium for $\xi = 0.1$. What does this tell you about the variation of G_{pure} with ξ ?

It tells you that ΔG_f° for A + B is less than that for C + D. If the ΔG_f° of reactants and products were nearly the same, ξ would be near 0.5. If the ΔG_f° for the products were less than those for the reactants, ξ would be near 1.

Q6.8) The reaction A + B \rightarrow C + D is at equilibrium for $\xi = 0.5$. What does this tell you about the variation of G_{pure} with ξ ?

It tells you that ΔG_f° for A + B is equal to that for C + D. If the ΔG_f° for the products were less than those for the reactants, ξ would be near 1. If the ΔG_f° for the reactants were less than those for the products, ξ would be much smaller than 0.5.

Q6.9) Why is it reasonable to set the chemical potential of a pure liquid or solid substance equal to its standard state chemical potential at that temperature independent of the pressure in considering chemical equilibrium?

The pressure dependence of G for solids and liquids is very small, because the volume of liquids and solids changes very little unless very high pressures are applied. Therefore, it is a good approximation to set the chemical potential of a pure liquid or solid substance equal to its standard state chemical potential at the temperature of interest.

Q6.10) Is the equation $\left(\frac{\partial U}{\partial V}\right)_T = \frac{\beta T - \kappa P}{\kappa}$ valid for liquids, solids, and gases?

Yes. No assumptions have been made in deriving this differential relationship.

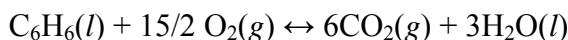
Q6.11) What is the relationship between the K_P for the two reactions $3/2\text{H}_2 + 1/2\text{N}_2 \rightarrow \text{NH}_3$ and $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$?

K_P for the second reaction is the square of K_P for the first reaction as can be seen the

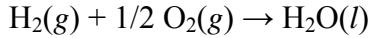
$$\text{reactions quotients } \frac{\left(\frac{P_{\text{NH}_3}}{P^\circ}\right)}{\left(\frac{P_{\text{H}_2}}{P^\circ}\right)^{3/2} \left(\frac{P_{\text{N}_2}}{P^\circ}\right)^{1/2}} \text{ and } \frac{\left(\frac{P_{\text{NH}_3}}{P^\circ}\right)^2}{\left(\frac{P_{\text{H}_2}}{P^\circ}\right)^3 \left(\frac{P_{\text{N}_2}}{P^\circ}\right)}.$$

Problems

P6.1) Calculate the maximum nonexpansion work that can be gained from the combustion of benzene(*l*) and of H₂(*g*) on a per gram and a per mole basis under standard conditions. Is it apparent from this calculation why fuel cells based on H₂ oxidation are under development for mobile applications?



$$\begin{aligned}
w_{\text{nonexpansion}}^{\max} &= \Delta G_R^\circ = 3\Delta G_f^\circ(\text{H}_2\text{O}, l) + 6\Delta G_f^\circ(\text{CO}_2, g) - \frac{15}{2}\Delta G_f^\circ(\text{O}_2, g) - \Delta G_f^\circ(\text{C}_6\text{H}_6, l) \\
&= 3 \times (-237.1 \text{ kJ mol}^{-1}) + 6 \times (-394.4 \text{ kJ mol}^{-1}) - \frac{15}{2} \times (0) - 124.5 - 124.5 \text{ kJ mol}^{-1} \\
&= -3202 \text{ kJ mol}^{-1} \\
&= -3202 \text{ kJ mol}^{-1} \times \frac{1 \text{ mol}}{78.18 \text{ g}} = -40.96 \text{ kJ g}^{-1}
\end{aligned}$$



$$\begin{aligned}
w_{\text{nonexpansion}}^{\max} &= \Delta G_R^\circ = \Delta G_f^\circ(\text{H}_2\text{O}, l) - \frac{1}{2}\Delta G_f^\circ(\text{O}_2, g) - \Delta G_f^\circ(\text{H}_2, g) \\
&= -237.1 \text{ kJ mol}^{-1} - 0 - 0 \\
&= -237.1 \text{ kJ mol}^{-1} \\
&= -237.1 \text{ kJ mol}^{-1} \times \frac{1 \text{ mol}}{2.016 \text{ g}} = -117.6 \text{ kJ g}^{-1}
\end{aligned}$$

On a per gram basis, nearly three times as much work can be extracted from the oxidation of hydrogen than benzene.

P6.2) Calculate ΔA for the isothermal compression of 2.00 mol of an ideal gas at 298 K from an initial volume of 35.0 L to a final volume of 12.0 L. Does it matter whether the path is reversible or irreversible?

$$dA = -SdT - PdV$$

At constant T, we consider the reversible process. Because A is a state function, any path whether reversible or irreversible, between the same initial and final states will give the same result.

$$\Delta A = - \int_{V_i}^{V_f} P dV = -nRT \ln \frac{V_f}{V_i} = -2.00 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln \frac{12.0 \text{ L}}{35.0 \text{ L}} = 5.30 \times 10^3 \text{ J}$$

P6.3) Calculate ΔG for the isothermal expansion of 2.50 mol of an ideal gas at 350 K from an initial pressure of 10.5 bar to a final pressure of 0.500 bar.

$$dG = -SdT + VdP$$

At constant T, we consider the reversible process. Because G is a state function, any path between the same initial and final states will give the same result.

$$\Delta G = \int_{P_i}^{P_f} V dP = nRT \ln \frac{P_f}{P_i} = 2.50 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 350 \text{ K} \times \ln \frac{0.500 \text{ bar}}{10.5 \text{ bar}} = -22.1 \times 10^3 \text{ J}$$

P6.4) A sample containing 2.50 mol of an ideal gas at 298 K is expanded from an initial volume of 10.0 L to a final volume of 50.0 L. Calculate ΔG and ΔA for this process for (a) an isothermal reversible path and (b) an isothermal expansion against a constant external pressure of 0.750 bar. Explain why ΔG and ΔA do or do not differ from one another.

a) for the isothermal reversible path

$$\begin{aligned}\Delta G &= \int_{P_i}^{P_f} V dP = nRT \ln \frac{P_f}{P_i} = nRT \ln \frac{V_i}{V_f} \\ &= 2.50 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln \frac{10.0 \text{ L}}{50.0 \text{ L}} = -9.97 \times 10^3 \text{ J} \\ \Delta A &= -\int_{V_i}^{V_f} P dV = -nRT \ln \frac{V_f}{V_i} \\ &= -2.50 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln \frac{50.0 \text{ L}}{10.0 \text{ L}} = -9.97 \times 10^3 \text{ J}\end{aligned}$$

b) Because A and G are state functions, the answers are the same as to part a) because the systems go between the same initial and final states, $T, V_i \rightarrow T, V_f$.

$\Delta G - \Delta A = \Delta H - \Delta U = \Delta(PV) = \Delta(nRT)$. Therefore, $\Delta G = \Delta A$ for an ideal gas if T is constant.

P6.5) The pressure dependence of G is quite different for gases and condensed phases. Calculate $G_m(C, \text{solid, graphite}, 100 \text{ bar}, 298.15 \text{ K})$ and $G_m(\text{He, g}, 100 \text{ bar}, 298.15 \text{ K})$ relative to their standard state values. By what factor is the change in G_m greater for He than for graphite?

For a solid or liquid,

$$\begin{aligned}\Delta G &= \int_{P_i}^{P_f} V dP = V \left(P_f - P_i \right) \\ G_m(C, s, 100 \text{ bar}) &= G_m(C, s, 1 \text{ bar}) + V_m \left(P_f - P_i \right) = G_m(C, s, 1 \text{ bar}) + \frac{M}{\rho} \left(P_f - P_i \right) \\ &= 0 + \frac{12.011 \times 10^{-3} \text{ kg}}{2250 \text{ kg m}^{-3}} \times 99.0 \times 10^5 \text{ Pa} = 52.8 \text{ J}\end{aligned}$$

Treating He as an ideal gas,

$$\begin{aligned}G_m(\text{He, g}, 100 \text{ bar}) &= G_m(\text{He, g}, 1 \text{ bar}) + \int_{P_i}^{P_f} V dP \\ &= 0 + RT \ln \frac{P_f}{P_i} = 1 \text{ mole} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times \ln \frac{100 \text{ bar}}{1 \text{ bar}} = 11.4 \times 10^3 \text{ J}\end{aligned}$$

This result is a factor of 216 greater than that for graphite.

P6.6) Assuming that ΔH_f° is constant in the interval 275 K – 600 K, calculate ΔG° for the process (H₂O, g, 298 K) → (H₂O, g, 525 K).

$$\begin{aligned}\Delta G^\circ &= T_2 \left[\frac{\Delta G_f^\circ(T_1)}{T_1} + \Delta H_f^\circ(T_1) \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right] \\ &= 525 \text{ K} \times \left[\frac{-228.6 \times 10^3 \text{ J mol}^{-1}}{298.15 \text{ K}} - 241.8 \times 10^3 \text{ J mol}^{-1} \times \left(\frac{1}{525 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \right] \\ \Delta G^\circ &= -218.5 \times 10^3 \text{ J mol}^{-1}\end{aligned}$$

P6.7) Calculate $\Delta G_{reaction}^\circ$ for the reaction CO(g) + ½ O₂(g) ↔ CO₂(g) at 298.15 K. Calculate $\Delta G_{reaction}^\circ$ at 650 K assuming that $\Delta H_{reaction}^\circ$ is constant in the temperature interval of interest.

$$\begin{aligned}\Delta G_{reaction}^\circ(298.15 \text{ K}) &= \Delta G_f^\circ(\text{CO}_2, g) - \Delta G_f^\circ(\text{CO}, g) - \frac{1}{2} \Delta G_f^\circ(\text{O}_2, g) \\ &= -394.4 \times 10^3 \text{ J mol}^{-1} + 137.2 \times 10^3 \text{ J mol}^{-1} - 0 \\ &= -257.2 \times 10^3 \text{ J mol}^{-1} \\ \Delta H_{reaction}^\circ(298.15 \text{ K}) &= \Delta H_f^\circ(\text{CO}_2, g) - \Delta H_f^\circ(\text{CO}, g) - \frac{1}{2} \Delta H_f^\circ(\text{O}_2, g) \\ &= -393.5 \times 10^3 \text{ J mol}^{-1} + 110.5 \times 10^3 \text{ J mol}^{-1} - 0 \\ &= -283.0 \times 10^3 \text{ J mol}^{-1} \\ \Delta G_{reaction}^\circ(T_2) &= T_2 \left[\frac{\Delta G_{reaction}^\circ(T_1)}{T_1} + \Delta H_{reaction}^\circ(T_1) \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right] \\ \Delta G_{reaction}^\circ(650 \text{ K}) &= 650 \text{ K} \times \left[\frac{-257.2 \times 10^3 \text{ J mol}^{-1}}{298.15 \text{ K}} - 283.0 \times 10^3 \text{ J mol}^{-1} \times \left(\frac{1}{650 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \right] \\ &= -226.8 \times 10^3 \text{ J mol}^{-1}\end{aligned}$$

P6.8) Calculate $\Delta A_{reaction}^\circ$ and $\Delta G_{reaction}^\circ$ for the reaction CH₄(g) + 2O₂(g) ↔ CO₂(g) + 2H₂O(l) at 298 K from the combustion enthalpy of methane and the entropies of the reactants and products.

All reactants and products are treated as ideal gases

$$\begin{aligned}\Delta G_{\text{combustion}}^{\circ} &= \Delta H_{\text{combustion}}^{\circ} - T \Delta S_{\text{combustion}}^{\circ} \\ \Delta S_{\text{combustion}}^{\circ} &= S^{\circ}(\text{CO}_2, g) + 2S^{\circ}(\text{H}_2\text{O}, l) - S^{\circ}(\text{CH}_4, g) - 2S^{\circ}(\text{O}_2, g) \\ &= 213.8 \text{ J mol}^{-1}\text{K}^{-1} + 2 \times 70.0 \text{ J mol}^{-1}\text{K}^{-1} - 186.3 \text{ J mol}^{-1}\text{K}^{-1} - 2 \times 205.2 \text{ J mol}^{-1}\text{K}^{-1} \\ &= -242.9 \text{ J mol}^{-1}\text{K}^{-1}\end{aligned}$$

$$\Delta G_{\text{combustion}}^{\circ} = -890.3 \times 10^3 \text{ J mol}^{-1} - 298.15 \text{ K} \times (-242.9 \text{ J mol}^{-1}\text{K}^{-1}) = -818.6 \times 10^3 \text{ J mol}^{-1}$$

$$\begin{aligned}\Delta A_{\text{combustion}}^{\circ} &= \Delta U_{\text{combustion}}^{\circ} - T \Delta S_{\text{combustion}}^{\circ} \\ &= \Delta H_{\text{combustion}}^{\circ} - \Delta(PV)_{\text{combustion}} - T \Delta S_{\text{combustion}}^{\circ} \\ &= \Delta G_{\text{combustion}}^{\circ} + T \Delta S_{\text{combustion}}^{\circ} - \Delta(PV) - T \Delta S_{\text{combustion}}^{\circ} \\ &= \Delta G_{\text{combustion}}^{\circ} - \Delta n RT\end{aligned}$$

where Δn is the change in the number of moles of gas phase species in the reaction

$$= -818.6 \times 10^3 \text{ J mol}^{-1} - (-2) \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298.15 \text{ K}$$

$$\Delta A_{\text{combustion}}^{\circ} = -813.6 \times 10^3 \text{ J mol}^{-1}$$

P6.9) Consider the equilibrium $\text{C}_2\text{H}_6(g) \leftrightarrow \text{C}_2\text{H}_4(g) + \text{H}_2(g)$. At 1000 K and a constant total pressure of 1 bar, $\text{C}_2\text{H}_6(g)$ is introduced into a reaction vessel. At equilibrium, the composition of the mixture in mole percent is $\text{H}_2(g)$: 26%, $\text{C}_2\text{H}_4(g)$: 26%, and $\text{C}_2\text{H}_6(g)$: 48%.

- Calculate K_P at 1000 K.
- If $\Delta H_{\text{reaction}}^{\circ} = 137.0 \text{ kJ mol}^{-1}$, calculate the value of K_P at 298.15 K.
- Calculate $\Delta G_{\text{reaction}}^{\circ}$ for this reaction at 298.15 K.



$$K_P = \frac{(P_{\text{C}_2\text{H}_6}/P^{\circ}) \times (P_{\text{H}_2}/P^{\circ})}{P_{\text{C}_2\text{H}_6}/P^{\circ}}$$

The partial pressure of each component, P_i , is $P_i = x_i P_{\text{total}}$ and $P_{\text{total}} = 1 \text{ bar}$.
By definition, $P^{\circ} = 1 \text{ bar}$.

$$K_P = \frac{0.26 \times 0.26}{0.48} = 0.1408$$

$$\text{b) } \ln K_p(1000 \text{ K}) = \ln K_p(298.15 \text{ K}) - \frac{\Delta H_{reaction}^\circ}{R} \left(\frac{1}{1000 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$\ln K_p(298.15 \text{ K}) = \ln K_p(1000 \text{ K}) + \frac{137.0 \times 10^3 \text{ J}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{1000 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) = -40.75$$

$$K_p(298.15 \text{ K}) = 2.00 \times 10^{-18}$$

$$\text{c) } \Delta G_{reaction}^\circ = -RT \ln K_p$$

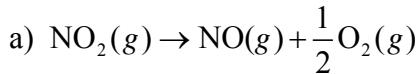
$$\Delta G_{reaction}^\circ(298.15 \text{ K}) = -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times (-40.75) = 101 \text{ kJ mol}^{-1}$$

P6.10) Consider the equilibrium $\text{NO}_2(g) \leftrightarrow \text{NO}(g) + 1/2\text{O}_2(g)$. One mole of $\text{NO}_2(g)$ is placed in a vessel and allowed to come to equilibrium at a total pressure of 1 bar. An analysis of the contents of the vessel gives the following results:

T	700 K	800 K
$\frac{P_{NO}}{P_{NO_2}}$	0.872	2.50

a. Calculate K_p at 700 and 800 K.

b. Calculate $\Delta G_{reaction}^\circ$ and $\Delta H_{reaction}^\circ$ for this reaction at 298.15 K. Assume that $\Delta H_{reaction}^\circ$ is independent of temperature.



$$K_p = \frac{(P_{NO}/P^\circ)(P_{O_2}/P_O)^{1/2}}{P_{NO_2}/P^\circ}$$

$$\text{At 700 K, } \frac{P_{NO}}{P_{NO_2}} = 0.872 \text{ and } P_{O_2} = \frac{1}{2} P_{NO}$$

$$P_{total} = P_{NO} + P_{NO_2} + P_{O_2} = 1 \text{ bar}$$

$$1 \text{ bar} = 0.872 P_{NO_2} + P_{NO_2} + 0.436 P_{NO_2}$$

$$1 \text{ bar} = 2.308 P_{NO_2}$$

$$P_{NO_2} = 0.433 \text{ bar}$$

$$K_p = \frac{(0.872 \times 0.433) \times \sqrt{0.436 \times 0.433}}{0.433} = 0.379$$

At 800 K, $\frac{P_{NO}}{P_{NO_2}} = 2.50$ and $P_{O_2} = \frac{1}{2} P_{NO}$

$$P_{Total} = P_{NO} + P_{NO_2} + P_{O_2}$$

$$1 \text{ bar} = 2.50 P_{NO_2} + P_{NO_2} + 1.25 P_{NO_2} = 4.75 P_{NO_2}$$

$$P_{NO_2} = 0.211 \text{ bar}$$

$$K_p = \frac{(2.50 \times 0.211) \times \sqrt{1.25 \times 0.211}}{0.211} = 1.284$$

b) Assuming that $\Delta H_{reaction}^\circ$ is independent of temperature,

$$\ln \frac{K_p(800 \text{ K})}{K_p(700 \text{ K})} = \frac{-\Delta H_{reaction}^\circ}{R} \left(\frac{1}{800 \text{ K}} - \frac{1}{700 \text{ K}} \right)$$

$$\Delta H_{reaction}^\circ = -\frac{R \times \ln \left(\frac{K_p(800 \text{ K})}{K_p(700 \text{ K})} \right)}{\left(\frac{1}{800 \text{ K}} - \frac{1}{700 \text{ K}} \right)} = 56.8 \times 10^3 \text{ J mol}^{-1}$$

$$\ln K_p(298.15 \text{ K}) = \ln K_p(700 \text{ K}) - \frac{\Delta H_{reaction}^\circ}{R} \times \left(\frac{1}{298.15 \text{ K}} - \frac{1}{700 \text{ K}} \right) = -14.12$$

$$\begin{aligned} \Delta G_{reaction}^\circ(298.15 \text{ K}) &= -RT \ln K_p(298.15 \text{ K}) \\ &= -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times (-14.12) \\ &= 35.0 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

P6.11) Consider the equilibrium $\text{CO}(g) + \text{H}_2\text{O}(g) \leftrightarrow \text{CO}_2(g) + \text{H}_2(g)$. At 1000 K, the composition of the reaction mixture is

Substance	$\text{CO}_2(g)$	$\text{H}_2(g)$	$\text{CO}(g)$	$\text{H}_2\text{O}(g)$
Mole %	27.1	27.1	22.9	22.9

a) Calculate K_p and $\Delta G_{reaction}^\circ$ at 1000 K.

b) Given the answer to part (a), use the ΔH_f° of the reaction species to calculate $\Delta G_{reaction}^\circ$ at 298.15 K. Assume that $\Delta H_{reaction}^\circ$ is independent of temperature.

a) $\text{CO}(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}_2(g) + \text{H}_2(g)$

$$K_p = \frac{\left(P_{CO_2} / P^\circ \right) \times \left(P_{H_2} / P^\circ \right)}{\left(P_{CO} / P^\circ \right) \times \left(P_{H_2O} / P^\circ \right)}$$

For each component, $P_i = x_i P_{total}$ because $\Delta \nu = 0$, $K_p = K_x$.

$$K_p = \frac{x_{CO_2} x_{H_2}}{x_{CO} x_{H_2O}} = \frac{0.271 \times 0.271}{0.229 \times 0.229} = 1.40$$

$$\begin{aligned}\Delta G_{reaction}^\circ &= -RT \ln K_p = -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 1000 \text{ K} \times \ln(1.40) \\ &= -2.80 \times 10^3 \text{ J mol}^{-1}\end{aligned}$$

b) $\Delta H_{reaction}^\circ = \Delta H_f^\circ(\text{CO}_2, g) + \Delta H_f^\circ(\text{H}_2, g) - \Delta H_f^\circ(\text{CO}, g) - \Delta H_f^\circ(\text{H}_2\text{O}, g)$
 $= -393.5 \text{ kJ mol}^{-1} + 110.5 \text{ kJ mol}^{-1} + 241.8 \text{ kJ mol}^{-1}$
 $= -41.2 \text{ kJ mol}^{-1}$

$$\begin{aligned}\ln K_p(298.15 \text{ K}) &= \ln K_p(1000 \text{ K}) - \frac{\Delta H_{reaction}^\circ}{R} \left(\frac{1}{298.15 \text{ K}} - \frac{1}{1000 \text{ K}} \right) \\ &= \frac{-41.2 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{298.15 \text{ K}} - \frac{1}{1000 \text{ K}} \right) = 12.0\end{aligned}$$

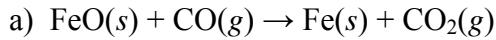
$$\Delta G_{reaction}^\circ = -RT \ln K_p(298.15 \text{ K}) = -29.7 \text{ kJ mol}^{-1}$$

P6.12) Consider the reaction $\text{FeO}(s) + \text{CO}(g) \leftrightarrow \text{Fe}(s) + \text{CO}_2(g)$ for which K_p is found to have the following values:

T	600°C	1000°C
K_p	0.900	0.396

a. Calculate $\Delta G_{reaction}^\circ$, $\Delta S_{reaction}^\circ$ and $\Delta H_{reaction}^\circ$ for this reaction at 600°C. Assume that $\Delta H_{reaction}^\circ$ is independent of temperature.

b. Calculate the mole fraction of $\text{CO}_2(g)$ present in the gas phase at 600°C.



$$\begin{aligned}K_p &= \frac{P_{CO_2} / P^\circ}{P_{CO} / P^\circ} \\ \ln \frac{K_p(1000^\circ\text{C})}{K_p(600^\circ\text{C})} &= \frac{\Delta H_{reaction}^\circ}{R} \left(\frac{1}{1273.15 \text{ K}} - \frac{1}{873.15 \text{ K}} \right)\end{aligned}$$

Assume that $\Delta H_{reaction}^\circ$ is independent of temperature.

$$\begin{aligned}
\Delta H_{reaction}^{\circ} &= \frac{-R \ln \frac{K_p(1000^\circ C)}{K_p(600^\circ C)}}{\left(\frac{1}{1273.15 \text{ K}} - \frac{1}{873.15 \text{ K}}\right)} \\
&= \frac{-8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \frac{0.0396}{0.900}}{\left(\frac{1}{1273.15 \text{ K}} - \frac{1}{873.15 \text{ K}}\right)} = -19.0 \text{ kJ mol}^{-1} \\
\Delta G_{reaction}^{\circ}(600^\circ C) &= -RT \ln K_p(600^\circ C) \\
&= -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 873.15 \text{ K} \times \ln(0.900) = 765 \text{ J mol}^{-1} \\
\Delta S_{reaction}^{\circ}(600^\circ C) &= \frac{\Delta H_{reaction}^{\circ} - \Delta G_{reaction}^{\circ}(600^\circ C)}{T} = \frac{-18960 \text{ J mol}^{-1} - 765 \text{ J mol}^{-1}}{873.15 \text{ K}} = -22.6 \text{ J mol}^{-1} \text{ K}^{-1}
\end{aligned}$$

b) because $K_P = P_{CO_2}/P_{CO} = 0.900$

$K_P = K_x$ because $\Delta v = 0$

$$\frac{x_{CO_2}}{x_{CO}} = 0.900 \text{ and } x_{CO_2} + x_{CO} = 1$$

$$x_{CO_2} = 0.47 \quad x_{CO} = 0.53$$

P6.13) If the reaction $Fe_2N(s) + 3/2H_2(g) \leftrightarrow 2Fe(s) + NH_3(g)$ comes to equilibrium at a total pressure of 1 bar, analysis of the gas shows that at 700 and 800 K, $\frac{P_{NH_3}}{P_{H_2}} = 2.165$ and 1.083, respectively, if only $H_2(g)$ was initially present in the gas phase and $Fe_2N(s)$ was in excess.

a. Calculate K_P at 700 and 800 K.

b. Calculate $\Delta S_{reaction}^{\circ}$ at 700 and 800 K and $\Delta H_{reaction}^{\circ}$, assuming that it is independent of temperature.

c. Calculate $\Delta G_{reaction}^{\circ}$ for this reaction at 298.15 K.

a) $FeN_2(s) + 3/2 H_2(g) \leftrightarrow 2Fe(s) + NH_3(g)$

$$K_P = \frac{P_{NH_3} / P^{\circ}}{(P_{H_2} / P^{\circ})^{3/2}}$$

$$P_{total} = 1 \text{ bar} = P_{NH_3} + P_{H_2}$$

At 700 K,

$$1 \text{ bar} = 2.165 P_{H_2} + P_{H_2} = 3.165 P_{H_2}$$

$$P_{H_2} = 0.316 \text{ bar}, P_{NH_3} = 0.684 \text{ bar}$$

$$K_p(700 \text{ K}) = \frac{0.684}{(0.316)^{3/2}} = 3.85$$

At 800 K

$$1 \text{ bar} = 1.083 P_{H_2} + P_{H_2} = 2.083 P_{H_2}$$

$$P_{H_2} = 0.480 \text{ bar}, P_{NH_3} = 0.520 \text{ bar}$$

$$K_p(800 \text{ K}) = \frac{0.520}{(0.480)^{3/2}} = 1.56$$

b) Assume that $\Delta H_{reaction}^\circ$ is independent of temperature

$$\ln \frac{K_p(800 \text{ K})}{K_p(700 \text{ K})} = \frac{-\Delta H_{reaction}^\circ}{R} \left(\frac{1}{800 \text{ K}} - \frac{1}{700 \text{ K}} \right)$$

$$\Delta H_{reaction}^\circ = \frac{-R \ln \frac{K_p(800 \text{ K})}{K_p(700 \text{ K})}}{\left(\frac{1}{800 \text{ K}} - \frac{1}{700 \text{ K}} \right)} = -42.1 \text{ kJ mol}^{-1}$$

$$\Delta G_{reaction}^\circ(700 \text{ K}) = -RT \ln K_p(700 \text{ K}) = -7.85 \text{ kJ mol}^{-1}$$

$$\Delta G_{reaction}^\circ(800 \text{ K}) = -RT \ln K_p(800 \text{ K}) = -2.96 \text{ kJ mol}^{-1}$$

$$\Delta S_{reaction}^\circ(700 \text{ K}) = \frac{\Delta H_{reaction}^\circ - \Delta G_{reaction}^\circ(700 \text{ K})}{700 \text{ K}} = 48.9 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S_{reaction}^\circ(800 \text{ K}) = 48.9 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\text{c) } \ln K_p(298.15 \text{ K}) = \ln K_p(700 \text{ K}) - \frac{\Delta H_{reaction}^\circ}{R} \left(\frac{1}{298.15 \text{ K}} - \frac{1}{700 \text{ K}} \right)$$

$$= \ln 3.85 + \frac{42.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{298.15 \text{ K}} - \frac{1}{700 \text{ K}} \right) = 11.1$$

$$\Delta G_{reaction}^\circ(298.15 \text{ K}) = -RT \ln K_p(298.15 \text{ K})$$

$$= -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times 11.1 = -27.5 \text{ kJ mol}^{-1}$$

P6.14) At 25°C, values for the formation enthalpy and Gibbs energy and $\log_{10} K_P$ for the formation reactions of the various isomers of C₅H₁₀ in the gas phase are given by the following table:

Substance	ΔH_f° (kJ mol ⁻¹)	ΔG_f° (kJ mol ⁻¹)	$\log_{10} K_P$
A = 1-pentene	-20.920	78.605	-13.7704
B = <i>cis</i> -2-pentene	-28.075	71.852	-12.5874
C = <i>trans</i> -2-pentene	-31.757	69.350	-12.1495
D = 2-methyl-1-butene	-36.317	64.890	-11.3680
E = 3-methyl-1-butene	-28.953	74.785	-13.1017
F = 2-methyl-2-butene	-42.551	59.693	-10.4572
G = cyclopentane	-77.24	38.62	-6.7643

Consider the equilibrium A \leftrightarrow B \leftrightarrow C \leftrightarrow D \leftrightarrow E \leftrightarrow F \leftrightarrow G, which might be established using a suitable catalyst.

- Calculate the mole ratios A/G, B/G, C/G, D/G, E/G, F/G present at equilibrium at 25°C.
- Do these ratios depend on the total pressure?
- Calculate the mole percentages of the various species in the equilibrium mixture.

a)

Reaction	$K_P = \exp\left(-\left[\frac{\Delta G_{product} - \Delta G_{reactant}}{RT}\right]\right)$
A \leftrightarrow B	$K_{B/A} = 15.27 = P_B / P_A = \frac{x_B}{x_A}$
B \leftrightarrow C	$K_{C/B} = 2.745 = P_C / P_B = \frac{x_C}{x_B}$
C \leftrightarrow D	$K_{D/C} = 6.050 = P_D / P_C = \frac{x_D}{x_C}$
D \leftrightarrow E	$K_{E/D} = 0.01843 = P_E / P_D = \frac{x_E}{x_D}$
E \leftrightarrow F	$K_{F/E} = 442 = P_F / P_E = \frac{x_F}{x_E}$
F \leftrightarrow G	$K_{F/G} = 4939 = P_G / P_F = \frac{x_G}{x_F}$

Because $\Delta v = 0$ for each reaction, $K_x = K_P$

$$\frac{x_F}{x_G} = \frac{1}{4939} = 2.025 \times 10^{-4}$$

$$\frac{x_E}{x_G} = \frac{x_E}{x_F} \times \frac{x_F}{x_G} = 4.581 \times 10^{-7}$$

$$\frac{x_D}{x_G} = \frac{x_D}{x_E} \times \frac{x_E}{x_F} \times \frac{x_F}{x_G} = 2.486 \times 10^{-5}$$

$$\frac{x_C}{x_G} = \frac{x_C}{x_D} \times \frac{x_D}{x_E} \times \frac{x_E}{x_F} \times \frac{x_F}{x_G} = 4.109 \times 10^{-6}$$

$$\frac{x_B}{x_G} = \frac{x_B}{x_C} \times \frac{x_C}{x_D} \times \frac{x_D}{x_E} \times \frac{x_E}{x_F} \times \frac{x_F}{x_G} = 1.497 \times 10^{-6}$$

$$\frac{x_A}{x_G} = \frac{x_A}{x_B} \times \frac{x_B}{x_C} \times \frac{x_C}{x_D} \times \frac{x_D}{x_E} \times \frac{x_E}{x_F} \times \frac{x_F}{x_G} = 9.803 \times 10^{-8}$$

b) The ratios do not depend on pressure because ΔV for each reaction is zero.

c) $x_G + x_F + x_E + x_D + x_C + x_B + x_A = 1$. Because x_G is much larger than all the other mole fractions, $x_G \approx 1$.

$x_F = 2.025 \times 10^{-4}$,	$\text{mol \%} = 2.025 \times 10^{-2}\%$
$x_E = 4.581 \times 10^{-7}$,	$\text{mol \%} = 4.581 \times 10^{-5}\%$
$x_D = 2.486 \times 10^{-5}$,	$\text{mol \%} = 2.486 \times 10^{-3}\%$
$x_C = 4.109 \times 10^{-6}$,	$\text{mol \%} = 4.109 \times 10^{-4}\%$
$x_B = 1.497 \times 10^{-6}$,	$\text{mol \%} = 1.497 \times 10^{-4}\%$
$x_A = 9.803 \times 10^{-8}$,	$\text{mol \%} = 9.803 \times 10^{-6}\%$

P6.15) The following data are given at 25°C:

Compound	CuO(s)	Cu(s)	O ₂ (g)
ΔH_f° (kJ mol ⁻¹)	-157		
ΔG_f° (kJ mol ⁻¹)	-130		
$C_{P,m}^\circ$ (J K ⁻¹ mol ⁻¹)	42.3	24.4	29.4

a. From equation 6.71, $\int_{K_P(T_0)}^{K_P(T_f)} d \ln K_P = \frac{1}{R} \int_{T_0}^{T_f} \frac{\Delta H_{\text{reaction}}^\circ}{T^2} dT$. To a good approximation, we

can assume that the heat capacities are independent of temperature over a limited range in temperature, giving $\Delta H_{\text{reaction}}^\circ(T) = \Delta H_{\text{reaction}}^\circ(T_0) + \Delta C_P(T - T_0)$ where

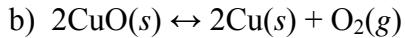
$\Delta C_P = \sum_i \nu_i C_{P,m}(i)$. By integrating equation 6.71, show that

$$\ln K_P(T) = \ln K_P(T_0) - \frac{\Delta H_{\text{reaction}}^\circ(T_0)}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \frac{T_0 \times \Delta C_P}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \frac{\Delta C_P}{R} \ln \frac{T}{T_0}$$

b. Using the result from part (a), calculate the equilibrium pressure of oxygen over copper and CuO(s) at 1200 K. How is this values related to K_P for the reaction $2\text{CuO}(s) \rightleftharpoons 2\text{Cu}(s) + \text{O}_2(g)$?

c. What value would you obtain if you assumed that $\Delta H_{reaction}^\circ$ were constant at its value for 298.15 K up to 1200 K?

$$\begin{aligned} \text{a) } & \int_{T_0}^{T_f} d \ln K_P = \frac{1}{R} \int_{T_0}^{T_f} \frac{\Delta H_{reaction}^\circ}{T^2} dT \\ & \ln K_P(T_f) - \ln K_P(T_0) = \frac{1}{R} \int_{T_0}^{T_f} \frac{\Delta H_{reaction}^\circ + \Delta C_P(T - T_0)}{T^2} dT \\ & = \frac{\Delta H_{reaction}^\circ(T_0)}{R} \times \int_{T_0}^{T_f} \frac{dT}{T^2} + \frac{\Delta C_P}{R} \int_{T_0}^{T_f} \frac{dT}{T} - \frac{\Delta C_P T_0}{R} \int_{T_0}^{T_f} \frac{dT}{T^2} \\ & = \frac{-\Delta H_{reaction}^\circ(T_0)}{R} \left(\frac{1}{T_f} - \frac{1}{T_0} \right) + \frac{\Delta C_P}{R} \ln \frac{T_f}{T_0} + \frac{\Delta C_P T_0}{R} \left(\frac{1}{T_f} - \frac{1}{T_0} \right) \end{aligned}$$



$$\Delta H_{reaction}^\circ(T_0) = 2 \times 157 \times 10^3 \text{ J mol}^{-1} = 314 \times 10^3 \text{ J mol}^{-1}$$

$$\begin{aligned} \Delta C_P &= 2C_{P,m}(\text{Cu}, s) + C_{P,m}(\text{O}_2, g) - 2C_{P,m}(\text{CuO}, s) \\ &= (2 \times 24.4 + 29.4 - 2 \times 42.3) \text{ J K}^{-1} \text{ mol}^{-1} \\ &= -6.4 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \ln K_P(1200 \text{ K}) &= -\frac{2 \times 130 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} \\ &\quad - \frac{2 \times 157 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{1200 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) - \frac{6.4 \text{ J K}^{-1} \text{ mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \ln \frac{1200 \text{ K}}{298.15 \text{ K}} \\ &\quad - \frac{6.4 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{1200 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \end{aligned}$$

$$\ln K_P(1200 \text{ K}) = -10.1818$$

$$K_P(1200 \text{ K}) = \frac{P_{O_2}}{P^\circ} = 3.78 \times 10^{-5}$$

$$P_{O_2} = 3.78 \times 10^{-5} \text{ bar}$$

c) This is equivalent to setting $\Delta C_P = 0$. Neglecting the last two terms in the calculation above gives $\ln K_P = -9.6884$ and $P_{O_2} = 6.20 \times 10^{-5}$ bar.

P6.16) Show that $\left[\frac{\partial(A/T)}{\partial(1/T)} \right]_V = U$. Write an expression analogous to Equation (6.37) that would allow you to relate ΔA at two temperatures.

$$\left(\frac{\partial A/T}{\partial T} \right)_V = \frac{1}{T} \left(\frac{\partial A}{\partial T} \right)_V - \frac{A}{T^2} = -\frac{S}{T} - \frac{A}{T^2} = -\frac{A + TS}{T^2} = -\frac{U}{T^2}$$

$$\left(\frac{\partial A/T}{\partial 1/T} \right)_V = \left(\frac{\partial A/T}{\partial T} \right)_V \left(\frac{\partial T}{\partial 1/T} \right)_V = \frac{\left(\frac{\partial A/T}{\partial T} \right)_V}{\left(\frac{\partial 1/T}{\partial T} \right)_V} = -T^2 \left(\frac{\partial A/T}{\partial T} \right)_V = U$$

At constant V ,

$$\int_{T_1}^{T_2} d\left(\frac{\Delta A}{T}\right) = \int_{T_1}^{T_2} d\left(\frac{\Delta U}{T}\right)$$

$$\frac{\Delta A(T_2)}{T_2} \approx \frac{\Delta A(T_1)}{T_1} + \Delta U(T_1) \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

P6.17) Calculate $\mu_{O_2}^{mixture}(298.15 \text{ K}, 1 \text{ bar})$ for oxygen in air, assuming that the mole fraction of O_2 in air is 0.200.

We calculate the conventional molar Gibbs energy as described in Example Problem 6.3.
 $\mu_{O_2}^\circ(T) = -TS^\circ(O_2, g, 298.15 \text{ K}) = -298.15 \text{ K} \times 205.2 \text{ J K}^{-1} \text{ mol}^{-1} = -61.2 \text{ kJ mol}^{-1}$

$$\begin{aligned} \mu_{O_2}^{mixture}(T, P) &= \mu_{O_2}^\circ(T) + RT \ln \frac{P}{P^\circ} + RT \ln x_{O_2} \\ &= -61.2 \text{ kJ mol}^{-1} + RT \ln \frac{1 \text{ bar}}{1 \text{ bar}} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times \ln 0.200 \\ &= -65.2 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

P6.18) A sample containing 2.25 moles of He (1 bar, 298 K) is mixed with 3.00 mol of Ne (1 bar, 298 K) and 1.75 mol of Ar (1 bar, 298 K). Calculate ΔG_{mixing} and ΔS_{mixing} .

$$\begin{aligned}
\Delta G_{mixing} &= nRT \sum_i x_i \ln x_i \\
&= (7.00 \text{ mol}) \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298.15 \text{ K} \times \left(\frac{2.25}{7.00} \ln \frac{2.25}{7.00} + \frac{3.00}{7.00} \ln \frac{3.00}{7.00} + \frac{1.75}{7.00} \ln \frac{1.75}{7.00} \right) \\
&= -18.6 \times 10^3 \text{ J} \\
\Delta S_{mixing} &= -nR \sum_i x_i \ln x_i \\
&= -(7.00 \text{ mol}) \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \left(\frac{2.25}{7.00} \ln \frac{2.25}{7.00} + \frac{3.00}{7.00} \ln \frac{3.00}{7.00} + \frac{1.75}{7.00} \ln \frac{1.75}{7.00} \right) \\
&= 62.5 \text{ J K}^{-1}
\end{aligned}$$

P6.19) You have containers of pure H₂ and He at 298 K and 1 atm pressure. Calculate ΔG_{mixing} relative to the unmixed gases of

- a mixture of 10 mol of H₂ and 10 mol of He
- b. a mixture of 10 mol of H₂ and 20 mol of He
- c. Calculate ΔG_{mixing} if 10 mol of pure He are added to the mixture of 10 mol of H₂ and 10 mole of He.

$$\Delta G_{mixing} = nRT(x_1 \ln x_1 + x_2 \ln x_2)$$

$$\text{a)} \quad \Delta G_{mixing} = 20 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \left(\frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right) = -34.4 \text{ kJ}$$

$$\text{b)} \quad \Delta G_{mixing} = 30 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \left(\frac{1}{3} \ln \frac{1}{3} + \frac{2}{3} \ln \frac{2}{3} \right) = -47.3 \text{ kJ}$$

$$\begin{aligned}
\text{c)} \quad \Delta G_{mixing} &= \Delta G_{mixing} \text{ (pure gases)} \\
&\quad - \Delta G_{mixing} \text{ (10 mol A + 10 mol B)} \\
&= -47.3 + 34.4 = -12.9 \text{ kJ}
\end{aligned}$$

P6.20) A gas mixture with 4 mol of Ar, x moles of Ne, and y moles of Xe is prepared at a pressure of 1 bar and a temperature of 298 K. The total number of moles in the mixture is three times that of Ar. Write an expression for ΔG_{mixing} in terms of x . At what value of x does the magnitude of ΔG_{mixing} have its maximum value? Calculate ΔG_{mixing} for this value of x .

If the number of moles of Ne is x , the number of moles of Xe is $y = 8 - x$.

$$\begin{aligned}
\Delta G_{mixing} &= nRT \sum_i x_i \ln x_i \\
&= nRT \left(\frac{4}{12} \ln \frac{4}{12} + \frac{x}{12} \ln \frac{x}{12} + \frac{8-x}{12} \ln \frac{8-x}{12} \right) \\
\frac{d\Delta G_{mixing}}{dx} &= nRT \left(\frac{1}{12} \ln \frac{x}{12} + \frac{x}{12} \frac{12}{x} - \frac{1}{12} \ln \frac{8-x}{12} + \frac{8-x}{12} \frac{12}{8-x} (-1) \right) = 0 \\
&= nRT \left(\frac{1}{12} \ln \frac{x}{12} + 1 - \frac{1}{12} \ln \frac{8-x}{12} - 1 \right) = \frac{nRT}{12} \ln \frac{x}{8-x} = 0 \\
\frac{x}{8-x} &= 1; \quad x = 4 \\
\Delta G_{mixing} &= nRT \left(\frac{4}{12} \ln \frac{4}{12} + \frac{4}{12} \ln \frac{4}{12} + \frac{4}{12} \ln \frac{4}{12} \right) \\
&= 12 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298.15 \text{ K} \times \ln \frac{1}{3} = -32.7 \times 10^3 \text{ J}
\end{aligned}$$

P6.21) In Example Problem 6.8, K_P for the reaction $\text{CO}(g) + \text{H}_2\text{O}(l) \leftrightarrow \text{CO}_2(g) + \text{H}_2(g)$ was calculated to be 3.32×10^3 at 298.15 K. At what temperature does $K_P = 5.00 \times 10^3$? What is the highest value that K_P can have by changing the temperature? Assume that $\Delta H_{reaction}^\circ$ is independent of temperature.

$$\begin{aligned}
\ln K_P(T_f) &= \ln K_P(298.15 \text{ K}) - \frac{\Delta H_{reaction}^\circ}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right) \\
\Delta H_{reaction}^\circ &= \Delta H_f^\circ(\text{CO}_2, g) + \Delta H_f^\circ(\text{H}_2, g) - \Delta H_f^\circ(\text{H}_2\text{O}, l) - \Delta H_f^\circ(\text{CO}, g) \\
&= -393.5 \times 10^3 \text{ J mol}^{-1} + 0 + 285.8 \times 10^3 \text{ J mol}^{-1} + 110.5 \times 10^3 \text{ J mol}^{-1} = 2.80 \times 10^3 \text{ J mol}^{-1} \\
\frac{1}{T_f} &= \frac{1}{298.15 \text{ K}} - \frac{R}{\Delta H_{reaction}^\circ} \ln \frac{K_P(T_f)}{K_P(298.15 \text{ K})} \\
&= \frac{1}{298.15 \text{ K}} - \frac{8.314 \text{ J K}^{-1}\text{mol}^{-1}}{2.80 \times 10^3 \text{ J mol}^{-1}} \times \ln \frac{5.00 \times 10^3}{3.32 \times 10^3} = 2.1382 \times 10^{-3} \text{ K}^{-1} \\
T_f &= 468 \text{ K}
\end{aligned}$$

Because the reaction is endothermic, K_P increases with temperature. As $T \rightarrow \infty$,

$$\begin{aligned}
\frac{1}{298.15 \text{ K}} - \frac{R}{\Delta H_{reaction}^\circ} \ln \frac{K_P(T_f \rightarrow \infty)}{K_P(298.15 \text{ K})} &= 0 \\
\ln \frac{K_P(T_f \rightarrow \infty)}{K_P(298.15 \text{ K})} &= \frac{\Delta H_{reaction}^\circ}{R \times 298.15 \text{ K}} = \frac{2.80 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298.15 \text{ K}} = 1.12957 \\
K_P(T_f \rightarrow \infty) &= 3.094 \times K_P(298.15 \text{ K}) = 3.094 \times 3.32 \times 10^3 = 1.03 \times 10^4
\end{aligned}$$

P6.22) Calculate K_P at 550 K for the reaction $\text{N}_2\text{O}_4(l) \leftrightarrow 2\text{NO}_2(g)$ assuming that $\Delta H_{reaction}^\circ$ is constant over the interval 298–600 K.

$$\begin{aligned}\Delta H_{reaction}^\circ &= 2\Delta H_f^\circ(\text{NO}_2, g) - \Delta H_f^\circ(\text{N}_2\text{O}_4, l) \\ &= 2 \times 33.2 \times 10^3 \text{ J mol}^{-3} + 19.5 \times 10^3 \text{ J mol}^{-3} = 85.9 \times 10^3 \text{ J mol}^{-3} \\ \Delta G_{reaction}^\circ &= 2\Delta G_f^\circ(\text{NO}_2, g) - \Delta G_f^\circ(\text{N}_2\text{O}_4, l) \\ &= 2 \times 51.3 \times 10^3 \text{ J mol}^{-3} - 97.5 \times 10^3 \text{ J mol}^{-3} = 5.1 \times 10^3 \text{ J mol}^{-3} \\ \ln K_P(T_f) &= -\frac{\Delta G_{reaction}^\circ(298.15 \text{ K})}{R \times 298.15 \text{ K}} - \frac{\Delta H_{reaction}^\circ}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right) \\ \ln K_P(550 \text{ K}) &= -\frac{5.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} - \frac{85.9 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{550 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \\ \ln K_P(550 \text{ K}) &= 13.81 \\ K_P(550 \text{ K}) &= 9.95 \times 10^5\end{aligned}$$

P6.23) Calculate K_P at 475 K for the reaction $\text{NO}(g) + \frac{1}{2}\text{O}_2(g) \leftrightarrow \text{NO}_2(g)$ assuming that $\Delta H_{reaction}^\circ$ is constant over the interval 298–600 K. Do you expect K_P to increase or decrease as the temperature is increased to 550 K?

$$\begin{aligned}\Delta H_{reaction}^\circ &= \Delta H_f^\circ(\text{NO}_2, g) - \Delta H_f^\circ(\text{NO}, g) \\ &= 33.2 \times 10^3 \text{ J mol}^{-3} - 91.3 \times 10^3 \text{ J mol}^{-3} = -58.1 \times 10^3 \text{ J mol}^{-3} \\ \Delta G_{reaction}^\circ &= 2\Delta G_f^\circ(\text{NO}_2, g) - \Delta G_f^\circ(\text{NO}, g) \\ &= 51.3 \times 10^3 \text{ J mol}^{-3} - 87.6 \times 10^3 \text{ J mol}^{-3} = -36.3 \times 10^3 \text{ J mol}^{-3} \\ \ln K_P(T_f) &= -\frac{\Delta G_{reaction}^\circ(298.15 \text{ K})}{R \times 298.15 \text{ K}} - \frac{\Delta H_{reaction}^\circ}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right) \\ \ln K_P(475 \text{ K}) &= \frac{36.3 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} + \frac{58.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{475 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \\ \ln K_P(475 \text{ K}) &= 5.9175 \\ K_P(475 \text{ K}) &= 371\end{aligned}$$

Because $\Delta H_{reaction}^\circ < 0$, K_P decreases as T increases.

P6.24) Calculate the degree of dissociation of N_2O_4 in the reaction $\text{N}_2\text{O}_4(g) \leftrightarrow 2\text{NO}_2(g)$ at 250 K and a total pressure of 0.500 bar. Do you expect the degree of dissociation to increase or decrease as the temperature is increased to 550 K?

We set up the following table

	$\text{N}_2\text{O}_4(g)$	\leftrightarrow	$2\text{NO}_2(g)$
Initial number of moles	n_0		0
Moles present at equilibrium	$n_0 - \xi$		2ξ
Mole fraction present at equilibrium	$\frac{n_0 - \xi}{n_0 + \xi}$		$\frac{2\xi}{n_0 + \xi}$
Partial pressure at Equilibrium, $P_i = x_i P$	$\left(\frac{n_0 - \xi}{n_0 + \xi}\right)P$		$\left(\frac{2\xi}{n_0 + \xi}\right)P$

We next express K_P in terms of n_0 , ξ , and P .

$$K_P(T) = \frac{\left(\frac{P_{Cl}^{eq}}{P^\circ}\right)^2}{\left(\frac{P_{Cl_2}^{eq}}{P^\circ}\right)} = \frac{\left[\left(\frac{2\xi}{n_0 + \xi}\right)\frac{P}{P^\circ}\right]^2}{\left(\frac{n_0 - \xi}{n_0 + \xi}\right)\frac{P}{P^\circ}} = \frac{4\xi^2}{(n_0 + \xi)(n_0 - \xi)} \frac{P}{P^\circ} = \frac{4\xi^2}{(n_0)^2 - \xi^2} \frac{P}{P^\circ}$$

We convert this expression for K_P to one in terms of α .

$$K_P(T) = \frac{4\xi^2}{(n_0)^2 - \xi^2} \frac{P}{P^\circ} = \frac{4\alpha^2}{1 - \alpha^2} \frac{P}{P^\circ}$$

$$\left(K_P(T) + 4 \frac{P}{P^\circ}\right) \alpha^2 = K_P(T)$$

$$\alpha = \sqrt{\frac{K_P(T)}{K_P(T) + 4 \frac{P}{P^\circ}}}$$

$$\begin{aligned}\Delta G_{reaction}^\circ &= 2\Delta G_f^\circ(\text{NO}_2, g) - \Delta G_f^\circ(\text{N}_2\text{O}_4, g) \\ &= 2 \times 51.3 \times 10^3 \text{ J mol}^{-3} - 99.8 \times 10^3 \text{ J mol}^{-3} = 2.8 \times 10^3 \text{ J mol}^{-3}\end{aligned}$$

$$\begin{aligned}\Delta H_{reaction}^\circ &= 2\Delta H_f^\circ(\text{NO}_2, g) - \Delta H_f^\circ(\text{N}_2\text{O}_4, g) \\ &= 2 \times 33.2 \times 10^3 \text{ J mol}^{-3} - 11.1 \times 10^3 \text{ J mol}^{-3} = 55.3 \times 10^3 \text{ J mol}^{-3}\end{aligned}$$

$$\ln K_P(T_f) = -\frac{\Delta G_{reaction}^\circ(298.15 \text{ K})}{R \times 298.15 \text{ K}} - \frac{\Delta H_{reaction}^\circ}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right)$$

$$\ln K_P(250 \text{ K}) = -\frac{2.8 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298.15 \text{ K}} - \frac{55.3 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1}\text{mol}^{-1}} \times \left(\frac{1}{250 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$\ln K_P(250 \text{ K}) = -5.426$$

$$K_P(250 \text{ K}) = 4.40 \times 10^{-3}$$

$$\alpha = \sqrt{\frac{4.40 \times 10^{-3}}{4.40 \times 10^{-3} + 4 \times 0.500}} = 4.68 \times 10^{-2}$$

Because $\Delta H_{reaction}^\circ > 0$, α increases as T increases.

P6.25) You wish to design an effusion source for Br atoms from $\text{Br}_2(g)$. If the source is to operate at a total pressure of 20 Torr, what temperature is required to produce a degree of dissociation of 0.50? What value of the pressure would increase the degree of dissociation to 0.65 at this temperature? Assume that $\Delta H_{reaction}^\circ$ is independent of temperature.

The following result for the degree of dissociation is derived in Example Problem 6.7

$$K_P(T) = \frac{4\alpha^2}{1-\alpha^2} \frac{P}{P^\circ} = \frac{4 \times (0.50)^2}{1 - (0.50)^2} \times \frac{20.0 \text{ Torr}}{760 \text{ Torr}} = 3.51 \times 10^{-2}$$

$$\ln K_P(T_f) = -\frac{\Delta G_{reaction}^\circ(298.15 \text{ K})}{R \times 298.15 \text{ K}} - \frac{\Delta H_{reaction}^\circ}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right)$$

$$\begin{aligned}\Delta H_{reaction}^\circ &= 2\Delta H_f^\circ(\text{Br}, g) - \Delta H_f^\circ(\text{Br}_2, g) \\ &= 2 \times 111.9 \times 10^3 \text{ J mol}^{-1} - 30.9 \times 10^3 \text{ J mol}^{-1} = 192.9 \times 10^3 \text{ J mol}^{-1} \\ \Delta G_{reaction}^\circ &= 2\Delta G_f^\circ(\text{Br}, g) - \Delta G_f^\circ(\text{Br}_2, g) \\ &= 2 \times 82.4 \times 10^3 \text{ J mol}^{-1} - 3.1 \times 10^3 \text{ J mol}^{-1} = 161.7 \times 10^3 \text{ J mol}^{-1}\end{aligned}$$

$$\begin{aligned}\frac{1}{T_f} &= \frac{1}{298.15 \text{ K}} - \frac{R}{\Delta H_{reaction}^\circ} \left(\ln K_P(T_f) + \frac{\Delta G_{reaction}^\circ(298.15 \text{ K})}{R \times 298.15 \text{ K}} \right) \\ &= \frac{1}{298.15 \text{ K}} - \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{192.9 \times 10^3 \text{ J mol}^{-1}} \times \left(\ln 3.51 \times 10^{-2} + \frac{161.7 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \right) \\ &= 6.868 \times 10^{-4} \text{ K}^{-1}\end{aligned}$$

$$T_f = 1456 \text{ K}$$

$$\alpha = \sqrt{\frac{K_p(T)}{K_p(T) + 4 \frac{P}{P^\circ}}}$$

$$\frac{P}{P^\circ} = \frac{K}{4} \left(\frac{1}{\alpha^2} - 1 \right) = \frac{0.0351}{4} \times \left(\frac{1}{0.65^2} - 1 \right) = 1.120 \times 10^{-2}$$

$$P = 1.120 \times 10^{-2} P^\circ = 1.120 \times 10^{-2} \times 760 \text{ Torr} = 9.12 \text{ Torr}$$

P6.26) A sample containing 2.00 moles of N₂ and 6.00 mol of H₂ are placed in a reaction vessel and brought to equilibrium at 20.0 bar and 750 K in the reaction $\frac{1}{2} \text{N}_2(g) + \frac{3}{2} \text{H}_2(g) \rightarrow \text{NH}_3(g)$.

- Calculate K_P at this temperature.
- Set up an equation relating K_P and the extent of reaction as in Example Problem 6.9.
- Using a numerical equation solver, calculate the number of moles of each species present at equilibrium.

	$\frac{1}{2} \text{N}_2(g) +$	$\frac{3}{2} \text{H}_2(g) \leftrightarrow$	$\text{NH}_3(g)$
Initial number of moles	2.00	6.00	0
Moles present at equilibrium	$2.00 - \xi$	$6.00 - 3\xi$	2ξ
Mole fraction present			

at equilibrium	$\frac{2.00 - \xi}{8 - 2\xi}$	$\frac{6.00 - 3\xi}{8 - 2\xi}$	$\frac{2\xi}{8 - 2\xi}$
Partial pressure at			
Equilibrium, $P_i = x_i P$	$\left(\frac{2.00 - \xi}{8 - 2\xi}\right)P$	$\left(\frac{6.00 - 3\xi}{8 - 2\xi}\right)P$	$\left(\frac{2\xi}{8 - 2\xi}\right)P$

We next express K_P in terms of n_0 , ξ , and P .

$$K_P(T) = \frac{\left(\frac{P_{NH_3}^{eq}}{P^\circ}\right)}{\left(\frac{P_{N_2}^{eq}}{P^\circ}\right)^{\frac{1}{2}} \left(\frac{P_{H_2}^{eq}}{P^\circ}\right)^{\frac{3}{2}}} = \frac{\left(\frac{2\xi}{8 - 2\xi}\right)P}{\left(\left(\frac{2.00 - \xi}{8 - 2\xi}\right)\frac{P}{P^\circ}\right)^{\frac{1}{2}} \left(\left(\frac{6.00 - 3\xi}{8 - 2\xi}\right)\frac{P}{P^\circ}\right)^{\frac{3}{2}}}$$

$$\Delta H_{reaction}^\circ = \Delta H_f^\circ(NH_3, g) = -45.9 \times 10^3 \text{ J mol}^{-1}$$

$$\Delta G_{reaction}^\circ = \Delta G_f^\circ(NH_3, g) = -16.5 \times 10^3 \text{ J mol}^{-1}$$

$$\ln K_P(T_f) = -\frac{\Delta G_{reaction}^\circ(298.15 \text{ K})}{R \times 298.15 \text{ K}} - \frac{\Delta H_{reaction}^\circ}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right)$$

$$\begin{aligned} \ln K_P(750 \text{ K}) &= \frac{16.5 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} + \frac{45.9 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{750 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \\ &= -4.4994 \end{aligned}$$

$$K_P(750 \text{ K}) = 1.11 \times 10^{-2}$$

The following equation can be solved numerically using a program such as Mathematica

$$K_P(T) = \frac{\left(\frac{2\xi}{8 - 2\xi}\right)20}{\left(\left(\frac{2.00 - \xi}{8 - 2\xi}\right)20\right)^{\frac{1}{2}} \left(\left(\frac{6.00 - 3\xi}{8 - 2\xi}\right)20\right)^{\frac{3}{2}}} = 1.11 \times 10^{-2}$$

The physically meaningful root of the cubic equation is $\xi = 0.241$. Therefore, there are 1.76 moles of $N_2(g)$, 5.28 moles of $H_2(g)$, and 0.48 moles of $NH_3(g)$ at equilibrium.

P6.27) Consider the equilibrium in the reaction $3O_2(g) \leftrightarrow 2O_3(g)$, with $\Delta H_{reaction}^\circ = 285.4 \times 10^3 \text{ J mol}^{-1}$ at 298 K.

- a. Without doing a calculation, predict whether the equilibrium position will shift toward reactants or products as the pressure is increased.
- b. Without doing a calculation, predict whether the equilibrium position will shift toward reactants or products as the temperature is increased.
- c. Calculate K_P at 550 K.
- d. Calculate K_x at 550 K and 0.500 bar.

- a) Without doing a calculation, predict if the equilibrium position will shift towards reactants or products as the pressure is increased.

The number of moles of products is fewer than the number of moles of reactants. Therefore, the equilibrium position will shift towards products as the pressure is increased.

- b) Without doing a calculation, predict if the equilibrium position will shift towards reactants or products as the temperature is increased.

Because $\Delta H_{reaction}^\circ > 0$, the equilibrium position will shift towards products as the temperature is increased.

- c) Calculate K_P at 550K.

$$\Delta G_{reaction}^\circ = 2\Delta G_f^\circ(O_3, g) = 2 \times 163.2 \times 10^3 \text{ J mol}^{-1}$$

$$\Delta H_{reaction}^\circ = 2\Delta H_f^\circ(O_3, g) = 2 \times 142.7 \times 10^3 \text{ J mol}^{-1}$$

$$\ln K_P(T_f) = -\frac{\Delta G_{reaction}^\circ(298.15 \text{ K})}{R \times 298.15 \text{ K}} - \frac{\Delta H_{reaction}^\circ}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right)$$

$$\ln K_P(550 \text{ K}) = -\frac{2 \times 163.2 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} - \frac{2 \times 142.7 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{550 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$\ln K_P(550 \text{ K}) = -78.954$$

$$K_P(550 \text{ K}) = 5.13 \times 10^{-35}$$

- d) Calculate K_X at 550 K and 0.500 bar.

$$K_X = K_P \left(\frac{P}{P^\circ} \right)^{-\Delta \nu} = 5.13 \times 10^{-35} \times \left(\frac{0.500 \text{ bar}}{1 \text{ bar}} \right)^{+1} = 2.57 \times 10^{-35}$$

P6.28) 2.00 moles of $\text{NOCl}(g)$ are placed in a reaction vessel and equilibrium is established with respect to the decomposition reaction $\text{NOCl}(g) \leftrightarrow \text{NO}(g) + \frac{1}{2} \text{Cl}_2(g)$.

- a. Derive an expression for K_P in terms of the degree of advancement ξ .

- b. Simplify your expression for part (a) in the limit that ξ is very small.
c. Calculate K_P , ξ and the degree of dissociation of NOCl in the limit that ξ is very small at 375 K and a total pressure of 0.500 bar.
d. Solve the expression derived in part (a) using a numerical equation solver for the conditions stated in the previous part. What is the relative error in ξ made using the approximation of part (b)?

a) Obtain an expression for K_P in terms of the degree of advancement ξ .

	$\text{NOCl}(g)$	\leftrightarrow	$\text{NO}(g)$	+	$\frac{1}{2} \text{Cl}_2(g)$
Initial number of moles	2.00		0		0
Moles present at equilibrium	2.00 - ξ		ξ		$\frac{1}{2} \xi$
Mole fraction present					
at equilibrium	$\frac{2.00 - \xi}{2 + \frac{1}{2} \xi}$		$\frac{\xi}{2 + \frac{1}{2} \xi}$		$\frac{\frac{1}{2} \xi}{2 + \frac{1}{2} \xi}$
Partial pressure at Equilibrium, $P_i = x_i P$	$\left(\frac{2.00 - \xi}{2 + \frac{1}{2} \xi} \right) P$		$\left(\frac{\xi}{2 + \frac{1}{2} \xi} \right) P$		$\left(\frac{\frac{1}{2} \xi}{2 + \frac{1}{2} \xi} \right) P$

We next express K_P in terms of ξ and P .

$$K_P(T) = \frac{\left(\frac{P_{\text{NO}}^{\text{eq}}}{P^\circ} \right) \left(\frac{P_{\text{Cl}_2}^{\text{eq}}}{P^\circ} \right)^{\frac{1}{2}}}{\left(\frac{P_{\text{NOCl}}^{\text{eq}}}{P^\circ} \right)} = \frac{\left(\frac{\xi}{2 + \frac{1}{2} \xi} \right) \frac{P}{P^\circ} \left(\left(\frac{\frac{1}{2} \xi}{2 + \frac{1}{2} \xi} \right) \frac{P}{P^\circ} \right)^{\frac{1}{2}}}{\left(\frac{2.00 - \xi}{2 + \frac{1}{2} \xi} \right) \frac{P}{P^\circ}}$$

b)

$$K_p(T) = \frac{\left(\frac{\xi}{2 + \frac{1}{2}\xi}\right) \frac{P}{P^\circ} \left(\left(\frac{\frac{1}{2}\xi}{2 + \frac{1}{2}\xi}\right) \frac{P}{P^\circ}\right)^{\frac{1}{2}}}{\left(\frac{2.00 - \xi}{2 + \frac{1}{2}\xi}\right) \frac{P}{P^\circ}} = \frac{\xi \left(\frac{\xi}{2(2 + \xi/2)} \frac{P}{P^\circ}\right)^{\frac{1}{2}}}{2.00 - \xi}$$

$$\approx \frac{\xi P \left(\frac{\xi}{4} \frac{P}{P^\circ}\right)^{\frac{1}{2}}}{P} = \frac{1}{4} \xi^{\frac{3}{2}} \left(\frac{P}{P^\circ}\right)^{\frac{1}{2}} \text{ if } \xi \ll 2$$

c) Calculate ξ and the degree of dissociation of NOCl in the above limit at 400 K and a pressure of 0.100 bar.

$$\Delta G_{reaction}^\circ = \Delta G_f^\circ(\text{NO}, g) - \Delta G_f^\circ(\text{NOCl}, g) = 87.6 \times 10^3 \text{ J mol}^{-1} - 66.1 \times 10^3 \text{ J mol}^{-1}$$

$$= 21.5 \times 10^3 \text{ J mol}^{-1}$$

$$\Delta H_{reaction}^\circ = \Delta H_f^\circ(\text{NO}, g) - \Delta H_f^\circ(\text{NOCl}, g) = 91.3 \times 10^3 \text{ J mol}^{-1} - 51.7 \times 10^3 \text{ J mol}^{-1}$$

$$= 39.6 \times 10^3 \text{ J mol}^{-1}$$

$$\ln K_p(T_f) = -\frac{\Delta G_{reaction}^\circ(298.15 \text{ K})}{R \times 298.15 \text{ K}} - \frac{\Delta H_{reaction}^\circ}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right)$$

$$\ln K_p(375 \text{ K}) = -\frac{21.5 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 298.15 \text{ K}} - \frac{39.6 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ JK}^{-1}\text{mol}^{-1}} \times \left(\frac{1}{375 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$\ln K_p(375 \text{ K}) = -5.3996$$

$$K_p(375 \text{ K}) = 4.52 \times 10^{-3}$$

$$K_p = \frac{1}{4} \xi^{\frac{3}{2}} \left(\frac{P}{P^\circ}\right)^{\frac{1}{2}}$$

$$\xi = \left[4K_p \left(\frac{P}{P^\circ} \right)^{\frac{1}{2}} \right]^{\frac{2}{3}} = \left[\frac{4 \times 4.52 \times 10^{-3}}{\sqrt{0.500}} \right]^{\frac{2}{3}} = 8.68 \times 10^{-2}$$

The degree of dissociation is $\frac{\xi}{2} = 0.044$.

d) Solve the expression derived in part a) using a numerical equation solver for the conditions stated in the previous part. What is the relative error in ξ made using the approximation of part b)?

Solving the expression of part a) without approximations gives $\xi = 8.49 \times 10^{-2}$.

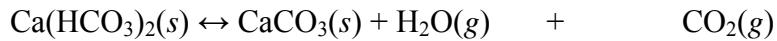
$$\text{The relative error is } \frac{8.68 \times 10^{-2} - 8.49 \times 10^{-2}}{8.49 \times 10^{-2}} = 2.2\%$$

P6.29) $\text{Ca}(\text{HCO}_3)_2(s)$ decomposes at elevated temperatures according to the stoichiometric equation $\text{Ca}(\text{HCO}_3)_2(s) \rightarrow \text{CaCO}_3(s) + \text{H}_2\text{O}(g) + \text{CO}_2(g)$.

a. If pure $\text{Ca}(\text{HCO}_3)_2(s)$ is put into a sealed vessel, the air is pumped out, and the vessel and its contents are heated, the total pressure is 0.115 bar. Determine K_P under these conditions.

b. If the vessel initially also contains 0.225 bar $\text{H}_2\text{O}(g)$, what is the partial pressure of $\text{CO}_2(g)$ at equilibrium?

a) If pure $\text{Ca}(\text{HCO}_3)_2(s)$ is put into a sealed vessel and heated, the total pressure is 0.115 bar. Determine K_P under these conditions.



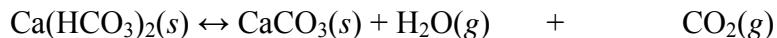
Partial pressure at

$$\text{Equilibrium, } P_i = x_i P \quad \xi P \quad \xi P$$

The total pressure is made up of equal partial pressures of $\text{H}_2\text{O}(g)$ and $\text{CO}_2(g)$.

$$K_P = \frac{P_{\text{H}_2\text{O}}}{P^\circ} \frac{P_{\text{CO}_2}}{P^\circ} = \left(\frac{P_{\text{H}_2\text{O}}}{P^\circ} \right)^2 = \left(\frac{0.115}{2} \right)^2 = 3.31 \times 10^{-3}$$

b) If one of the products is originally present



Partial pressure at

$$\text{Equilibrium, } P_i = x_i P \quad \xi P + P_i \quad \xi P$$

$$K_P = \frac{P_{\text{H}_2\text{O}}}{P^\circ} \frac{P_{\text{CO}_2}}{P^\circ} = \left(\frac{P + P_i}{P^\circ} \right) \left(\frac{P}{P^\circ} \right) = \left(\frac{P}{P^\circ} + 0.225 \right) \left(\frac{P}{P^\circ} \right) = 3.31 \times 10^{-3}$$

$$\frac{P}{P^\circ} = \frac{P_{\text{CO}_2}}{P^\circ} = 0.0139; \quad P_{\text{CO}_2} = 0.0139 \text{ bar}$$

P6.30) Assume that a sealed vessel at constant pressure of 1 bar initially contains 2.00 mol of $\text{NO}_2(g)$. The system is allowed to equilibrate with respect to the reaction $2 \text{NO}_2(g) \leftrightarrow \text{N}_2\text{O}_4(g)$. The number of moles of $\text{NO}_2(g)$ and $\text{N}_2\text{O}_4(g)$ at equilibrium is $2.00 - 2\xi$ and ξ , respectively, where ξ is the extent of reaction.

a. Derive an expression for the entropy of mixing as a function of ξ .

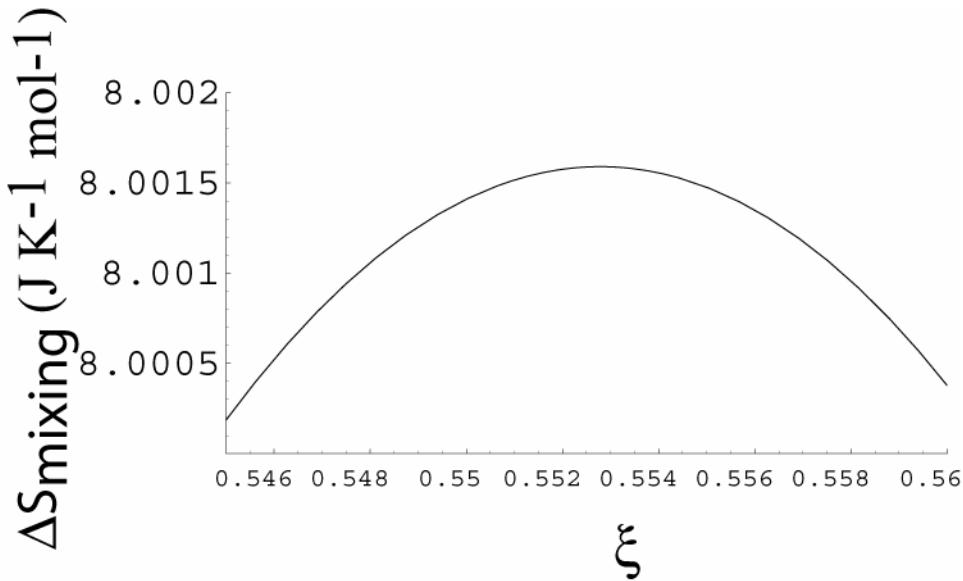
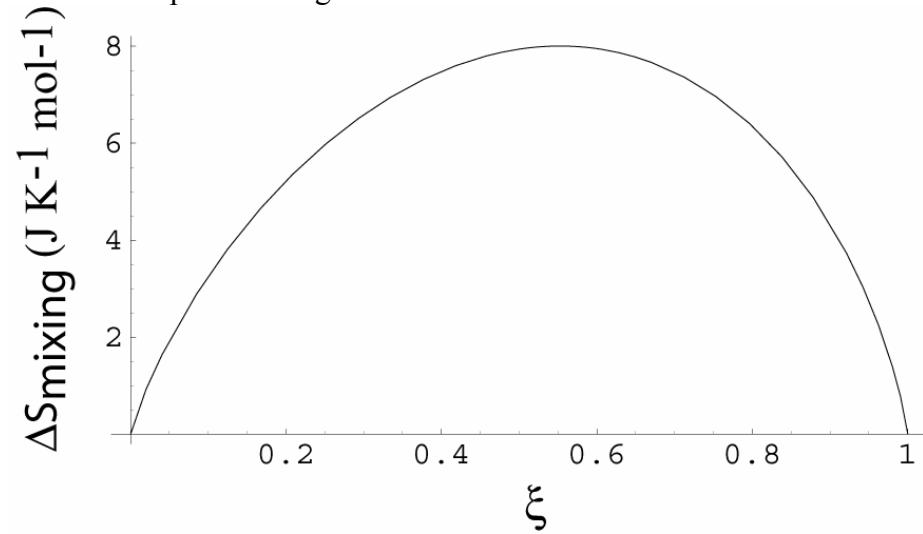
b. Graphically determine the value of ξ for which ΔS_{mixing} has its maximum value.

- c. Write an expression for G_{pure} as a function of ξ .
d. Plot $\Delta G_{reaction} = G_{pure} + \Delta G_{mixing}$ as a function of ξ for $T = 298$ K and graphically determine the value of ξ for which $\Delta G_{reaction}$ has its minimum value. Is this value the same as for part (b)?

- a) Derive an expression for the entropy of mixing as a function of ξ .

$$\begin{aligned}\Delta S_{mixing} &= -nR(x_{NO_2} \ln x_{NO_2} + x_{N_2O_4} \ln x_{N_2O_4}) \\ &= -(2.00 - \xi)R \left(\frac{2.00 - 2\xi}{2.00 - \xi} \ln \frac{2.00 - 2\xi}{2.00 - \xi} + \frac{\xi}{2.00 - \xi} \ln \frac{\xi}{2.00 - \xi} \right)\end{aligned}$$

- b) A plot and a detail plot locating the maximum are shown below.

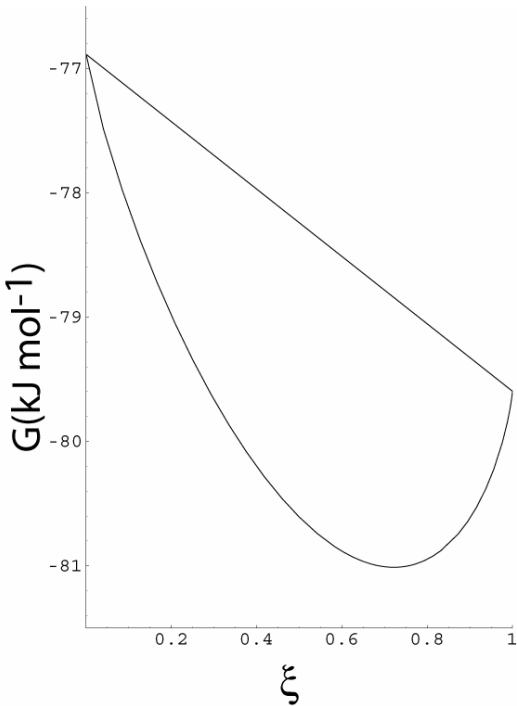


The value of ξ at the maximum is $\xi = 0.55$.

- c) Write an expression for G_{pure} as a function of ξ .

$$\Delta G_{pure} = (2.00 - 2\xi) \Delta G_f^\circ (\text{NO}_2, g) + \xi \Delta G_f^\circ (\text{N}_2\text{O}_4, g)$$

d) Plot $\Delta G_{reaction} = G_{pure} + \Delta G_{mixing}$ as a function of ξ for $T = 298$ K and graphically determine the value of ξ for which $\Delta G_{reaction}$ has its minimum value. Is this value the same as for part b)?



The minimum is at $\xi = 0.72$. The minimum is shifted to higher values of ξ relative to the ΔS vs ξ curve for mixing because of the contribution of G_{pure} to $\Delta G_{reaction}$.

Thermo Chapter 7

Questions on Concepts

Q7.1) Explain why the oscillations in the two-phase coexistence region using the Redlich-Kwong and van der Waals equations of state (see Figure 7.4) do not correspond to reality.

The oscillations predict that as V increases, P will increase. No real gas exhibits this behavior.

Q7.2) Explain the significance of the Boyle temperature.

The Boyle temperature provides a way to classify the way in which z varies with P at low values of P for different gases. If $T > T_B$, z increases with increasing P ; if $T < T_B$, z decreases with increasing P .

Q7.3) The value of the Boyle temperature increases with the strength of the attractive interactions between molecules. Arrange the Boyle temperatures of the gases Ar, CH₄, and C₆H₆ in increasing order.

Ar < CH₄ < C₆H₆

Q7.4) Will the fugacity coefficient of a gas above the Boyle temperature be less than one at low pressures?

No. The integral $\int_0^P \frac{z-1}{P'} dP'$ is always greater than zero for this case. Therefore, $\gamma > 1$ for all P .

Q7.5) Using the concept of the intermolecular potential, explain why two gases in corresponding states can be expected to have the same value for z .

Two different gases will have different values for the depth of the intermolecular potential and for the distance at which the potential becomes positive. By normalizing P , T , and V to their critical values, the differences in the intermolecular potential are to a significant extent also normalized.

Q7.6) By looking at the a and b values for the van der Waals equation of state, decide whether 1 mole of O₂ or H₂O has the higher pressure at the same value of T and V .

A is significantly larger for H₂O. Therefore, the attractive forces between H₂O molecules are greater than between O₂ molecules. Consequently, O₂ will have a higher pressure.

Q7.7) Consider the comparison made between accurate results and those based on calculations using the van der Waals and Redlich-Kwong equations of state in Figures 7.1 and 7.5. Is it clear that one of these equations of state is better than the other under all conditions?

The Redlich-Kwong gives more accurate results for almost all of the values of pressure shown in these figures. However, it is not better under all conditions.

Q7.8) Why is the standard state of fugacity, f° , equal to the standard state of pressure, P° ?

If this were not the case the fugacity would not become equal to the pressure in the limit of low pressures.

Q7.9) For a given set of conditions, the fugacity of a gas is greater than the pressure. What does this tell you about the interaction between the molecules of the gas?

If the fugacity is greater than the pressure, the repulsive part of the potential dominates the interaction between the molecules.

Q7.10) A system containing argon gas is at pressure P_1 and temperature T_1 . How would you go about estimating the fugacity coefficient of the gas?

Use the critical constants of the gas to determine the reduced pressure and temperature. With these results, estimate the fugacity coefficient using figure 7.11.

Problems

P7.1) A sample containing 35.0 g of Ar is enclosed in a container of volume 0.165 L at 390 K. Calculate P using the ideal gas, van der Waals, and Redlich-Kwong equations of state. Based on your results, does the attractive or repulsive contribution to the interaction potential dominate under these conditions?

$$V_m = \frac{0.165 \text{ L}}{35.0 \text{ g}} \times \frac{39.95 \text{ g}}{\text{mol}} = 0.1883 \text{ L mol}^{-1}$$

$$P_{\text{ideal gas}} = \frac{RT}{V_m} = \frac{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 390 \text{ K}}{0.1883 \text{ L mol}^{-1}} = 172 \text{ bar}$$

$$P_{\text{vdW}} = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 390 \text{ K}}{0.1883 \text{ L mol}^{-1} - 0.0320 \text{ L mol}^{-1}} - \frac{1.355 \text{ L}^2 \text{ bar mol}^{-2}}{(0.1883 \text{ L mol}^{-1})^2}$$

$$= 169 \text{ bar}$$

$$P_{\text{RK}} = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}} \frac{1}{V_m (V_m + b)}$$

$$= \frac{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 390 \text{ K}}{0.1883 \text{ L mol}^{-1} - 0.02219 \text{ L mol}^{-1}}$$

$$- \frac{16.86 \text{ L}^2 \text{ bar mol}^{-2} \text{ K}^{\frac{1}{2}}}{\sqrt{390 \text{ K}}} \frac{1}{0.1883 \text{ L mol}^{-1} (0.1883 \text{ L mol}^{-1} + 0.02219 \text{ L mol}^{-1})}$$

$$P_{\text{RK}} = 174 \text{ bar}$$

Because $P_{\text{vdW}} < P_{\text{ideal gas}}$, the attractive part of the interaction appears to dominate using the van der Waals equation of state. However, because $P_{\text{RK}} > P_{\text{ideal gas}}$, the repulsive part of the interaction appears to dominate using the Redlich-Kwong equation of state. This is a case where a more accurate equation of state is needed to answer the question.

P7.2) Calculate the density of $\text{O}_2(g)$ at 375 K and 385 bar using the ideal gas and the van der Waals equations of state. Use a numerical equation solver to solve the van der Waals equation for V_m or use an iterative approach starting with V_m equal to the ideal gas result. Based on your result, does the attractive or repulsive contribution to the interaction potential dominate under these conditions?

$$V_m = \frac{RT}{P} = \frac{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 375 \text{ K}}{385 \text{ bar}} = 8.10 \times 10^{-2} \text{ L}$$

$$P_{\text{vdW}} = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 370 \text{ K}}{V_m - 0.0319 \text{ L mol}^{-1}} - \frac{1.382 \text{ L}^2 \text{ bar mol}^{-2}}{(V_m)^2}$$

The three solutions to this equation are

$$V_m = (0.0131 \pm 0.0339i) \text{ L mol}^{-1} \text{ and } V_m = 0.0867 \text{ L mol}^{-1}$$

Only the real solution is of significance.

$$\rho_{\text{ideal gas}} = \frac{M}{V_m} = \frac{32.0 \text{ g mol}^{-1}}{0.0867 \text{ L mol}^{-1}} = 395 \text{ g L}^{-1}$$

$$\rho_{\text{vdW}} = \frac{M}{V_m} = \frac{32.0 \text{ g mol}^{-1}}{0.0867 \text{ L mol}^{-1}} = 369 \text{ g L}^{-1}$$

Because the van der Waals density is less than the ideal gas density, the repulsive part of the potential dominates.

P7.3) At 500 K and 400 bar, the experimentally determined density of O₂ is 7.90 mol L⁻¹. Compare this with values calculated from the ideal and Redlich-Kwong equations of state. Use a numerical equation solver to solve the Redlich-Kwong equation for V_m. Discuss your results.

For the ideal gas,

$$\frac{1}{V_m} = \frac{P}{RT} = \frac{400 \text{ bar}}{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 500 \text{ K}} = 9.62 \text{ mol L}^{-1}$$

$$P_{RK} = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}} \frac{1}{V_m(V_m + b)}$$

$$400 \text{ bar} = \frac{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 500 \text{ K}}{V_m - 0.02208 \text{ L mol}^{-1}}$$

$$-\frac{17.40 \text{ L}^2 \text{ bar mol}^{-2} \text{ K}^{\frac{1}{2}}}{\sqrt{500 \text{ K}}} \frac{1}{V_m(V_m + 0.02208 \text{ L mol}^{-1})}$$

The three solutions to this equation are

$$V_m = (-0.00529 \pm 0.0186i) \text{ L mol}^{-1} \text{ and } V_m = 0.1145 \text{ L mol}^{-1}$$

Only the real solution is of significance.

$$\frac{1}{V_m} = \frac{1}{0.1145 \text{ L mol}^{-1}} = 8.73 \text{ mol L}^{-1}$$

The ideal gas density is greater than that calculated with the Redlich-Kwong equation of state and the experimental result showing that the repulsive part of the potential dominates. The Redlich-Kwong result is in error by +10%.

P7.4) The observed Boyle temperatures of H₂, N₂, and CH₄ are 107.3, 324, and 509.7 K, respectively. Compare these values with those calculated for a van der Waals gas with the appropriate parameters.

$$T_B = \frac{a}{Rb} \text{ for a van der Waals gas.}$$

In solving this problem, keep in mind that $1 \text{ dm}^3 = 1 \text{ L} = 10^{-3} \text{ m}^3$.

$$T_B(\text{H}_2) = \frac{0.2452 \text{ dm}^6 \text{ bar mol}^{-2}}{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 0.0265 \text{ dm}^3 \text{ mol}} = 111 \text{ K}$$

This value is slightly higher than the experimental value.

$$T_B(\text{N}_2) = \frac{1.370 \text{ dm}^6 \text{ bar mol}^{-2}}{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 0.0387 \text{ dm}^3 \text{ mol}^{-1}} = 426 \text{ K}$$

This value is substantially larger than the experimental value.

$$T_B(\text{CH}_4) = \frac{2.303 \text{ dm}^6 \text{ bar mol}^{-2}}{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 0.0431 \text{ dm}^3 \text{ mol}^{-1}} = 643 \text{ K}$$

This value is substantially larger than the experimental value.

P7.5) Calculate the van der Waals parameters of methane from the values of the critical constants.

$$b = \frac{RT_c}{8P_c} = \frac{8.314 \times 10^{-2} \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1} \times 190.56 \text{ K}}{8 \times 45.99 \text{ bar}} = 0.0431 \text{ dm}^3 \text{ mol}^{-1}$$

$$a = \frac{27R^2 T_c^2}{64P_c} = \frac{27 \times (8.314 \times 10^{-2} \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1})^2 \times (190.56 \text{ K})^2}{64 \times 45.99 \text{ bar}} = 2.303 \text{ dm}^6 \text{ bar mol}^{-2}$$

P7.6) Calculate the Redlich-Kwong parameters of methane from the values of the critical constants.

$$a = \frac{R^2 T_c^{5/2}}{9P_c (2^{1/3} - 1)} = \frac{(8.314 \times 10^{-2} \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1})^2 \times (190.56)^{5/2}}{9 \times 45.99 \text{ bar} (2^{1/3} - 1)} = 32.20 \text{ dm}^6 \text{ bar K}^{1/2} \text{ mol}^{-2}$$

$$b = \frac{(2^{1/3} - 1) RT_c}{3P_c} = \frac{(2^{1/3} - 1) \times 8.3145 \times 10^{-2} \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1} \times 190.56 \text{ K}}{3 \times 45.99 \text{ bar}} = 0.02985 \text{ dm}^3 \text{ mol}^{-1}$$

P7.7) Use the law of corresponding states and Figure 7.8 to estimate the molar volume of methane at $T = 285 \text{ K}$ and $P = 180 \text{ bar}$.

$$T_r = \frac{285 \text{ K}}{190.56 \text{ K}} = 1.5 \quad P_r = \frac{180 \text{ bar}}{45.99 \text{ bar}} = 3.91. \text{ Therefore, } z \approx 0.8$$

$$\frac{PV_m}{RT} = 0.8; \quad V_m = 0.8 \frac{RT}{P} = 0.8 \times \frac{8.314 \times 10^{-2} \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1} \times 285 \text{ K}}{180 \text{ bar}}$$

$$V_m = 0.105 \text{ L mol}^{-1}$$

P7.8) Calculate the P and T values for which $\text{H}_2(g)$ is in a corresponding state to $\text{Xe}(g)$ at 450 K and 85.0 bar.

$$T_R^{Xe} = \frac{T_C^{Xe}}{T_C^{Xe}} = \frac{450 \text{ K}}{289.74 \text{ K}} = 1.55; \quad T^{H_2} = 1.55 T_C^{H_2} = 1.55 \times 32.98 \text{ K} = 51.2 \text{ K}$$

$$P_R^{Xe} = \frac{P_C^{Xe}}{P_C^{Xe}} = \frac{85.0 \text{ bar}}{58.40 \text{ bar}} = 1.46; \quad P^{H_2} = 1.46 P_C^{H_2} = 1.46 \times 12.93 \text{ bar} = 18.8 \text{ bar}$$

P7.9) Assume that the equation of state for a gas can be written in the form

$P(V_m - b(T)) = RT$. Derive an expression for $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$ and $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$ for such a gas in terms of $b(T)$, $\frac{db(T)}{dT}$, P , and V_m .

$$P \left(\frac{V}{n} - b(T) \right) = RT; \quad \frac{V}{n} = \frac{RT}{P} + b(T)$$

$$V = nb(T) + \frac{nRT}{P}$$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \left(\frac{ndb(T)}{dT} + \frac{nR}{P} \right) = \frac{1}{V_m} \left(\frac{db(T)}{dT} + \frac{R}{P} \right)$$

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left(-\frac{nRT}{P^2} \right) = \frac{RT}{V_m P^2}$$

P7.10) One mole of Ar initially at 298 K undergoes an adiabatic expansion against a pressure $P_{external} = 0$ from a volume of 20.0 L to a volume of 65.0 L. Calculate the final temperature using the ideal gas and van der Waals equations of state.

$w = q = 0$, $\Delta U = 0$ for an ideal gas and $\Delta T = 0$ because U is a function of T only. Using the results of Example Problem 3.5 for a van der Waals gas,

$$\begin{aligned}
\Delta U_{T,m} &= a \left(\frac{1}{V_{m,i}} - \frac{1}{V_{m,f}} \right)_m \\
&= 1.355 \text{ dm}^6 \text{ bar mol}^{-2} \times \frac{10^5 \text{ Pa}}{\text{bar}} \times \frac{10^6 \text{ m}^3}{\text{dm}^6} \times \left(\frac{1}{65.0 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}} - \frac{1}{20.0 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}} \right) \\
&= -4.69 \text{ J} \\
\Delta T &= \frac{\Delta U_{T,m}}{C_{V,m}} = -\frac{4.69 \text{ J mol}^{-1}}{12.5 \text{ J K}^{-1} \text{ mol}^{-1}} = -0.376 \text{ K} \\
T_f &= 297.6 \text{ K}
\end{aligned}$$

P7.11) One mole of Ar undergoes an isothermal reversible expansion from an initial volume of 1.00 L to a final volume of 65.0 L at 298 K. Calculate the work done in this process using the ideal gas and van der Waals equations of state. What percentage of the work done by the van der Waals gas arises from the attractive potential?

For the ideal gas,

$$w = -nRT \ln \frac{V_f}{V_i} = -1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln \frac{65.0 \text{ L}}{1.00 \text{ L}} = -10.34 \times 10^3 \text{ J}$$

For the van der Waals gas,

$$\begin{aligned}
w &= - \int_{V_i}^{V_f} \left(\frac{nRT}{V-nb} - \frac{n^2a}{V^2} \right) dV = - \left[nRT \ln(V-nb) + \frac{an^2}{V} \right]_{V_i}^{V_f} \\
&= - \left[1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln(V - 3.20 \times 10^{-5} \text{ m}^3) + \frac{0.1355 \text{ Pa m}^6}{V} \right]_{0.001 \text{ m}^3}^{0.065 \text{ m}^3} \\
&= -10.42 \times 10^3 \text{ J} + 133 \text{ J} = -10.29 \times 10^3 \text{ J} \\
100 \times \frac{133 \text{ J}}{10.29 \times 10^3 \text{ J}} &= 1.3\%
\end{aligned}$$

P7.12) For a van der Waals gas, $z = \frac{V_m}{V_m - b} - \frac{a}{RTV_m}$. Expand the first term of this

expression in a Taylor series in the limit $V_m \gg b$ to obtain $z \approx 1 + \left(b - \frac{a}{RT} \right) \frac{1}{V_m}$.

$$f(x) = f(0) + \left(\frac{df(x)}{dx} \right)_{x=0} x + \dots \text{ In this case, } f(x) = \frac{1}{1 - \frac{b}{V_m}} \text{ and } x = \frac{b}{V_m}$$

$$z = \frac{V_m}{V_m - b} - \frac{a}{RTV_m} = \frac{1}{1 - \frac{b}{V_m}} - \frac{a}{RTV_m}$$

$$\frac{1}{1 - \frac{b}{V_m}} \approx \left(1 \left/ \left[1 - \frac{b}{V_m} \right] \right. \right)_{\frac{b}{V_m} = 1} + \left[\frac{d \left(1 \left/ \left[1 - \frac{b}{V_m} \right] \right. \right)}{d \left(\frac{b}{V_m} \right)} \right]_{\frac{b}{V_m} = 1} \frac{b}{V_m} = 1 + \frac{b}{V_m}$$

$$z \approx 1 + \frac{b}{V_m} - \frac{a}{RTV_m} = 1 + \frac{1}{V_m} \left(b - \frac{a}{RT} \right)$$

P7.13) Show that $T\beta = 1 + T \left(\frac{\partial \ln z}{\partial T} \right)_P$ and that $P\kappa = 1 - P \left(\frac{\partial \ln z}{\partial P} \right)_T$.

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P ; \quad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$z = \frac{PV}{RT} ; \quad \left(\frac{\partial z}{\partial T} \right)_P = -\frac{VP}{RT^2} + \frac{P}{RT} \left(\frac{\partial V}{\partial T} \right)_P = -\frac{VP}{RT^2} + \frac{PV}{RT} \beta$$

$$\left(\frac{\partial \ln z}{\partial T} \right)_P = \frac{1}{z} \left(\frac{\partial z}{\partial T} \right)_P = \frac{RT}{VP} \left(-\frac{VP}{RT^2} + \frac{PV}{RT} \beta \right) = -\frac{1}{T} + \beta$$

$$\text{Therefore } 1 + T \left(\frac{\partial \ln z}{\partial T} \right)_P = 1 + T \left(-\frac{1}{T} + \beta \right) = \beta T$$

$$\left(\frac{\partial z}{\partial P} \right)_T = \frac{V}{RT} + \frac{P}{RT} \left(\frac{\partial V}{\partial P} \right)_T = \frac{V}{RT} - \frac{PV}{RT} \kappa$$

$$\left(\frac{\partial \ln z}{\partial P} \right)_T = \frac{1}{z} \left(\frac{\partial z}{\partial P} \right)_T = \frac{RT}{PV} \left(\frac{V}{RT} - \frac{PV}{RT} \kappa \right) = \frac{1}{P} - \kappa$$

$$\text{Therefore } 1 - P \left(\frac{\partial \ln z}{\partial P} \right)_T = 1 - P \left(\frac{1}{P} - \kappa \right) = P\kappa$$

P7.14) A van der Waals gas has a value of $z = 1.00084$ at 298 K and 1 bar and the Boyle temperature of the gas is 125 K. Because the density is low, you can use the ideal gas law to calculate V_m . Use this information and the result of Problem 7.12 to estimate a and b .

$$z - 1 = \frac{1}{V_m} \left(b - \frac{a}{RT} \right); \quad T_B = \frac{a}{Rb}$$

$$z - 1 = \frac{b}{V_m} \left(1 - \frac{T_B}{T} \right)$$

$$b = \frac{z - 1}{1 - \frac{T_B}{T}} \frac{RT}{P} = \frac{0.00084}{1 - \frac{125 \text{ K}}{298 \text{ K}}} \times \frac{8.314 \times 10^{-2} \text{ dm}^3 \text{ bar mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{1 \text{ bar}}$$

$$= 0.0359 \text{ dm}^3 \text{ mol}^{-1} = 3.59 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

$$a = RbT_B = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 3.59 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \times 125 \text{ K} = 3.73 \times 10^{-2} \text{ m}^6 \text{ Pa mol}^{-2}$$

P7.15) The experimental critical constants of H₂O are $T_c = 647.14 \text{ K}$, $P_c = 220.64 \text{ bar}$, and $V_c = 55.95 \times 10^{-3} \text{ L}$. Use the values of P_c and T_c to calculate V_c . Assume that H₂O behaves as (a) an ideal gas, (b) a van der Waals gas, and (c) a Redlich-Kwong gas at the critical point. For parts (b) and (c), use the formulas for the critical compression factor. Compare your answers with the experimental value.

Assuming an ideal gas,

$$V_c = \frac{RT_c}{P_c} = \frac{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 647.14 \text{ K}}{220.64 \text{ bar}} = 0.2438 \text{ L}$$

For a van der Waals gas,

$$z_c = \frac{PV_c}{RT_c} = \frac{3}{8}; \quad V_c = \frac{3}{8} \frac{RT_c}{P_c} = \frac{3}{8} \times 0.2438 \text{ L} = 91.4 \times 10^{-3} \text{ L}$$

For a Redlich-Kwong gas,

$$z_c = \frac{PV_c}{RT_c} = 0.333; \quad V_c = 0.333 \frac{RT_c}{P_c} = 0.333 \times 0.2438 \text{ L} = 81.2 \times 10^{-3} \text{ L}$$

Although the agreement with experiment is better for the van der Waals and Redlich-Kwong models than for the ideal gas model, all results differ significantly from the true value.

P7.16) Another equation of state is the Bertholet equation, $V_m = \frac{RT}{P} + b - \frac{a}{RT^2}$. Derive expressions for $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$ and $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$ from the Bertholet equation in terms of V , T , and P .

$$V = \frac{nRT}{P} + nb - \frac{na}{RT^2}$$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \left(\frac{nR}{P} + \frac{2na}{RT^3} \right) = \frac{1}{V_m} \left(\frac{R}{P} + \frac{2a}{RT^3} \right)$$

$$\kappa = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = - \frac{1}{V} \left(- \frac{nRT}{P^2} \right) = \frac{nRT}{P^2V} = \frac{RT}{P^2V_m}$$

P7.17) For the Bertholet equation, $V_m = \frac{RT}{P} + b - \frac{a}{RT^2}$, find an expression for the Boyle temperature in terms of a , b , and R .

$$z = \frac{PV_m}{RT} = 1 + \frac{Pb}{RT} - \frac{Pa}{R^2T^3}$$

$$\left(\frac{\partial z}{\partial P} \right)_T = b - \frac{a}{R^2T^3} \text{ and at } T = T_B, \left(\frac{\partial z}{\partial P} \right)_T = 0$$

Therefore $b - \frac{a}{R^2T_B^3} = 0$

$$T_B = \sqrt{\frac{a}{Rb}}$$

P7.18) The experimentally determined density of H₂O at 1200 bar and 800 K is 537 g L⁻¹. Calculate z and V_m from this information. Compare this result with what you would have estimated from Figure 7.8. What is the relative error in using Figure 7.8 for this case?

$$V_m = \frac{M}{\rho} = \frac{18.02 \text{ g mol}^{-1}}{537 \text{ g L}^{-1}} = 3.34 \times 10^{-2} \text{ L mol}^{-1}$$

$$z = \frac{PV_m}{RT} = \frac{1200 \text{ bar} \times 3.34 \times 10^{-2} \text{ L mol}^{-1}}{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 800 \text{ K}} = 0.602$$

Because $P_r = \frac{1200 \text{ bar}}{220.64 \text{ bar}} = 5.44$ and $T_r = \frac{800 \text{ K}}{647.14 \text{ K}} = 1.24$, figure 7.7 predicts $z = 0.75$. The relative error in z is 25%.

P7.19) The volume of a spherical molecule can be estimated as $V = b/4N_A$ where b is the van der Waals parameter and N_A is Avogadro's number. Justify this relationship by considering a spherical molecule of radius r , with volume $V_{molecule} = \frac{4}{3}\pi r^3$. What is the volume centered at the molecule that is excluded for the center of mass of a second molecule in terms of V ? Multiply this volume by N_A and set it equal to b . Apportion this

volume equally among the molecules to arrive at $V_{molecule} = b/4N_A$. Calculate the radius of a methane molecule from the value of its van der Waals parameter b .

The excluded volume is $\frac{4}{3}\pi(2r)^3 = 8V_{molecule}$, or $4V_{molecule}$ per molecule. Therefore, $b = 4N_A V_{molecule}$ and $V_{molecule} = b/4N_A$.

$$N_A \frac{16}{3}\pi r^3 = b$$

$$r = \left(\frac{3b}{16N_A\pi} \right)^{\frac{1}{3}} = \left(\frac{3 \times 4.31 \times 10^{-5} \text{ m}^3}{16\pi \times 6.022 \times 10^{23}} \right)^{\frac{1}{3}} = 1.63 \times 10^{-10} \text{ m}$$

P7.20) At what temperature does the slope of the z versus P curve as $P \rightarrow 0$ have its maximum value for a van der Waals gas? What is the value of the maximum slope?

$$\left(\frac{\partial Z}{\partial P} \right)_{T,P \rightarrow 0} = \frac{1}{RT} \left(b - \frac{a}{RT} \right) \text{ for a van der Waals gas}$$

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial Z}{\partial P} \right)_T \right)_{P \rightarrow 0} = -\frac{1}{RT^2} \left(b - \frac{a}{RT} \right) + \frac{1}{RT^3} = -\frac{1}{RT^2} \left(b - \frac{2a}{RT} \right)$$

Setting this derivative equal to zero gives

$$b - \frac{2a}{RT_{max}} = 0 \quad T_{max} = \frac{2a}{Rb}$$

$$\text{The maximum slope is } \frac{1}{RT_{max}} \left(b - \frac{a}{RT_{max}} \right) = \frac{b}{2a} \left[b - a \left(\frac{b}{2a} \right) \right] = \frac{b^2}{4a}$$

P7.21) Show that the van der Waals and Redlich-Kwong equations of state reduce to the ideal gas equation of state in the limit of low density.

$\frac{RT}{V_m - b} - \frac{a}{V_m^2}$: In the limit of low density, V_m is large and $V_m \gg b$. The second term in

the van der Waals equation can be neglected because it goes as $\frac{1}{V_m^2}$, and in the first term,

$$\frac{RT}{V_m - b} \rightarrow \frac{RT}{V_m}.$$

$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}} \frac{1}{V_m(V_m + b)}$: In the limit of low density, V_m is large and $V_m \gg b$. As

for the van der Waals equation, the second term in the Redlich-Kwong equation can be neglected because it goes as $\frac{1}{V_m^2}$. In the limit, the first term becomes $\frac{RT}{V_m - b} \rightarrow \frac{RT}{V_m}$.

P7.22) Show that the second virial coefficient for a van der Waals gas is given by

$$B(T) = \frac{1}{RT} \left(\frac{\partial z}{\partial \frac{1}{V_m}} \right)_T = b - \frac{a}{RT}$$

Let $u = \frac{1}{V_m}$. The virial expansion takes the form

$$P = RT \left([P(u)]_{u=0} + \left[\frac{dP(u)}{du} \right]_{u=0} u + \frac{1}{2} \left[\frac{d^2 P(u)}{du^2} \right]_{u=0} u^2 + \dots \right)$$

Therefore, the second virial coefficient is $B(T) = \frac{1}{2RT} \left[\frac{d^2 P(u)}{du^2} \right]_{u=0}$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{RT}{1/u - b} - au^2$$

$$\frac{dP}{du} = -\frac{RT}{(1/u - b)^2} \frac{d}{du}(1/u) - 2au = \frac{RT}{u^2 (1/u - b)^2} - 2au = \frac{RT}{(1 - ub)^2} - 2au$$

$$\frac{d^2 P}{du^2} = \frac{2bRT}{(1 - ub)^3} - 2a$$

$$\lim_{u \rightarrow 0} \frac{2bRT}{(1 - ub)^3} - 2a = 2bRT - 2a \text{ and}$$

$$B(T) = \frac{1}{2RT} \left[\frac{d^2 P(u)}{du^2} \right]_{u=0} = b - \frac{a}{RT}$$

P7.23) For a gas at a given temperature, the compressibility is described by the

empirical equation $z = 1 - 9.00 \times 10^{-3} \frac{P}{P^\circ} + 4.00 \times 10^{-5} \left(\frac{P}{P^\circ} \right)^2$, where $P^\circ = 1$ bar. Calculate

the activity coefficient for $P = 100, 200, 300, 400$, and 500 bar. For which of these values is the activity coefficient greater than one?

$$\ln \gamma = \int_0^P \frac{z-1}{P'} dP' = \int_0^P \frac{\left(1 - 9.00 \times 10^{-3} P' + 4.00 \times 10^{-5} (P')^2\right) - 1}{P'} dP'$$

$$\ln \gamma = -9.00 \times 10^{-3} P + 2.00 \times 10^{-5} P^2$$

$\gamma = 0.497, 0.368, 0.407, 0.670,$ and 1.65 at $100, 200, 300, 400,$ and 500 bar respectively.

P7.24) For values of z near one, it is a good approximation to write

$$z(P) = 1 + \left(\frac{\partial z}{\partial P}\right)_T P. \text{ If } z = 1.00054 \text{ at } 0^\circ\text{C and 1 bar, and the Boyle temperature of the}$$

gas is 220 K, estimate the values of V_m, a and b for the van der Waals gas. An equation solver will be useful for this problem.

From Example Problem 7.2,

$$\left(\frac{\partial z}{\partial P}\right)_T = \frac{1}{RT} \left(b - \frac{a}{RT}\right)$$

We can write three equations in three unknowns:

$$z - 1 = \left(b - \frac{a}{RT}\right) \frac{P}{RT}$$

$$5.4 \times 10^{-4} = \left(b - \frac{a}{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 273.15 \text{ K}}\right) \times \frac{1 \text{ bar}}{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 273.15 \text{ K}}$$

$$T_B = \frac{a}{Rb} = \frac{a}{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times b} = 220 \text{ K}$$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m} = \frac{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 273.15 \text{ K}}{V_m - b} - \frac{a}{V_m} = 1 \text{ bar}$$

Using an equation solver, the results are

$$a = 1.15 \text{ L}^2 \text{ bar mol}^{-2}, b = 0.0630 \text{ L mol}^{-1}, V_m = 22.72 \text{ L}.$$

P7.25) Calculate the critical volume for ethane using the data for T_c and P_c in Table 7.2 assuming a) the ideal gas equation of state, and b) the van der Waals equation of state. Use an iterative approach to obtain V_c from the van der Waals equation, starting with the ideal gas result. How well do the calculations agree with the tabulated values for V_c ?

Using the ideal gas law,

$$V_c = \frac{RT_c}{P_c} = \frac{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 305.32 \text{ K}}{48.72 \text{ bar}} = 0.5211 \text{ L}$$

Using the van der Waals equation of state,

$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} = \frac{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 305.32 \text{ K}}{V_c - 0.0651 \text{ L mol}^{-1}} - \frac{5.580 \text{ L}^2 \text{ bar mol}^{-2}}{V_c^2}$$

Setting $V_c = 0.5211$ L gives $P_c = 35.13$ bar, which is below the experimental value $P_c = 48.72$ bar. Setting $V_c = 0.300$ L gives $P_c = 46.06$ bar, and setting $V_c = 0.1784$ L gives $P_c = 48.72$ bar. The relative error of this value for V_c is $100 \times \frac{0.1874 \text{ L} - 0.1455 \text{ L}}{0.1455 \text{ L}} = +29\%$.

Thermo Chapter 8

Questions on Concepts

Q8.1) At a given temperature, a liquid can coexist with its gas at a single value of the pressure. However, you can sense the presence of $\text{H}_2\text{O}(g)$ above the surface of a lake by the humidity, and it is still there if the barometric pressure rises or falls at constant temperature. How is this possible?

The statement that at a given temperature, a liquid can coexist with its gas at a single value of the pressure holds for a system with only one substance. For the case described, the system consists of water and air. The change in barometric pressure is equivalent to an external pressure exerted on a liquid. As discussed in Section 8.5, this will change the vapor pressure only slightly.

Q8.2) Why is it reasonable to show the μ versus T segments for the three phases as straight lines as is done in <LINK>Figure 8.1? More realistic curves would have some curvature. Is the curvature upward or downward on a μ versus T plot?

$\left(\frac{\partial \mu}{\partial T}\right)_P = -S$. Because S increases with T , the realistic curves will curve downward.

Q8.3) Figure 8.5 is not drawn to scale. What would be the relative lengths on the q_P axis of the liquid + solid, liquid, and liquid + gas segments for water if the drawing were to scale and the system consisted of H_2O ?

For the liquid + solid segment, the length of the segment is ΔH_{fusion} , for the liquid segment, the length is $C_{P,m}^{liquid} \Delta T$, and for the liquid + gas segment, the length is $\Delta H_{vaporization}$. Numerically, for water, the relative lengths are 6008 : 7550 : 40656.

Q8.4) Why is $\Delta H_{sublimation} = \Delta H_{fusion} + \Delta H_{vaporization}$?

Because H is a state function, ΔH for the process solid \rightarrow liquid \rightarrow gas must be the same as for the process solid \rightarrow gas if the initial and final states are the same.

Q8.5) A triple point refers to a point in a P - T phase diagram for which three phases are in equilibrium. Do all triple points correspond to gas–liquid–solid equilibrium?

No. If there are several solid phases, there can be a triple point corresponding to equilibrium between 3 solid phases.

Q8.6) Why are the triple point temperature and the normal freezing point very close in temperature for most substances?

This is the case because the freezing point changes only slightly with temperature.

Q8.7) As the pressure is increased at -45°C , ice I is converted to ice II. Which of these phases has the lower density?

The higher density phase, in this case ice II, is more stable as the pressure is increased. Therefore ice I is the less dense phase.

Q8.8) What is the physical origin of the pressure difference across a curved liquid–gas interface?

The origin is the cohesive forces in the liquid. Across an interface, the resultant force vector is not zero in magnitude. If the interface is curved, the resultant force tends to minimize the surface area, leading to a pressure difference across the interface.

Q8.9) Why does the triple point in a P - T diagram become a triple line in a P - V diagram?

This is the case because a gas and a liquid are in equilibrium for the range of values of volume from that of the pure liquid to that of the pure gas at a given temperature.

Q8.10) Give a molecular level explanation why the surface tension of $\text{Hg}(l)$ is not zero.

Hg atoms have a strong attractive interaction. Therefore, those atoms at the surface of a droplet that have fewer nearest neighbors than an atom in the liquid experience a net force perpendicular to the surface that will lead to a pressure increase inside the droplet.

Problems

P8.1) In this problem, you will calculate the differences in the chemical potentials of ice and supercooled water, and of steam and superheated water all at 1 atm pressure shown schematically in Figure 8.1. For this problem, $S_{\text{H}_2\text{O},s}^{\circ} = 48.0 \text{ J mol}^{-1} \text{ K}^{-1}$, $S_{\text{H}_2\text{O},l}^{\circ} = 70.0 \text{ J mol}^{-1} \text{ K}^{-1}$, and $S_{\text{H}_2\text{O},g}^{\circ} = 188.8 \text{ J mol}^{-1} \text{ K}^{-1}$.

- By what amount does the chemical potential of water exceed that of ice at -5.00°C ?
- By what amount does the chemical potential of water exceed that of steam at 105.00°C ?

- By what amount does the chemical potential of water exceed that of ice at -5.00°C ?
$$\Delta\mu = \Delta G_m = -\Delta S_m \Delta T \text{ at constant } P$$

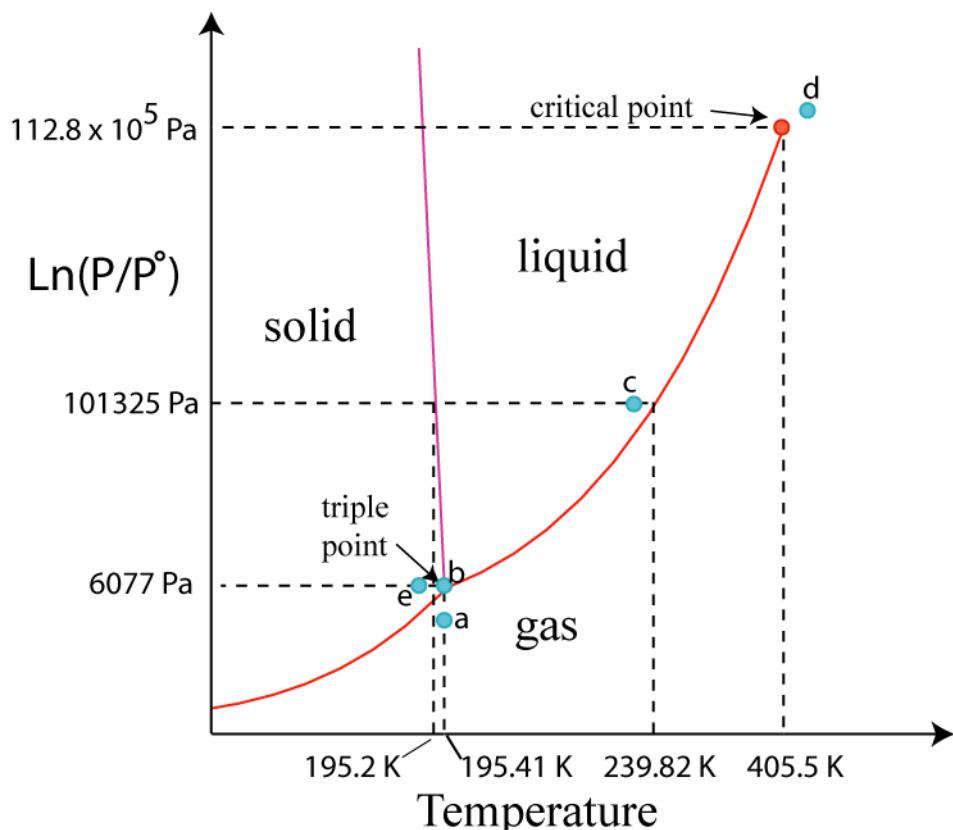
$$\begin{aligned}\Delta\mu &= \Delta G_m = -\left(S_{\text{H}_2\text{O},l}^{\circ} - S_{\text{H}_2\text{O},s}^{\circ}\right)(\Delta T) = -\left(70.0 \text{ J K}^{-1} \text{ mol}^{-1} - 48.0 \text{ J K}^{-1} \text{ mol}^{-1}\right)(-5.00^{\circ}\text{C}) \\ &= 110 \text{ J mol}^{-1}\end{aligned}$$

- By what amount does the chemical potential of water exceed that of steam at 105.00°C ?

$$\Delta\mu = \Delta G_m = -\left(S_{H_2O,l}^\circ - S_{H_2O,g}^\circ\right)(\Delta T) = -\left(70.0 \text{ J K}^{-1}\text{mol}^{-1} - 188.8 \text{ J K}^{-1}\text{mol}^{-1}\right) \times (5.00^\circ C)$$

$$= 594 \text{ J mol}^{-1}$$

P8.2) The phase diagram of NH₃ can be characterized by the following information. The normal melting and boiling temperatures are 195.2 and 239.82 K, respectively, the triple point pressure and temperature are 6077 Pa and 195.41 K, respectively. The critical point parameters are $112.8 \times 10^5 \text{ Pa}$ and 405.5 K. Make a sketch of the *P-T* phase diagram (not necessarily to scale) for NH₃. Make a point in the phase diagram for the following conditions. State which and how many phases are present.



- | | |
|--|----------------------------------|
| a) $195.41 \text{ K}, 1050 \text{ Pa}$ | single phase gas |
| b) $195.41 \text{ K}, 6077 \text{ Pa}$ | triple point: gas, liquid, solid |
| c) $237.51 \text{ K}, 101325 \text{ Pa}$ | single phase liquid |
| d) $420 \text{ K}, 130 \times 10^5 \text{ Pa}$ | single phase supercritical fluid |
| e) $190 \text{ K}, 6077 \text{ Pa}$ | single phase solid |

P8.3) Within what range can you restrict the values of *P* and *T* if the following information is known about CO₂?

- a. As the temperature is increased, the solid is first converted to the liquid and subsequently to the gaseous state.

The temperature and pressure are greater than the values for the triple point, -56.6°C and 5.11 atm.

- b. As the pressure on a cylinder containing pure CO_2 is increased from 65 to 80 atm, no interface delineating liquid and gaseous phases is observed.

The temperature is greater than the critical temperature, 31.0°C .

- c. Solid, liquid, and gas phases coexist at equilibrium.

The system is at the triple point, -56.6°C and 5.11 atm.

- d. An increase in pressure from 10 to 50 atm converts the liquid to the solid.

The temperature is slightly greater than the triple point value of -56.6°C .

- e. An increase in temperature from -80° to 20°C converts a solid to a gas with no intermediate liquid phase.

The pressure is below the triple point pressure value of 5.11 atm.

P8.4) Within what range can you restrict the values of P and/or T if the following information is known about sulfur?

- a. Only the monoclinic solid phase is observed for $P = 1 \text{ atm}$.

$$95.39^{\circ}\text{C} < T < 115.18^{\circ}\text{C}$$

- b. When the pressure on the vapor is increased, the liquid phase is formed.

$$T > 115.18^{\circ}\text{C}, P > 3.2 \times 10^{-5} \text{ atm}$$

- c. Solid, liquid, and gas phases coexist at equilibrium.

$$P = 3.2 \times 10^{-5} \text{ atm}, T = 115.18^{\circ}\text{C}$$

- d. As the temperature is increased, the rhombic solid phase is converted to the liquid directly.

$$T > 153^{\circ}\text{C}, P > 1420 \text{ atm}$$

e. As the temperature is increased at 1 atm, the monoclinic solid phase is converted to the liquid directly.

$$115.21^\circ\text{C} > T > 95.39^\circ\text{C}$$

P8.5) The vapor pressure of liquid SO₂ is 2232 Pa at 201 K, and $\Delta H_{vaporization} = 24.94 \text{ kJ mol}^{-1}$. Calculate the normal and standard boiling points. Does your result for the normal boiling point agree with that in Table 8.2? If not, suggest a possible cause.

$$\ln \frac{P_f}{P_i} = -\frac{\Delta H_{m,vaporization}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$T_f = \frac{\Delta H_{m,vaporization}}{R \left(\frac{\Delta H_{m,vaporization}}{RT_i} - \ln \frac{P_f}{P_i} \right)}$$

At the normal boiling point, $P = 101325 \text{ Pa}$.

$$T_{b,normal} = \frac{24.94 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \left(\frac{24.94 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 201 \text{ K}} - \ln \frac{101325}{2232} \right)} = 271.8 \text{ K}$$

At the standard boiling point, $P = 10^5 \text{ Pa}$.

$$T_{b,standard} = \frac{24.94 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \left(\frac{24.94 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 201 \text{ K}} - \ln \frac{100000}{2232} \right)} = 269.6 \text{ K}$$

The result for the normal boiling point is $\sim 8 \text{ K}$ higher than the value tabulated in Table 8.2. The most probable reason for this difference is that the calculation above has assumed that $\Delta H_{vaporization}$ is independent of T .

P8.6) For water, $\Delta H_{vaporization}$ is $40.65 \text{ kJ mol}^{-1}$, and the normal boiling point is 373.15 K . Calculate the boiling point for water on the top of a mountain of height 5500 m, where the normal barometric pressure is 380 Torr.

$$\ln \frac{P_f}{P_i} = -\frac{\Delta H_m^{\text{vaporization}}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$T_f = \frac{\Delta H_m^{\text{vaporization}}}{R \left(\frac{\Delta H_m^{\text{vaporization}}}{RT_i} - \ln \frac{P_f}{P_i} \right)}$$

At the normal boiling point, $P = 760 \text{ Pa}$.

$$T_{b,\text{normal}} = \frac{40.656 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \left(\frac{40.656 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 373.15 \text{ K}} - \ln \frac{380 \text{ Torr}}{760 \text{ Torr}} \right)} = 354.4 \text{ K}$$

P8.7) Use the values for ΔG_f° (ethanol, *l*) and ΔG_f° (ethanol, *g*) in Appendix A to calculate the vapor pressure of ethanol at 298.15 K.

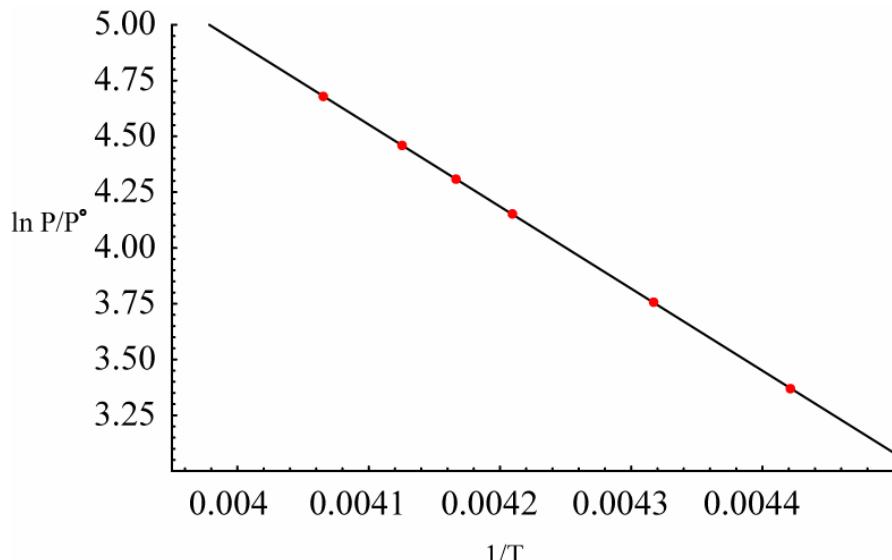
For the transformation $\text{C}_2\text{H}_5\text{OH} (\text{l}) \rightarrow \text{C}_2\text{H}_5\text{OH} (\text{g})$

$$\begin{aligned} \ln K_P &= \frac{\ln P_{\text{C}_2\text{H}_5\text{OH}(\text{g})}}{P^\circ} = -\frac{\Delta G_f^\circ (\text{C}_2\text{H}_5\text{OH}, \text{g}) - \Delta G_f^\circ (\text{C}_2\text{H}_5\text{OH}, \text{l})}{RT} \\ &= -\frac{-167.9 \times 10^3 \text{ J mol}^{-1} + 174.8 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K}} = 2.785 \end{aligned}$$

$$K_P = \frac{P_{\text{C}_2\text{H}_5\text{OH}(\text{g})}}{1 \text{ bar}} = 0.0617 \text{ bar} = 6.17 \times 10^3 \text{ Pa}$$

P8.8) Use the vapor pressures of ClF_3 given in the following table to calculate the enthalpy of vaporization using a graphical method or a least squares fitting routine.

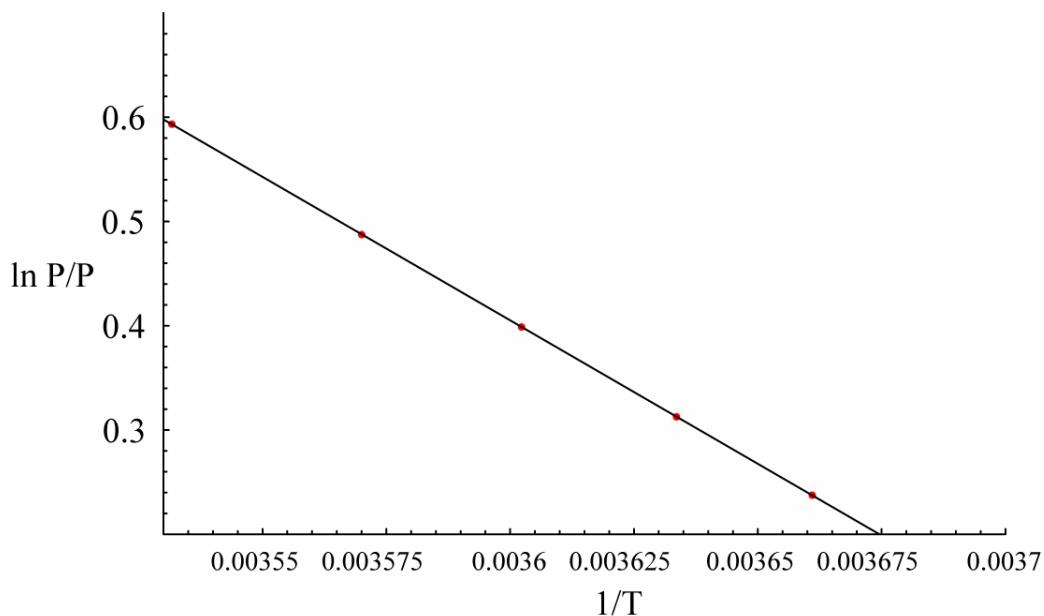
$T (\text{°C})$	$P (\text{Torr})$	$T (\text{°C})$	$P (\text{Torr})$
-46.97	29.06	-33.14	74.31
-41.51	42.81	-30.75	86.43
-35.59	63.59	-27.17	107.66



A least squares fit of $\ln P$ versus $1/T$ gives the result $\Delta H_{vaporization} = 30.58 \text{ kJ mol}^{-1}$.

P8.9) Use the following vapor pressures of 1-butene given here to calculate the enthalpy of vaporization using a graphical method or a least squares fitting routine.

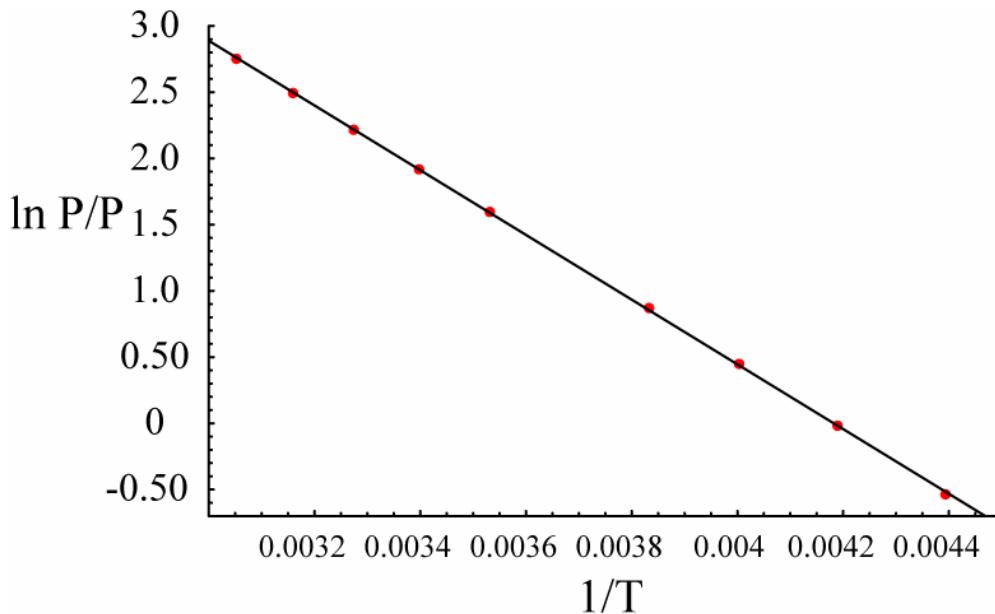
$T(\text{K})$	$P(\text{atm})$
273.15	1.268
275.21	1.367
277.60	1.490
280.11	1.628
283.15	1.810



A least squares fit of $\ln P$ versus $1/T$ gives the result $\Delta H_{vaporization} = 22.88 \text{ kJ mol}^{-1}$.

P8.10) Use the vapor pressures of Cl_2 given in the following table to calculate the enthalpy of vaporization using a graphical method or a least squares fitting routine.

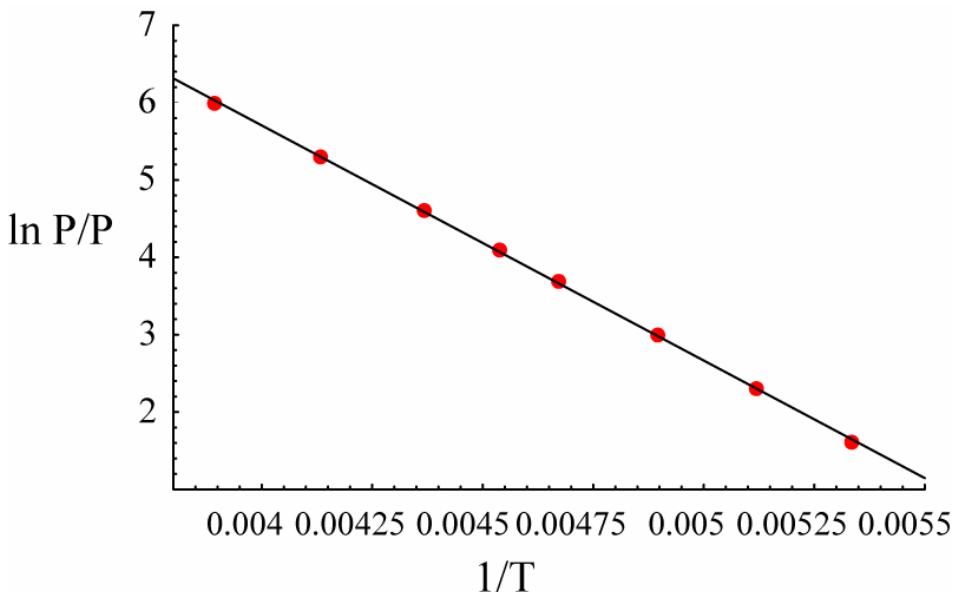
T (K)	P (atm)	T (K)	P (atm)
227.6	0.585	283.15	4.934
238.7	0.982	294.3	6.807
249.8	1.566	305.4	9.173
260.9	2.388	316.5	12.105
272.0	3.483	327.6	15.676



A least squares fit of $\ln P$ versus $1/T$ gives the result $\Delta H_{\text{vaporization}} = 20.32 \text{ kJ mol}^{-1}$.

P8.11) Use the vapor pressures of *n*-butane given in the following table to calculate the enthalpy of vaporization using a graphical method or a least squares fitting routine.

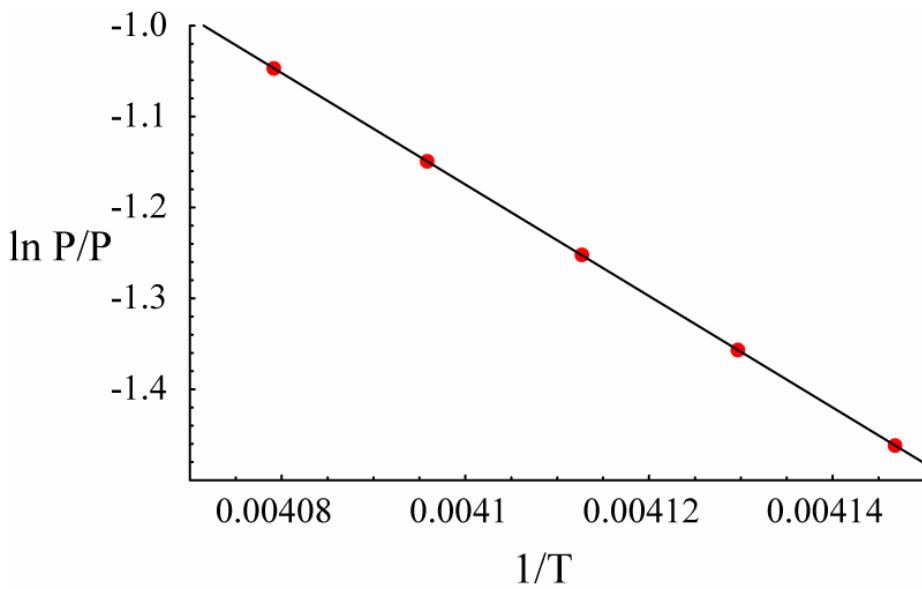
T (K)	P (Torr)	T (K)	P (Torr)
187.45	5.00	220.35	60.00
195.35	10.00	228.95	100.00
204.25	20.00	241.95	200.0
214.05	40.00	256.85	400.0



A least squares fit of $\ln P$ versus $1/T$ gives the result $\Delta H_{vaporization} = 25.28 \text{ kJ mol}^{-1}$.

P8.12) Use the vapor pressures of ice given here to calculate the enthalpy of sublimation using a graphical method or a least squares fitting routine.

$T(\text{°C})$	$P(\text{Torr})$
-28.00	0.3510
-29.00	0.3169
-30.00	0.2859
-31.00	0.2575
-32.00	0.2318



A least squares fit of $\ln P$ versus $1/T$ gives the result $\Delta H_{vaporization} = 50.99 \text{ kJ mol}^{-1}$.

P8.13) Carbon tetrachloride melts at 250 K. The vapor pressure of the liquid is 10539 Pa at 290 K and 74518 Pa at 340 K. The vapor pressure of the solid is 270 Pa at 232 K and 1092 Pa at 250 K.

- Calculate $\Delta H_{vaporization}$ and $\Delta H_{sublimation}$.
- Calculate ΔH_{fusion} .
- Calculate the normal boiling point and $\Delta S_{vaporization}$ at the boiling point.
- Calculate the triple point pressure and temperature.

- a) Calculate $\Delta H_{vaporization}$ and $\Delta H_{sublimation}$.

$$\ln \frac{P_f}{P_i} = -\frac{\Delta H_m^{vaporization}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$\Delta H_m^{vaporization} = -\frac{R \ln \frac{P_f}{P_i}}{\left(\frac{1}{T_f} - \frac{1}{T_i} \right)}$$

$$\Delta H_m^{vaporization} = -\frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \ln \frac{74518 \text{ Pa}}{10539 \text{ Pa}}}{\left(\frac{1}{340 \text{ K}} - \frac{1}{290 \text{ K}} \right)} = 32.1 \times 10^3 \text{ J mol}^{-1}$$

$$\ln \frac{P_f}{P_i} = -\frac{\Delta H_m^{sublimation}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$\Delta H_m^{sublimation} = -\frac{R \ln \frac{P_f}{P_i}}{\left(\frac{1}{T_f} - \frac{1}{T_i} \right)}$$

$$\Delta H_m^{sublimation} = -\frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times \ln \frac{1092 \text{ Pa}}{270 \text{ Pa}}}{\left(\frac{1}{250 \text{ K}} - \frac{1}{232 \text{ K}} \right)} = 37.4 \times 10^3 \text{ J mol}^{-1}$$

- b) Calculate ΔH_{fusion} .

$$\begin{aligned} \Delta H_{fusion} &= \Delta H_{sublimation} - \Delta H_{vaporization} = 37.4 \times 10^3 \text{ J mol}^{-1} - 32.1 \times 10^3 \text{ J mol}^{-1} \\ &= 5.3 \times 10^3 \text{ J mol}^{-1}. \end{aligned}$$

- c) Calculate the normal boiling point and $\Delta S_{vaporization}$ at the boiling point.

$$\ln \frac{P_f}{P_i} = -\frac{\Delta H_m^{\text{vaporization}}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$T_f = \frac{\Delta H_m^{\text{vaporization}}}{R \left(\frac{\Delta H_m^{\text{vaporization}}}{RT_i} - \ln \frac{P_f}{P_i} \right)}$$

At the normal boiling point, $P = 101325 \text{ Pa}$.

$$T_{b,\text{normal}} = \frac{32.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \left(\frac{32.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 340 \text{ K}} - \ln \frac{101325 \text{ Pa}}{74518 \text{ Pa}} \right)} = 349.5 \text{ K}$$

$$\Delta S_m^{\text{vaporization}} = \frac{\Delta H_m^{\text{vaporization}}}{T_{\text{vaporization}}} = \frac{32.1 \times 10^3 \text{ J mol}^{-1}}{349.5 \text{ K}} = 91.8 \text{ J mol}^{-1} \text{ K}^{-1}$$

d) Calculate the triple point pressure and temperature.

From Example Problem 8.2,

$$T_{tp} = \frac{\left(\Delta H_m^{\text{vaporization}} - \Delta H_m^{\text{sublimation}} \right)}{R \left(\ln \frac{P_i^{\text{liquid}}}{P^\circ} - \ln \frac{P_i^{\text{solid}}}{P^\circ} - \frac{\Delta H_m^{\text{sublimation}}}{RT_i^{\text{solid}}} + \frac{\Delta H_m^{\text{vaporization}}}{RT_i^{\text{liquid}}} \right)}$$

$$T_{tp} = \frac{\left(32.1 \times 10^3 \text{ J mol}^{-1} - 37.4 \times 10^3 \text{ J mol}^{-1} \right)}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times \left(\ln \frac{10539 \text{ Pa}}{10^5 \text{ Pa}} - \ln \frac{270 \text{ Pa}}{10^5 \text{ Pa}} - \frac{37.4 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 232 \text{ K}} + \frac{32.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 290 \text{ K}} \right)} = 264 \text{ K}$$

$$\ln \frac{P_{tp}}{P_i} = -\frac{\Delta H_m^{\text{vaporization}}}{R} \left(\frac{1}{T_{tp}} - \frac{1}{T_i} \right)$$

$$\ln \frac{P_{tp}}{10539 \text{ Pa}} = -\frac{32.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{264 \text{ K}} - \frac{1}{290 \text{ K}} \right) = -1.3112$$

$$\frac{P_{tp}}{10539 \text{ Pa}} = 0.269$$

$$P_{tp} = 2.84 \times 10^3 \text{ Pa}$$

P8.14) It has been suggested that the surface melting of ice plays a role in enabling speed skaters to achieve peak performance. Carry out the following calculation to test this hypothesis. At 1 atm pressure, ice melts at 273.15 K, $\Delta H_{\text{fusion}} = 6010 \text{ J mol}^{-1}$, the density of ice is 920 kg m^{-3} , and the density of liquid water is 997 kg m^{-3} .

a. What pressure is required to lower the melting temperature by 5.0°C ?

- b. Assume that the width of the skate in contact with the ice has been reduced by sharpening to 25×10^{-3} cm, and that the length of the contact area is 15 cm. If a skater of mass 85 kg is balanced on one skate, what pressure is exerted at the interface of the skate and the ice?
- c. What is the melting point of ice under this pressure?
- d. If the temperature of the ice is -5.0°C , do you expect melting of the ice at the ice-skate interface to occur?

a) What pressure is required to lower the melting temperature by 5.0°C ?

$$\left(\frac{dP}{dT}\right)_{fusion} = \frac{\Delta S_m^{fusion}}{\Delta V_m^{fusion}} \approx \frac{\Delta S_m^{fusion}}{\frac{M}{\rho_{H_2O,l}} - \frac{M}{\rho_{H_2O,l}}} = \frac{22.0 \text{ J mol}^{-1}\text{K}^{-1}}{\frac{18.02 \times 10^{-3} \text{ kg}}{998 \text{ kg m}^{-3}} - \frac{18.02 \times 10^{-3} \text{ kg}}{920 \text{ kg m}^{-3}}} \\ = -1.44 \times 10^7 \text{ Pa K}^{-1} = -144 \text{ bar K}^{-1}$$

The pressure must be increased by 720 bar to lower the melting point by 5.0°C .

b) Assume that the width of the skate in contact with the ice is 25×10^{-3} cm, and that the length of the contact area is 15 cm. If a skater of mass 85 kg is balanced on one skate, what pressure is exerted at the interface of the skate and the ice?

$$P = \frac{F}{A} = \frac{85 \text{ kg} \times 9.81 \text{ m s}^{-2}}{15 \times 10^{-2} \text{ m} \times 25 \times 10^{-5} \text{ m}} = 2.2 \times 10^7 \text{ Pa} = 2.2 \times 10^2 \text{ bar}$$

c) What is the melting point of ice under this pressure?

$$\Delta T = \left(\frac{dT}{dP}\right)_{fusion} \quad \Delta P = \frac{1^\circ\text{C}}{144 \text{ bar}} \times 2.20 \times 10^2 \text{ bar} = 1.5^\circ\text{C} ; T_m = -1.5^\circ\text{C}$$

d) If the temperature of the ice is -5.0°C , do you expect melting of the ice at the ice-skate interface to occur?

No, because the lowering of the melting temperature is less than the temperature of the ice.

P8.15) Solid iodine at 25°C has an enthalpy of sublimation of $56.30 \text{ kJ mol}^{-1}$. The $C_{P,m}$ of the vapor and solid phases at that temperature are 36.9 and $54.4 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. The sublimation pressure at 25°C is 0.30844 Torr. Calculate the sublimation pressure of the solid at the melting point (113.6°C) assuming

a) that the enthalpy of sublimation and the heat capacities do not change with temperature.

b) that the enthalpy of sublimation at T can be calculated from the equation

$$\Delta H_{sublimation}^\circ(T) = \Delta H_{sublimation}^\circ(T_0) + \Delta C_P(T - T_0).$$

a) If the enthalpy of sublimation is constant

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{sublimation}}^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln P_2 = \ln 0.30844 - \frac{56.30 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{386.8 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$P_2 = 56.22 \text{ Torr}$$

b) If the enthalpy of sublimation is given by $\Delta H_{\text{sublimation}}^{\circ}(T) = \Delta H_{\text{sublimation}}^{\circ}(T_0) + \Delta C_P(T - T_0)$

$$\int \frac{dP}{P} = \int_{T_0}^T \frac{\Delta H_{\text{sublimation}}^{\circ}}{RT^2} dT = \int_{T_0}^T \frac{\Delta H_{\text{sublimation}}^{\circ}(T_0) + \Delta C_P(T - T_0)}{RT^2} dT$$

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{sublimation}}^{\circ}(T_0)}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \frac{\Delta C_P T_0}{R} \left[\frac{1}{T} - \frac{1}{T_0} \right] + \frac{\Delta C_P}{R} \ln \frac{T}{T_0}$$

$$\ln P_2 = \ln 0.30844 - \frac{56.30 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{386.8 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$+ \frac{(36.9 - 54.4) \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{386.8 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$+ \frac{(36.9 - 54.4) \text{ J K}^{-1} \text{ mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \ln \frac{386.8 \text{ K}}{298.15 \text{ K}}$$

$$\ln P_2 = 3.964$$

$$P_2 = 52.65 \text{ Torr}$$

P8.16) Carbon disulfide ($\text{CS}_2(l)$) at 25°C has a vapor pressure of 0.4741 bar and an enthalpy of vaporization of $27.66 \text{ kJ mol}^{-1}$. The $C_{P,m}$ of the vapor and liquid phases at that temperature are 45.4 and $75.7 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. Calculate the vapor pressure of $\text{CS}_2(l)$ at 100.0°C assuming

a) that the enthalpy of vaporization and the heat capacities do not change with temperature.

b) that the enthalpy of vaporization at T can be calculated from the relationship

$$\Delta H_{\text{vaporization}}^{\circ}(T) = \Delta H_{\text{vaporization}}^{\circ}(T_0) + \Delta C_P(T - T_0).$$

a) If the enthalpy of vaporization is current

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{vaporization}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln P_2 = \ln(0.4741) - \frac{27.66 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{373.15 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) = 1.4964$$

$$P_2 = 4.66 \text{ barr}$$

b) If the enthalpy of vaporization is given by

$$\Delta H_{vaporization}^\circ(T) = \Delta H_{vaporization}^\circ(T_0) + \Delta C_P(T - T_0)$$

$$\int \frac{dP}{P} = \int_{T_0}^T \frac{\Delta H_{vaporization}^\circ}{RT^2} dT = \int_{T_0}^T \frac{\Delta H_{vaporization}^\circ(T_0) + \Delta C_P(T - T_0)}{RT^2} dT$$

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{vaporization}^\circ(T_0)}{8.314} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \frac{\Delta C_P T_0}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \frac{\Delta C_P}{R} \ln \frac{T}{T_0}$$

$$\ln P_2 = \ln(0.4741) - \frac{27.66 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{373.15} - \frac{1}{298.15} \right)$$

$$+ \frac{(45.4 - 75.7) \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{373.15 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$+ \frac{(45.4 - 75.7) \text{ J mol}^{-1} \text{ K}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \ln \frac{373.15 \text{ K}}{298.15 \text{ K}}$$

$$\ln P_2 = 1.411$$

$$P_2 = 4.10 \text{ bar}$$

P8.17) Consider the transition between two forms of solid tin,

$\text{Sn}(s, \text{gray}) \rightleftharpoons \text{Sn}(s, \text{white})$. The two phases are in equilibrium at 1 bar and 18°C. The densities for gray and white tin are 5750 and 7280 kg m⁻³, respectively, and $\Delta S_{transition} = 8.8 \text{ J K}^{-1} \text{ mol}^{-1}$. Calculate the temperature at which the two phases are in equilibrium at 200 bar.

In going from 1 atm, 18°C to 200 atm, T

$$\Delta G^{gray} = V_m^{gray} \Delta P - S^{gray} \Delta T$$

$$\Delta G^{white} = V_m^{white} \Delta P - S^{white} \Delta T$$

At equilibrium

$$\Delta G^{gray} - \Delta G^{white} = 0 = (V_m^{gray} - V_m^{white}) \Delta P - (S^{gray} - S^{white}) \Delta T$$

$$\Delta T = \frac{(V_m^{gray} - V_m^{white}) \Delta P}{(S^{gray} - S^{white})} = \frac{M_{Sn} \left(\frac{1}{\rho_{gray}} - \frac{1}{\rho_{white}} \right) \Delta P}{\Delta S_{transition}}$$

$$= \frac{118.71 \times 10^{-3} \text{ kg mol}^{-1} \times \left(\frac{1}{5750 \text{ kg m}^{-3}} - \frac{1}{7280 \text{ kg m}^{-3}} \right) \times 199 \times 10^5 \text{ Pa}}{-8.8 \text{ J K}^{-1} \text{ mol}^{-1}} = -9.8^\circ \text{C}$$

$$T_f = 8.2^\circ \text{C}$$

P8.18) You have collected a tissue specimen that you would like to preserve by freeze drying. To ensure the integrity of the specimen, the temperature should not exceed -10.5°C . The vapor pressure of ice at 273.16 K is 611 Pa; $\Delta H_{fusion}^\circ = 6.01 \text{ kJ mol}^{-1}$ and $\Delta H_{vaporization}^\circ = 40.65 \text{ kJ mol}^{-1}$. What is the maximum pressure at which the freeze drying can be carried out?

$$\ln \frac{P_f}{P_i} = -\frac{\Delta H_{sublimation}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$\ln \frac{P_f}{P_i} = -\frac{6.008 \times 10^3 \text{ J mol}^{-1} + 40.656 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{262.65 \text{ K}} - \frac{1}{273.16 \text{ K}} \right) = 0.822205$$

$$\frac{P_f}{P_i} = 0.439; \quad P_f = 0.439 \times 611 \text{ Pa} = 269 \text{ Pa}$$

P8.19) The vapor pressure of methanol (*l*) is given by $\ln \left(\frac{P}{\text{Pa}} \right) = 23.593 - \frac{3.6791 \times 10^3}{\frac{T}{\text{K}} - 31.317}$.

a. Calculate the standard boiling temperature.

b. Calculate $\Delta H_{vaporization}$ at 298 K and at the standard boiling temperature.

a.

$$\ln\left(\frac{P}{\text{Pa}}\right) = 23.593 - \frac{3.6791 \times 10^3}{\frac{T_b}{\text{K}} - 31.317} = \ln 10^5 = 11.5129$$

$$3.6791 \times 10^3 = (23.593 - 11.5129) \left(\frac{T_b}{\text{K}} - 31.317 \right)$$

$$\frac{T_b}{\text{K}} = \frac{3.6791 \times 10^3}{(23.593 - 11.5129)} + 31.317 = 335.9$$

b.

$$\begin{aligned}\Delta H_{\text{vaporization}} &= RT^2 \frac{d \ln P}{dT} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 3679.1 \times (298 \text{ K})^2}{(T - 31.37)^2} \\ &= 38.19 \text{ kJ mol}^{-1} \text{ at } 298 \text{ K and } 37.20 \text{ kJ mol}^{-1} \text{ at } 335.9 \text{ K}\end{aligned}$$

P8.20) The vapor pressure of a liquid can be written in the empirical form known as the Antoine equation, where $A(1)$, $A(2)$, and $A(3)$ are constants determined from measurements:

$$\ln \frac{P(T)}{\text{Pa}} = A(1) - \frac{A(2)}{\frac{T}{\text{K}} + A(3)} .$$

Starting with this equation, derive an equation giving $\Delta H_{\text{vaporization}}$ as a function of temperature.

For a liquid-gas equilibrium involving a single species, $K_p = \frac{P}{P^\circ}$

$$\Delta H = -R \frac{d \ln K_p}{d\left(\frac{1}{T}\right)} = RT^2 \frac{d \ln K_p}{dT} = RT^2 \frac{d}{dT} \left(A(1) - \frac{A(2)}{\frac{T}{\text{K}} + A(3)} \right)$$

$$\Delta H = \frac{RT^2 A(2)}{\left[\frac{T}{\text{K}} + A(3) \right]^2}$$

P8.21) The vapor pressure of an unknown solid is approximately given by

$\ln \frac{P}{\text{Torr}} = 22.413 - 2035 \frac{\text{K}}{T}$ and the vapor pressure of the liquid phase of the same

substance is approximately given by $\ln \frac{P}{\text{Torr}} = 18.352 - 1736 \frac{\text{K}}{T}$.

a. Calculate $\Delta H_{vaporization}$ and $\Delta H_{sublimation}$.

From Equation 8.16

$$\frac{d \ln P}{dT} = \frac{\Delta H_{sublimation}}{RT^2}$$

$$\frac{d \ln P}{d\left(\frac{1}{T}\right)} = \frac{d \ln P}{dT} \frac{dT}{d\left(\frac{1}{T}\right)} = -T^2 \frac{d \ln P}{dT} = -\frac{\Delta H_{sublimation}}{R}$$

For this specific case

$$\frac{\Delta H_{sublimation}}{R} = 2035 \quad \Delta H_{sublimation} = 16.92 \times 10^3 \text{ J mol}^{-1}$$

Following the same procedure as above,

$$\frac{\Delta H_{vaporization}}{R} = 1736 \quad \Delta H_{vaporization} = 14.43 \times 10^3 \text{ J mol}^{-1}$$

b. Calculate ΔH_{fusion} .

$$\begin{aligned} \Delta H_{fusion} &= \Delta H_{sublimation} - \Delta H_{vaporization} \\ &= 16.92 \times 10^3 \text{ J mol}^{-1} - 14.43 \times 10^3 \text{ J mol}^{-1} \\ &= 2.49 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

c. Calculate the triple point temperature and pressure.

At the triple point, the vapor pressures of the solid and liquid are equal. Therefore

$$22.413 - 2035 \frac{K}{T_{tp}} = 18.352 - 1736 \frac{K}{T_{tp}}$$

$$4.061 = 299 \frac{K}{T_{tp}}$$

$$T_{tp} = 73.62 \text{ K}$$

$$\ln \frac{P_{tp}}{\text{Torr}} = 22.413 - \frac{2035}{73.62} = -5.22895$$

$$P_{tp} = 5.36 \times 10^{-3} \text{ Torr}$$

P8.22) The density of a given solid and liquid of molecular weight 122.5 at its normal melting temperature of 427.15 K are 1075 and 1012 kg m^{-3} , respectively. If the pressure is increased to 120 bar, the melting temperature increases to 429.35 K. Calculate ΔH_{fusion}° and ΔS_{fusion}° for this substance.

$$\frac{\Delta P}{\Delta T} \approx \frac{\Delta S}{\Delta V}; \quad \Delta S \approx \frac{\Delta P}{\Delta T} \Delta V$$

$$\Delta S_{fusion} = \frac{\Delta P}{\Delta T} M \left(\frac{1}{\rho_{liquid}} - \frac{1}{\rho_{solid}} \right)$$

$$\Delta S_{fusion} = \frac{119 \times 10^5 \text{ Pa}}{429.35 \text{ K} - 427.15 \text{ K}} \times 122.5 \times 10^{-3} \text{ kg mol}^{-1} \times \left(\frac{1}{1012 \text{ kg m}^{-3}} - \frac{1}{1075 \text{ kg m}^{-3}} \right) \\ = 38.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H_{fusion} = T_{fusion} \Delta S_{fusion} = 427.15 \text{ K} \times 38.4 \text{ J K}^{-1} \text{ mol}^{-1} = 16.4 \times 10^3 \text{ J mol}^{-1} \text{ at 1 bar}$$

P8.23) In Equation (8.13), $\left(\frac{dP}{dT}\right)_{vaporization}$ was calculated by assuming that $V_m^{gas} \gg V_m^{liquid}$.

In this problem, you will test the validity of this approximation. For water at its normal boiling point of 373.13 K, $\Delta H_{vaporization} = 40.65 \times 10^3 \text{ J mol}^{-1}$, $\rho_{liquid} = 958.66 \text{ kg m}^{-3}$, and

$\rho_{gas} = 0.58958 \text{ kg m}^{-3}$. Compare the calculated values for $\left(\frac{dP}{dT}\right)_{vaporization}$ with and without

the assumption discussed in Equation (8.13). What is the relative error in making the approximation?

$$\left(\frac{dP}{dT}\right)_{vaporization} = \frac{\Delta S_m^{vaporization}}{\Delta V_m^{vaporization}} = \frac{\Delta H_m^{vaporization}}{T_{vaporization} M \left(\frac{1}{\rho_{gas}} - \frac{1}{\rho_{liquid}} \right)}$$

$$\left(\frac{dP}{dT}\right)_{vaporization} = \frac{40.656 \times 10^3 \text{ J mol}^{-1}}{373.15 \text{ K} \times 18.02 \times 10^{-3} \text{ kg} \times \left(\frac{1}{0.58958 \text{ kg m}^{-3}} - \frac{1}{958.66 \text{ kg m}^{-3}} \right)} = 3566.9 \text{ Pa K}^{-1}$$

$$\left(\frac{dP}{dT}\right)_{vaporization} \approx \frac{40.656 \times 10^3 \text{ J mol}^{-1}}{373.15 \text{ K} \times 18.03 \times 10^{-3} \text{ kg} \times \left(\frac{1}{0.58958 \text{ kg m}^{-3}} \right)} = 3564.8 \text{ Pa K}^{-1}$$

$$\text{Relative Error} = 100 \times \frac{3566.9 \text{ Pa K}^{-1} - 3564.8 \text{ Pa K}^{-1}}{3566.9 \text{ Pa K}^{-1}} = 0.061\%$$

P8.24) The variation of the vapor pressure of the liquid and solid forms of a pure substance near the triple point are given by $\ln \frac{P_{solid}}{\text{Pa}} = -8750 \frac{\text{K}}{T} + 31.143$ and

$\ln \frac{P_{liquid}}{\text{Pa}} = -4053 \frac{\text{K}}{T} + 21.10$. Calculate the temperature and pressure at the triple point.

At the triple point, $P_{solid} = P_{liquid}$.

$$-8750 \frac{\text{K}}{T} + 31.143 = -4053 \frac{\text{K}}{T} + 21.10$$

$$31.143 - 21.10 = (8750 - 4053) \frac{\text{K}}{T}$$

$$T = \frac{(8750 - 4053)}{31.143 - 21.10} = 467.7 \text{ K}$$

$$\ln \frac{P_{tp}}{\text{Pa}} = \frac{-8750}{467.7} + 31.143 = 12.4344$$

$$\frac{P_{tp}}{\text{Pa}} = 2.513 \times 10^5$$

P8.25) Calculate the vapor pressure of CS₂ at 298 K if He is added to the gas phase at a partial pressure of 200 bar. The vapor pressure of CS₂ is given by the empirical equation

$$\ln \frac{P(T)}{\text{Pa}} = 20.801 - \frac{2.6524 \times 10^3}{\frac{T}{\text{K}} - 33.402}$$

The density of CS₂ at this temperature is 1255.5 kg m⁻³.

$$\ln \frac{P(298 \text{ K})}{\text{Pa}} = 20.801 - \frac{2.6524 \times 10^3}{298 - 33.402}$$

$$\frac{P(298 \text{ K})}{\text{Pa}} = 4.79 \times 10^4$$

$$\ln \left(\frac{P}{P_0} \right) = \frac{V_m^{liquid} (\mathbf{P} - P_0)}{RT} = \frac{\frac{M}{\rho_{liquid}} (\mathbf{P} - P_0)}{RT}$$

$$\ln \left(\frac{P}{P_0} \right) = \frac{\frac{76.14 \times 10^{-3} \text{ kg mol}^{-1}}{1255 \text{ kg m}^{-3}} \times (200 \times 10^5 \text{ Pa} - 4.789 \times 10^4 \text{ Pa})}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 0.488576$$

$$P = 1.6299 P_0 = 1.6299 \times 4.789 \times 10^4 \text{ Pa} = 7.806 \times 10^4 \text{ Pa}$$

P8.26) Use the vapor pressures for PbS given in the following table to estimate the temperature and pressure of the triple point and also the enthalpies of fusion, vaporization, and sublimation.

Phase	T (°C)	P (Torr)
Solid	1048	40.0
Solid	1108	100
Liquid	1221	400
Liquid	1281	760

To estimate $\Delta H_{\text{sublimation}}$, use the vapor pressures of the solid phase

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{sublimation}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\Delta H_{\text{sublimation}} = \frac{R \ln \frac{P_2}{P_1}}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \left(\frac{100 \text{ Torr}}{400 \text{ Torr}} \right)}{\frac{1}{(1048 + 273.15) \text{ K}} - \frac{1}{(1108 + 273.15) \text{ K}}}$$

$$= 231.7 \text{ kJ mol}^{-1}$$

To estimate $\Delta H_{\text{vaporization}}$, use the vapor pressures of the liquid phase

$$\Delta H_{\text{vaporization}} = \frac{R \ln \frac{P_2}{P_1}}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \left(\frac{760}{400} \right)}{\frac{1}{1221 + 273.15} - \frac{1}{1281 + 273.15}}$$

$$\Delta H_{\text{vaporization}} = 206.5 \text{ kJ mol}^{-1}$$

$$\begin{aligned}\Delta H_{\text{fusion}} &= \Delta H_{\text{sublimation}} - \Delta H_{\text{vaporization}} \\ &= 231.7 \text{ kJ mol}^{-1} - 206.5 \text{ kJ mol}^{-1} \\ &= 25.2 \text{ kJ mol}^{-1}\end{aligned}$$

At the triple point, the solid and liquid have the same vapor pressure

$$\begin{aligned}\ln \left(\frac{P_{\text{solid}}}{P_{\text{solid,ref}}} \right) &= \frac{\Delta H_{\text{sublimation}}^{\circ}}{R} \left(\frac{1}{T_{\text{solid,ref}}} - \frac{1}{T} \right) \\ \ln \left(\frac{P_{\text{liquid}}}{P_{\text{liquid,ref}}} \right) &= \frac{\Delta H_{\text{vaporization}}^{\circ}}{R} \left(\frac{1}{T_{\text{liquid,ref}}} - \frac{1}{T} \right) \\ \frac{\Delta H_{\text{sublimation}}^{\circ}}{R} \left(\frac{1}{T_{\text{solid,ref}}} - \frac{1}{T} \right) &+ \ln P_{\text{solid,ref}} \\ &= \frac{\Delta H_{\text{vaporization}}^{\circ}}{R} \left(\frac{1}{T_{\text{liquid,ref}}} - \frac{1}{T} \right) + \ln P_{\text{liquid,ref}} \\ \frac{1}{T} &= \frac{1}{\Delta H_{\text{sublimation}}^{\circ} - \Delta H_{\text{vaporization}}^{\circ}} \left(\frac{\Delta H_{\text{sublimation}}^{\circ}}{T_{\text{solid,ref}}} - \frac{\Delta H_{\text{vaporization}}^{\circ}}{T_{\text{liquid,ref}}} + R \ln P_{\text{solid,ref}} - R \ln P_{\text{liquid,ref}} \right)\end{aligned}$$

for

$$P_{solid,ref} = 100 \text{ Torr}, \quad P_{liquid,ref} = 400 \text{ Torr}$$

$$T_{solid,ref} = 1381 \text{ K}, \quad T_{liquid,ref} = 1494 \text{ K}$$

$$\begin{aligned} \frac{1}{T} &= \frac{1}{(232 - 207) \times 10^3 \text{ J mol}^{-1}} \times \left[\frac{232 \times 10^3 \text{ J mol}^{-1}}{1381 \text{ K}} - \frac{207 \times 10^3 \text{ J mol}^{-1}}{1494 \text{ K}} \right. \\ &\quad \left. + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln\left(\frac{100 \text{ Torr}}{400 \text{ Torr}}\right) \right] \\ &= 7.16 \times 10^{-4} \text{ K}^{-1} \end{aligned}$$

$$T_{tp} = 1398 \text{ K}$$

The pressure at the triple point can be obtained from either the equation for vapor pressure of the solid or the liquid phases.

$$P_{solid}(T) = P_{solid,ref} \exp\left[\frac{\Delta H_{sublimation}^\circ}{R} \left(\frac{1}{T_{solid,ref}} - \frac{1}{T}\right)\right]$$

$$P_{tp} = 100 \text{ Torr} \times \exp\left[\frac{232 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{1381 \text{ K}} - \frac{1}{1398 \text{ K}}\right)\right]$$

$$P_{tp} = 128 \text{ Torr}$$

P8.27) Use the vapor pressures for C₂N₂ given in the following table to estimate the temperature and pressure of the triple point and also the enthalpies of fusion, vaporization, and sublimation.

Phase	T (°C)	P (Torr)
Solid	-62.7	40.0
Solid	-51.8	100
Liquid	-33.0	400
Liquid	-21.0	760

We follow the same procedures as in P8.26.

$$\Delta H_{\text{sublimation}}^{\circ} = \frac{R \ln \frac{P_2}{P_1}}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \left(\frac{100 \text{ Torr}}{40.0 \text{ Torr}} \right)}{\left(\frac{1}{210.5 \text{ K}} - \frac{1}{221.4 \text{ K}} \right)} = 32.6 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{vaporization}}^{\circ} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \left(\frac{760 \text{ Torr}}{400 \text{ Torr}} \right)}{\left(\frac{1}{240.2 \text{ K}} - \frac{1}{252.2 \text{ K}} \right)} = 26.9 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{fusion}}^{\circ} = (32.6 - 26.9) \text{ kJ mol}^{-1} = 5.6 \text{ kJ mol}^{-1}$$

to calculate the triple point temperature, take

$$T_{\text{solid,ref}} = 221.4 \text{ K} \quad P_{\text{solid,ref}} = 100 \text{ Torr}$$

$$T_{\text{liquid,ref}} = 240.2 \text{ K} \quad P_{\text{liquid,ref}} = 400 \text{ Torr}$$

$$\frac{1}{T_{\text{tp}}} = \frac{1}{(32.6 - 26.9) \times 10^3 \text{ J mol}^{-1}} \times \left[\frac{32.6 \times 10^3 \text{ J mol}^{-1}}{221.4 \text{ K}} - \frac{26.9 \times 10^3 \text{ J mol}^{-1}}{240.2 \text{ K}} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \left(\frac{100 \text{ Torr}}{400 \text{ Torr}} \right) \right]$$

$$\frac{1}{T_{\text{tp}}} = 0.00416 \text{ K}^{-1}, \quad T_{\text{tp}} = 240.3 \text{ K}$$

$$P_{\text{tp}} = 100 \text{ Torr} \times \exp \left[\frac{32.6 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{221.4 \text{ K}} - \frac{1}{240.3 \text{ K}} \right) \right] = 402 \text{ Torr}$$

P8.28) A reasonable approximation to the vapor pressure of krypton is given by

$$\log_{10} \frac{P}{\text{Torr}} = b - 0.05223 \frac{a}{T} .$$

For solid krypton, $a = 10065$ and $b = 7.1770$. For liquid krypton, $a = 9377.0$ and $b = 6.92387$. Use these formulas to estimate the triple point temperature and pressure and also the enthalpies of vaporization, fusion, and sublimation of krypton.

At the triple point, the vapor pressures of the solid and liquid are equal.

$$7.1770 - 0.05223 \times \frac{10065}{T_{tp}} = 6.92387 - 0.05223 \times \frac{9377.0}{T_{tp}}$$

$$0.2531 = 0.05223 \times \frac{688}{T_{tp}}$$

$$T_{tp} = 142 \text{ K}$$

$$\log_{10} \frac{P_{tp}}{\text{Torr}} = 7.1770 - 0.05223 \times \frac{10065}{142} = 3.7492$$

$$P_{tp} = 2984 \text{ Torr}$$

We next calculate the enthalpies of sublimation and vaporization.

From Equation 8.16

$$\frac{d \ln P}{dT} = \frac{\Delta H_{\text{sublimation}}}{RT^2}$$

$$\frac{d \ln P}{d\left(\frac{1}{T}\right)} = \frac{d \ln P}{dT} \frac{dT}{d\left(\frac{1}{T}\right)} = -T^2 \frac{d \ln P}{dT} = -\frac{\Delta H_{\text{sublimation}}}{R}$$

$$\frac{d \log_{10} P}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H_{\text{sublimation}}}{2.303 R}$$

For this specific case

$$\frac{\Delta H_{\text{sublimation}}}{R} = 0.05223 \times 2.303 \times 10065 \quad \Delta H_{\text{sublimation}} = 10.07 \times 10^3 \text{ J mol}^{-1}$$

Following the same reasoning

$$\frac{\Delta H_{\text{vaporization}}}{R} = 0.05223 \times 2.303 \times 9377 \quad \Delta H_{\text{vaporization}} = 9.38 \times 10^3 \text{ J mol}^{-1}$$

$$\Delta H_{\text{fusion}} = \Delta H_{\text{sublimation}} - \Delta H_{\text{vaporization}} = 10.07 \times 10^3 \text{ J mol}^{-1} - 9.38 \times 10^3 \text{ J mol}^{-1} = 0.69 \times 10^3 \text{ J mol}^{-1}$$

P8.29) The normal melting point of H₂O is 273.15 K, and $\Delta H_{\text{fusion}} = 6010 \text{ J mol}^{-1}$.

Calculate the decrease in the normal freezing point at 100 and 500 bar assuming that the density of the liquid and solid phases remains constant at 997 and 917 kg m⁻³, respectively.

$$\left(\frac{dP}{dT}\right)_{fusion} = \frac{\Delta S_m^{fusion}}{\Delta V_m^{fusion}} = \frac{\Delta H_m^{fusion}}{T_{fusion} M \left(\frac{1}{\rho_{liquid}} - \frac{1}{\rho_{solid}} \right)}$$

$$= \frac{6010 \text{ J mol}^{-1}}{273.15 \text{ K} \times 18.02 \times 10^{-3} \text{ kg mol}^{-1} \times \left(\frac{1}{997 \text{ kg m}^{-3}} - \frac{1}{917 \text{ kg m}^{-3}} \right)} = -1.40 \times 10^7 \text{ Pa K}^{-1}$$

$$\left(\frac{dP}{dT}\right)_{fusion} = -140 \text{ bar K}^{-1}$$

$$\Delta T = -\frac{\Delta P}{140 \text{ bar K}^{-1}} = -0.714 \text{ K at 100 bar and } -3.57 \text{ K at 500 bar}$$

P8.30) Autoclaves that are used to sterilize surgical tools require a temperature of 120°C to kill bacteria. If water is used for this purpose, at what pressure must the autoclave operate? The normal boiling point of water is 373.15 K, and $\Delta H_{vaporization}^\circ = 40.656 \times 10^3 \text{ J mol}^{-1}$ at the normal boiling point.

$$\ln \frac{P_f}{P_i} = -\frac{\Delta H_m^{vaporization}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$\ln \frac{P_f}{P_i} = -\frac{40.656 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{393.15 \text{ K}} - \frac{1}{373.15 \text{ K}} \right) = 0.6667$$

$$\frac{P_f}{P_i} = 1.95; \quad P_f = 1.95 \text{ atm}$$

P8.31) The vapor pressure of $\text{H}_2\text{O}(l)$ is 23.766 Torr at 298.15 K. Use this value to calculate $\Delta G_f^\circ(\text{H}_2\text{O}, g) - \Delta G_f^\circ(\text{H}_2\text{O}, l)$. Compare your result with those in Table 4.1.

$$\Delta G_f^\circ(\text{H}_2\text{O}, g) - \Delta G_f^\circ(\text{H}_2\text{O}, l) = -RT \ln K_P = \frac{\ln P_{\text{H}_2\text{O},g}}{P^\circ}$$

$$\Delta G_f^\circ(\text{H}_2\text{O}, g) - \Delta G_f^\circ(\text{H}_2\text{O}, l) = -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln \frac{23.766 \text{ Torr}}{760 \text{ Torr}} \text{ From the tables, } \Delta G_f^\circ(\text{H}_2\text{O}, g) - \Delta G_f^\circ(\text{H}_2\text{O}, l) = 8.585 \times 10^3 \text{ J mol}^{-1}$$

$$\Delta G_f^\circ(\text{H}_2\text{O}, g) - \Delta G_f^\circ(\text{H}_2\text{O}, l) = -228.6 \text{ kJ mol}^{-1} + 237.1 \text{ kJ mol}^{-1} = 8.5 \text{ kJ mol}^{-1}$$

This result is in good agreement with the ΔG_f° values calculated above.

P8.32) Calculate the difference in pressure across the liquid–air interface for a water droplet of radius 150 nm.

From equation 8.26

$$P_{inner} - P_{outer} = \frac{2\gamma}{r} = \frac{2 \times 71.99 \times 10^{-3} \text{ Nm}^{-1}}{150 \times 10^{-9} \text{ m}} = 9.60 \times 10^5 \text{ Pa}$$

P8.33) Calculate the factor by which vapor pressure of a droplet of methanol of radius $1.00 \times 10^{-8} \text{ m}$ at 325 K in equilibrium with its vapor is increased with respect to a very large droplet. Use the tabulated value of the density and surface tension in Appendix A for this problem. (*Hint:* You need to calculate the vapor pressure of methanol at this temperature.)

$$\ln \frac{P(T)}{\text{Pa}} = A(1) - \frac{A(2)}{\frac{T}{\text{K}} + A(3)} = 23.593 - \frac{3.6971 \times 10^3}{325 - 31.317} = 11.0043$$

$$P = 6.01 \times 10^4 \text{ Pa}$$

$$\Delta P = \frac{2\gamma}{r} = \frac{2 \times 22.07 \times 10^{-3} \text{ N m}^{-1}}{10^{-8} \text{ m}} = 4.41 \times 10^6 \text{ Pa}$$

$$P_{inside} = P_{vapor} + \Delta P = 6.01 \times 10^4 \text{ Pa} + 4.41 \times 10^6 \text{ Pa} = 4.47 \times 10^6 \text{ Pa}$$

For a very large droplet, $\Delta P \rightarrow 0$, and the vapor pressure is $6.01 \times 10^4 \text{ Pa}$. For the small droplet, the vapor pressure is increased by the factor

$$\ln \left(\frac{P}{P_0} \right) = \frac{\frac{\rho}{M} (\mathbf{P} - P_0)}{RT} = \frac{\frac{32.04 \times 10^{-3} \text{ kg mol}^{-1}}{791.4 \text{ kg m}^{-3}} \times (4.47 \times 10^6 - 6.01 \times 10^4) \text{ Pa}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 325 \text{ K}} = 6.607 \times 10^{-2}$$

$$P = 1.068 P_0$$

P8.34) Calculate the vapor pressure of water droplets of radius $1.25 \times 10^{-8} \text{ m}$ at 360 K in equilibrium with water vapor. Use the tabulated value of the density and surface tension in Appendix A for this problem. (*Hint:* You need to calculate the vapor pressure of water at this temperature.)

$$\ln \frac{P(T)}{\text{Pa}} = A(1) - \frac{A(2)}{\frac{T}{\text{K}} + A(3)} = 23.195 - \frac{3.8140 \times 10^3}{360 - 46.290} = 11.0373$$

$$P = 6.21 \times 10^4 \text{ Pa}$$

$$\Delta P = \frac{2\gamma}{r} = \frac{2 \times 71.99 \times 10^{-3} \text{ N m}^{-1}}{1.25 \times 10^{-8} \text{ m}} = 1.15 \times 10^7 \text{ Pa}$$

$$P_{inside} = P_{vapor} + \Delta P = 6.21 \times 10^4 \text{ Pa} + 1.15 \times 10^7 \text{ Pa} = 1.16 \times 10^7 \text{ Pa}$$

$$\ln\left(\frac{P}{P_0}\right) = \frac{\frac{\rho}{M}(\mathbf{P} - P_0)}{RT} = \frac{\frac{18.02 \times 10^{-3} \text{ kg mol}^{-1}}{998 \text{ kg m}^{-3}} \times (1.17 \times 10^7 - 6.21 \times 10^4) \text{ Pa}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 360 \text{ K}} = 7.0208 \times 10^{-2}$$

$$P = 1.0727P_0 = 1.0727 \times 6.21 \times 10^4 \text{ Pa} = 6.66 \times 10^4 \text{ Pa}$$

P8.35) In Section 8.7, it is stated that the maximum height of a water column in which cavitation does not occur is ~ 9.7 m. Show that this is the case at 298 K.

Combining the two parts of equation 8.28,

$$h = \frac{P_{inner} - P_{outer}}{\rho g}$$

bubbles will form when P_{outer} has the value of the vapor pressure of water.

For the equilibrium



$$\Delta G_f^\circ(\text{H}_2\text{O}, g) - \Delta G_f^\circ(\text{H}_2\text{O}, l) = -228.6 \text{ kJ mol}^{-1} + 237.1 \text{ kJ mol}^{-1} = 8.5 \text{ kJ mol}^{-1}.$$

For this equilibrium

$$K_p = -\frac{\Delta G_{reaction}^\circ}{RT} = P_{H_2O,g}$$

$$\frac{P}{1 \text{ bar}} = \exp\left(\frac{-8.5 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}}\right)$$

$$P = 0.032 \text{ bar} = 3242 \text{ Pa}$$

Suppose that $P_{inner} = 1 \text{ atm} = 101325 \text{ Pa}$

Using $\rho = 998 \text{ kg m}^{-3}$

$$h = \frac{(101325 - 3242) \text{ Pa}}{998 \text{ kg m}^{-3} \times 9.81 \text{ m s}^{-2}} = 10.0 \text{ m}$$

Questions on Concepts

Q9.1) Show using the differential form of G that if $\Delta G_{mixing} = nRT \sum_i x_i \ln x_i$, then

$$\Delta H_{mixing} = \Delta V_{mixing} = 0.$$

$$\Delta G_{mixing} = nRT \sum_i x_i \ln x_i$$

$$\Delta S_{mixing} = -\left(\frac{\partial \Delta G_{mixing}}{\partial T}\right)_P = -nR \sum_i x_i \ln x_i \text{ and}$$

$$\Delta V_{mixing} = \left(\frac{\partial \Delta G_{mixing}}{\partial P}\right)_{T,n_1,n_2} = 0$$

$$\Delta H_{mixing} = \Delta G_{mixing} + T\Delta S_{mixing} = nRT \sum_i x_i \ln x_i - T \left(nR \sum_i x_i \ln x_i \right) = 0$$

Q9.2) For a pure substance, the liquid and gaseous phases can only coexist for a single value of the pressure at a given temperature. Is this also the case for an ideal solution of two volatile liquids?

No, an ideal solution of two volatile liquids can exist over a range of pressures that are limited by the pressure for which only a trace of liquid remains, and the pressure for which only a trace of gas remains.

Q9.3) Fractional distillation of a binary liquid mixture leaves behind a liquid consisting of both components in which the composition does not change as the liquid is boiled off. Is this behavior characteristic of a maximum or a minimum boiling point azeotrope?

This behavior is characteristic of a maximum-boiling azeotrope. After initially giving off the more volatile component, the liquid remaining tends to the composition of the maximum boiling point at intermediate composition. After the more volatile component has boiled away, the azeotrope evaporates at constant composition.

Q9.4) Why is the magnitude of the boiling point elevation less than that of the freezing point depression?

The boiling point elevation is less than the freezing point depression because the chemical potential of the vapor is a much more steeply decreasing function of temperature than the solid, as seen in Figure 9.11a. This is due to the relation $d\mu = -SdT$ at constant P and the fact that the molar entropy of a vapor is much larger than that of a solid. When the μ_{liquid} curve is displaced down by the addition of the solute, (see Fig. 9.11a), the intersection of the μ_{liquid} curve with the μ_{solid} curve and the μ_{gas} curve determine the shift in the freezing and boiling temperatures. Because the magnitude of

the slope of the μ_{gas} curve is greater than that of the μ_{solid} curve, T_b moves up less than the T_m moves down.

Q9.5) The natural standard state for the solvent in an ideal dilute solution is the Raoult's law standard state, and the standard state for the solute in an ideal dilute solution is the Henry's law standard state. Is there a natural standard state for the solution for which $x_{solvent} = x_{solute} = 0.5$?

Raoult's law defines the appropriate standard state of the solvent in a dilute solution because in this limit the solute has only a weak effect on the solvent. Henry's law defines the appropriate standard state for the solute at a low solute concentration. However, neither standard state adequately describes the standard state for $x_{solvent} = x_{solute} = 0.5$. In this case, either standard state can be used, but neither has a firm physical basis.

Q9.6) Is a whale likely to get the bends when it dives deep into the ocean and resurfaces? Answer this question by considering the likelihood of a diver getting the bends if he or she dives and resurfaces on one lung full of air as opposed to breathing air for a long time at the deepest point of the dive.

The whale is unlikely to get the bends on one lungful of air. There is not enough N₂ present in a single lungful to yield a saturated solution of N₂ in the blood. Breathing air for a long time at depth, however, will result in saturated blood for the diver. For this reason, the diver is more susceptible to getting the bends than the whale.

Q9.7) The statement "The boiling point of a typical liquid mixture can be reduced by approximately 100°C if the pressure is reduced from 760 to 20 Torr" is found in Section 9.4. What figure(s) in Chapter 8 can you identify to support this statement in a qualitative sense?

Figure 9.11 (b) shows the *P-T* phase diagram of a pure substance (and a corresponding solution). By looking at the liquid-vapor coexistence curves, the dependence of boiling point on pressure can be traced. Qualitatively, it is seen that a decrease in *P* leads to a decrease in T_b .

Q9.8) Explain why chemists doing quantitative work using liquid solutions prefer to express concentration in terms of molality rather than molarity.

The molality of a solution is the preferred unit because it is independent of *P* and *T*. A kilogram of a substance is a conserved quantity, independent of temperature and pressure. The volume, however, changes as *T* or *P* are varied because the thermal expansion coefficient and the isothermal compressibility are not zero. Moles per kilogram is thus a more useful concentration unit than moles per liter, which changes with the thermodynamic state.

Q9.9) Explain the usefulness of a tie line on a *P-Z* phase diagram such as that of Figure 9.4.

The tie line allows the compositions of the liquid and vapor phases to be determined geometrically for a given total composition and pressure. Specifically, the ratio of moles in liquid and vapor phase is inversely proportional to the ratio of tie line distances.

Q9.10) Explain why colligative properties depend only on the concentration, and not on the identity of the molecule.

The origin of the colligative properties is the dilution of the solvent, which lowers its vapor pressure. This is the case because solute molecules at the surface of the liquid affects the relative rates of evaporation and condensation. This statistical likelihood of being near the interface doesn't depend on the identity of the solute – only the number in solution. Therefore, colligative properties (ideally) depend only on the number of species in solution.

Problems

P9.1) At 303 K, the vapor pressure of benzene is 118 Torr and that of cyclohexane is 122 Torr. Calculate the vapor pressure of a solution for which $x_{benzene} = 0.25$ assuming ideal behavior.

$$\begin{aligned} P_{total} &= x_{benzene} P_{benzene}^* + x_{cyclohexene} P_{cyclohexene}^* \\ &= 0.25 \times 118 \text{ Torr} + (1 - 0.25) \times 122 \text{ Torr} = 121 \text{ Torr} \end{aligned}$$

P9.2) A volume of 5.50 L of air is bubbled through liquid toluene at 298 K, thus reducing the mass of toluene in the beaker by 2.38 g. Assuming that the air emerging from the beaker is saturated with toluene, determine the vapor pressure of toluene at this temperature.

$$P = \frac{nRT}{V} = \frac{\frac{2.38 \text{ g}}{78.11 \text{ g mol}^{-1}} \times \frac{1 \text{ mol}}{0.08314 \text{ L bar K}^{-1}} \times 298 \text{ K}}{5.50 \text{ L}} = 0.116 \text{ bar}$$

P9.3) An ideal solution is formed by mixing liquids A and B at 298 K. The vapor pressure of pure A is 180 Torr and that of pure B is 82.1 Torr. If the mole fraction of A in the vapor is 0.450, what is the mole fraction of A in the solution?

$$x_A = \frac{y_A P_B^*}{P_A^* + (P_B^* - P_A^*) y_A} = \frac{0.450 \times 82.1 \text{ Torr}}{180 \text{ Torr} + (82.1 \text{ Torr} - 180 \text{ Torr}) \times 0.450} = 0.272$$

P9.4) A and B form an ideal solution. At a total pressure of 0.900 bar, $y_A = 0.450$ and $x_A = 0.650$. Using this information, calculate the vapor pressure of pure A and of pure B.

$$P_{total} = x_A P_a^* + y_B P_{total}$$

$$P_a^* = \frac{P_{total} - y_B P_{total}}{x_A} = \frac{0.900 \text{ bar}_x (1 - 0.550)}{0.450} = 0.623 \text{ bar}$$

$$x_A = \frac{y_A P_B^*}{P_a^* + (P_B^* - P_A^*) y_A}$$

$$0.650 = \frac{0.450 P_B^*}{P_A^* + 0.450 (P_B^* - P_A^*)}$$

$$\frac{P_B^*}{P_A^*} = \frac{0.650 \times (1 - 0.450)}{0.450 \times (1 - 0.650)} = 2.27$$

$$P_B^* = 1.414 \text{ bar}$$

P9.5) A and B form an ideal solution at 298K, with $x_A = 0.600$, $P_A^* = 105 \text{ Torr}$ and $P_B^* = 63.5 \text{ Torr}$.

- Calculate the partial pressures of A and B in the gas phase.
- A portion of the gas phase is removed and condensed in a separate container. Calculate the partial pressures of A and B in equilibrium with this liquid sample at 298 K.

a) Calculate the partial pressures of A and B in the gas phase.

$$P_A = x_A P_A^* = 0.600 \times 105 \text{ Torr} = 63.0 \text{ Torr}$$

$$P_B = (1 - x_A) P_B^* = 0.400 \times 63.5 \text{ Torr} = 25.4 \text{ Torr}$$

b) A portion of the gas phase is removed and condensed in a separate container. Calculate the partial pressures of A and B in equilibrium with this liquid sample at 298K.

The composition of the initial gas is given by

$$y_A = \frac{P_A}{P_A + P_B} = \frac{63.0 \text{ Torr}}{88.4 \text{ Torr}} = 0.71; \quad y_B = 0.287$$

For the portion removed, the new x_A and x_B values are the previous y_A and y_B values.

$$P_A = x_A P_A^* = 0.713 \times 105 \text{ Torr} = 74.9 \text{ Torr}$$

$$P_B = (1 - x_A) P_B^* = 0.287 \times 63.5 \text{ Torr} = 18.2 \text{ Torr}$$

P9.6) The vapor pressures of 1-bromobutane and 1-chlorobutane can be expressed in the form $\ln \frac{P_{bromo}}{\text{Pa}} = 17.076 - \frac{1584.8}{\frac{T}{\text{K}} - 111.88}$ and $\ln \frac{P_{chloro}}{\text{Pa}} = 20.612 - \frac{2688.1}{\frac{T}{\text{K}} - 55.725}$ Assuming

ideal solution behavior, calculate x_{bromo} and y_{bromo} at 300.0 K and a total pressure of 8741 Pa.

At 300.0K, $P_{bromo}^{\circ} = 5719$ Pa and $P_{chloro}^{\circ} = 14877$ Pa.

$$P_{total} = x_{bromo} P_{bromo}^{\circ} + (1 - x_{bromo}) P_{chloro}^{\circ}$$

$$x_{bromo} = \frac{P_{total} - P_{chloro}^{\circ}}{P_{bromo}^{\circ} - P_{chloro}^{\circ}} = \frac{8741 \text{ Pa} - 14877 \text{ Pa}}{5719 \text{ Pa} - 14877 \text{ Pa}} = 0.67$$

$$y_{bromo} = \frac{x_{bromo} P_{bromo}^{\circ}}{P_{total}} = \frac{0.67 \times 5719 \text{ Pa}}{8741 \text{ Pa}} = 0.44$$

P9.7) Assume that 1-bromobutane and 1-chlorobutane form an ideal solution. At 273 K, $P_{chloro}^{*} = 3790$ Torr and $P_{bromo}^{*} = 1394$ Torr. When only a trace of liquid is present at 273 K, $y_{chloro} = 0.75$.

- a. Calculate the total pressure above the solution.
- b. Calculate the mole fraction of 1-chlorobutane in the solution.
- c. What value would Z_{chloro} have in order for there to be 4.86 mol of liquid and 3.21 mol of gas at a total pressure equal to that in part (a)? [Note: This composition is different from that of part (a).]

- a) Calculate the total pressure above the solution.

$$y_{chloro} = \frac{P_{chloro}^{*} P_{total} - P_{chloro}^{*} P_{bromo}^{*}}{P_{total} (P_{chloro}^{*} - P_{bromo}^{*})}$$

$$0.75 = \frac{3790 \text{ Pa} \times P_{total} - 3790 \text{ Pa} \times 1394 \text{ Pa}}{P_{total} \times (3790 \text{ Pa} - 1394 \text{ Pa})}$$

$$P_{total} = \frac{3790 \text{ Pa} \times 1394 \text{ Pa}}{3790 \text{ Pa} - 0.75 \times (3790 \text{ Pa} - 1394 \text{ Pa})} = 2651 \text{ Pa}$$

- b) Calculate the mole fraction of 1-chlorobutane in the solution.

$$P_{total} = x_{chloro} P_{chloro}^{*} + (1 - x_{chloro}) P_{bromo}^{*}$$

$$x_{chloro} = \frac{P_{total} - P_{bromo}^{*}}{P_{chloro}^{*} - P_{bromo}^{*}} = \frac{2651 \text{ Pa} - 1394 \text{ Pa}}{3790 \text{ Pa} - 1394 \text{ Pa}} = 0.525$$

- c) What value would Z_{chloro} have in order that there are 4.86 moles of liquid and 3.21 moles of gas at a total pressure equal to that in part a)? (This composition is different than that in part a).

$$y_{chloro} = \frac{P_{chloro}^* P_{total} - P_{chloro}^* P_{bromo}^*}{P_{total} (P_{chloro}^* - P_{bromo}^*)}$$

$$= \frac{3790 \text{ Pa} \times 2651 \text{ Pa} - 3790 \text{ Pa} \times 1394 \text{ Pa}}{2651 \text{ Pa} \times (3790 \text{ Pa} - 1394 \text{ Pa})} = 0.750$$

$$x_{chloro} = \frac{y_{chloro} P_{bromo}^*}{P_{chloro}^* + (P_{bromo}^* - P_{chloro}^*) y_{chloro}}$$

$$= \frac{0.750 \times 1394 \text{ Pa}}{3790 \text{ Pa} + (1394 \text{ Pa} - 3790 \text{ Pa}) \times 0.750} = 0.525$$

$$n_{liq}^{tot} (Z_{chloro} - x_{chloro}) = n_{vapor}^{tot} (y_{chloro} - Z_{chloro})$$

$$Z_{chloro} = \frac{n_{vapor}^{tot} y_{chloro} + n_{liq}^{tot} x_{chloro}}{n_{vapor}^{tot} + n_{liq}^{tot}} = \frac{3.21 \text{ mol} \times 0.750 + 4.86 \text{ mol} \times 0.525}{3.21 \text{ mol} + 4.86 \text{ mol}} = 0.614$$

P9.8) An ideal solution at 298 K is made up of the volatile liquids A and B, for which $P_A^* = 125$ Torr and $P_B^* = 46.3$ Torr. As the pressure is reduced from 450 Torr, the first vapor is observed at a pressure of 70.0 Torr. Calculate x_A .

The first vapor is observed at a pressure of

$$P_{total} = x_A P_A^* + (1 - x_A) P_B^*$$

$$x_A = \frac{P_{total} - P_B^*}{P_A^* - P_B^*} = \frac{70.0 \text{ Torr} - 46.3 \text{ Torr}}{125 \text{ Torr} - 46.3 \text{ Torr}} = 0.301$$

P9.9) At -47°C , the vapor pressure of ethyl bromide is 10.0 Torr and that of ethyl chloride is 40.0 Torr. Assume that the solution is ideal. Assume there is only a trace of liquid present and the mole fraction of ethyl chloride in the vapor is 0.80 and answer these questions:

- What is the total pressure and the mole fraction of ethyl chloride in the liquid?
- If there are 5.00 mol of liquid and 3.00 mol of vapor present at the same pressure as in part (a), what is the overall composition of the system?

$$\text{a) } P_{total} = \frac{P_{EB}^* - P_{EC}^*}{P_{EC}^* + (P_{EB}^* - P_{EC}^*) y_{EC}}$$

$$= \frac{10.0 \text{ Torr} - 40 \text{ Torr}}{40.0 \text{ Torr} + (10 \text{ Torr} - 40 \text{ Torr}) \times 0.80}$$

$$= 25.0 \text{ Torr}$$

$$P_{total} = x_{EC} P_{EC}^* + (1 - x_{EC}) P_{EB}^*$$

$$x_{EC} = \frac{P_{total} - P_{EB}^*}{P_{EC}^* - P_{EB}^*} = \frac{25.0 \text{ Torr} - 10.0 \text{ Torr}}{40.0 \text{ Torr} - 10.0 \text{ Torr}}$$

$$= 0.50$$

b) We use the lever rule.

$$n_{liq}^{tot} (Z_B - x_B) = n_{vap}^{tot} (y_B - Z_B)$$

$$Z_B - x_B = (1 - Z_A) - (1 - x_A) = x_A - Z_A$$

$$y_B - z_B = (1 - y_A) - (1 - z_A) = Z_A - y_A$$

therefore

$$\frac{n_{liq}^{tot}}{n_{vap}^{tot}} = \frac{y_{EC} - Z_{EC}}{Z_{EC} - x_{EC}} = \frac{5}{3}$$

we know that $x_{EC} = 0.50$ and $y_{EC} = 0.80$

$$(0.80 - Z_{EC}) = \frac{5}{3}(Z_{EC} - 0.50)$$

$$Z_{EC} = 0.613$$

$$Z_{EB} = (1 - Z_{EC}) = 0.387$$

P9.10) At -31.2°C , pure propane and *n*-butane have a vapor pressure of 1200 and 200 Torr, respectively.

- Calculate the mole fraction of propane in the liquid mixture that boils at -31.2°C at a pressure of 760 Torr.
- Calculate the mole fraction of propane in the vapor that is in equilibrium with the liquid of part (a).

$$a) P_{total} = x_p P_p^* + (1 - x_p) P_B^*$$

$$760 \text{ Torr} = 1200x_p + 200(1 - x_p)$$

$$x_p = 0.560$$

$$\begin{aligned}
 \text{b) } y_B &= \frac{x_p P_p^*}{P_p^* + (P_p^* - P_B^*) x_p} \\
 &= \frac{0.56 \times 1200 \text{ Torr}}{200 \text{ Torr} + 0.56 \times (1200 \text{ Torr} - 200 \text{ Torr})} \\
 &= 0.884
 \end{aligned}$$

P9.11) In an ideal solution of A and B, 3.50 mol are in the liquid phase and 4.75 mol are in the gaseous phase. The overall composition of the system is $Z_A = 0.300$ and $x_A = 0.250$. Calculate y_A .

$$\begin{aligned}
 n_{liq}^{tot} (Z_B - x_B) &= n_{vapor}^{tot} (y_B - Z_B) \\
 y_B &= \frac{n_{liq}^{tot} (Z_B - x_B) + n_{vapor}^{tot} Z_B}{n_{vapor}^{tot}} = \frac{3.50 \text{ mol} \times (0.300 - 0.250) + 4.75 \text{ mol} \times 0.300}{4.75 \text{ mol}} = 0.337
 \end{aligned}$$

P9.12) Given the vapor pressures of the pure liquids and the overall composition of the system, what are the upper and lower limits of pressure between which liquid and vapor coexist in an ideal solution?

Referring to Figure 9.4, it is seen that the maximum pressure results if $Z_A = x_A$.

$$P_{\max} = Z_A P_A^* + (1 - Z_A) P_B^*$$

The minimum pressure results if $Z_A = y_A$. Using equation 9.12,

$$P_{\min} = \frac{P_A^* P_B^*}{P_A^* + (P_B^* - P_A^*) Z_A}$$

P9.13) At 39.9°C, a solution of ethanol ($x_1 = 0.9006$, $P_1^* = 130.4$ Torr) and isoctane ($P_2^* = 43.9$ Torr) forms a vapor phase with $y_1 = 0.6667$ at a total pressure of 185.9 Torr.

- Calculate the activity and activity coefficient of each component.
- Calculate the total pressure that the solution would have if it were ideal.

- The activity and activity coefficient for ethanol are given by

$$a_1 = \frac{y_1 P_{total}}{P_1^*} = \frac{0.6667 \times 185.9 \text{ Torr}}{130.4 \text{ Torr}} = 0.9504$$

$$\gamma_1 = \frac{a_1}{x_1} = \frac{0.9504}{0.9006} = 1.055$$

Similarly, the activity and activity coefficient for isoctane are given by

$$a_2 = \frac{(1 - y_1) P_{total}}{P_2^*} = \frac{0.3333 \times 185.9 \text{ Torr}}{43.9 \text{ Torr}} = 1.411$$

$$\gamma_2 = \frac{a_2}{x_2} = \frac{1.411}{1 - 0.9006} = 14.20$$

b) If the solution were ideal, Raoult's law would apply.

$$\begin{aligned} P_{Total} &= x_1 P_1^* + x_2 P_2^* \\ &= 0.9006 \times 130.4 \text{ Torr} + (1 - 0.9006) \times 43.9 \text{ Torr} \\ &= 121.8 \text{ Torr} \end{aligned}$$

P9.14) Ratcliffe and Chao [*Canadian Journal of Chemical Engineering* 47, (1969), 148] obtained the following tabulated results for the variation of the total pressure above a solution of isopropanol ($P_1^* = 1008 \text{ Torr}$) and *n*-decane ($P_2^* = 48.3 \text{ Torr}$) as a function of the mole fraction of the *n*-decane in the solution and vapor phases. Using these data, calculate the activity coefficients for both components using a Raoult's law standard state.

(Torr)	x_2	y_2
942.6	0.1312	0.0243
909.6	0.2040	0.0300
883.3	0.2714	0.0342
868.4	0.3360	0.0362
830.2	0.4425	0.0411
786.8	0.5578	0.0451
758.7	0.6036	0.0489

a) for isopropanol $P_1^* = 1008 \text{ Torr}$

for *n*-decane $P_2^* = 48.3 \text{ Torr}$

Using the relations $P_i = y_i P_{total}$, $a_i = P_i / P_i^*$, and $\gamma_i = \frac{a_i}{x_i}$, the calculated activities and activity coefficients are shown below.

$P(\text{Torr})$	x_2	y_2	a_1	a_2	γ_1	γ_2
942.6	0.1312	0.0243	0.912	0.474	1.05	3.61
909.6	0.2040	0.0300	0.875	0.565	1.10	2.77
883.3	0.2714	0.0342	0.846	0.625	1.16	2.30
868.4	0.3360	0.0362	0.831	0.651	1.25	1.94
830.2	0.4425	0.0411	0.790	0.706	1.42	1.60

786.8	0.5578	0.0451	0.745	0.735	1.69	1.32
758.7	0.6036	0.0489	0.716	0.768	1.81	1.27+

P9.15) At 39.9°C, the vapor pressure of water is 55.03 Torr (component A) and that of methanol (component B) is 255.6 Torr. Using data from the following table, calculate the activity coefficients for both components using a Raoult's law standard state.

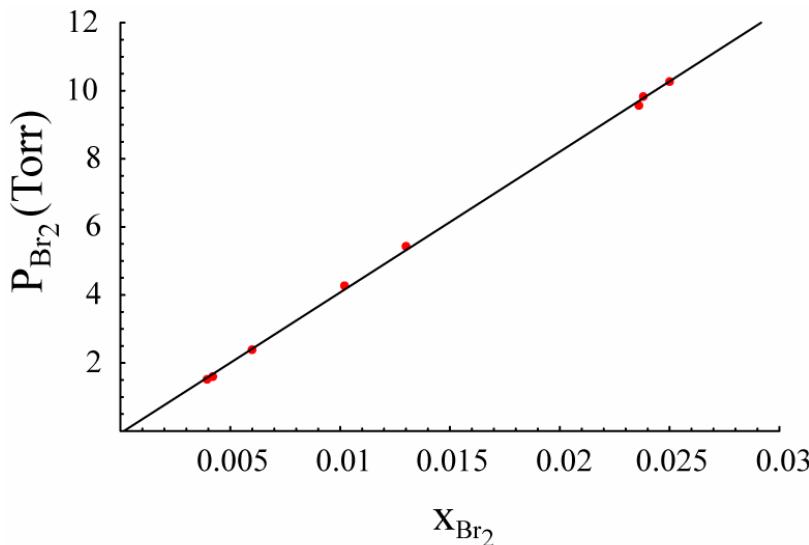
See the solution to Problem 9.14 for the method used. The results are shown below.

x_A	y_A	P (Torr)
0.0490	0.0175	257.9
0.3120	0.1090	211.3
0.4750	0.1710	184.4
0.6535	0.2550	156.0
0.7905	0.3565	125.7

x_A	y_A	P (Torr)	a_A	a_B	γ_A	γ_B
0.0490	0.0175	257.9	0.082	0.991	1.67	1.04
0.3120	0.1090	211.3	0.419	0.737	1.34	1.07
0.4750	0.1710	184.4	0.573	0.598	1.21	1.14
0.6535	0.2550	156.0	0.723	0.455	1.11	1.31
0.7905	0.3565	125.7	0.814	0.316	1.03	1.55

P9.16) The partial pressures of Br₂ above a solution containing CCl₄ as the solvent at 25°C are found to have the values listed in the following table as a function of the mole fraction of Br₂ in the solution [G. N. Lewis and H. Storch, *J. American Chemical Society* 39 (1917), 2544]. Use these data and a graphical method to determine the Henry's law constant for Br₂ in CCl₄ at 25°C.

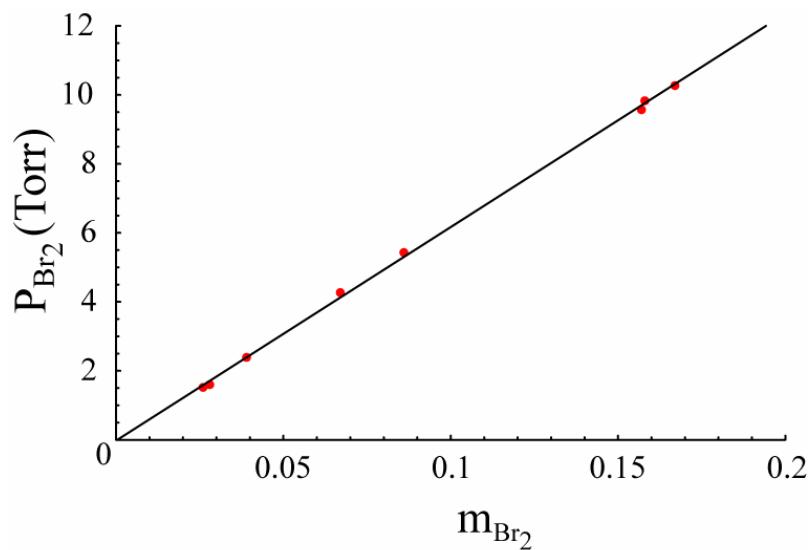
x_{Br_2}	P (Torr)	x_{Br_2}	P (Torr)
0.00394	1.52	0.0130	5.43
0.00420	1.60	0.0236	9.57
0.00599	2.39	0.0238	9.83
0.0102	4.27	0.0250	10.27



The best fit line in the plot is $P_{Br_2} \text{ (Torr)} = 413 x_{Br_2} - 0.063$. Therefore, the Henry's law constant in terms of mole fraction is 413 Torr.

P9.17) The data from Problem P9.16 can be expressed in terms of the molality rather than the mole fraction of Br₂. Use the data from the following table and a graphical method to determine the Henry's law constant for Br₂ in CCl₄ at 25°C in terms of molality.

m_{Br_2}	$P \text{ (Torr)}$	m_{Br_2}	$P \text{ (Torr)}$
0.026	1.52	0.086	5.43
0.028	1.60	0.157	9.57
0.039	2.39	0.158	9.83
0.067	4.27	0.167	10.27



The best fit line in the plot is $P_{B_2} \text{ (Torr)} = 61.9 m_{B_2} - 0.0243$. Therefore, the Henry's law constant in terms of molality is 61.9 Torr.

P9.18) The partial molar volumes of water and ethanol in a solution with $x_{H_2O} = 0.60$ at 25°C are 17.0 and 57.0 cm³ mol⁻¹, respectively. Calculate the volume change upon mixing sufficient ethanol with 2.00 mol of water to give this concentration. The densities of water and ethanol are 0.997 and 0.7893 g cm⁻³, respectively, at this temperature.

$$V = n_{H_2O} \bar{V}_{H_2O} + n_{Et} \bar{V}_{Et}$$

$$\bar{V}_{H_2O} = 17.0 \text{ cm}^3 \text{ mol}^{-1} \text{ and } \bar{V}_{Et} = 57.0 \text{ cm}^3 \text{ mol}^{-1}$$

$$n_{H_2O} = 2.00 \text{ and } x_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{Et}} = 0.600$$

$$\frac{2 \text{ mol}}{2 \text{ mol} + n_{Et}} = 0.600; \quad n_{Et} = 1.333$$

The total mixed volume is given by

$$V_{mixed} = n_{H_2O} \bar{V}_{H_2O} + n_{Et} \bar{V}_{Et}$$

$$= 2.00 \text{ mol} \times 17.0 \text{ cm}^3 \text{ mol}^{-1} + 1.333 \text{ mol} \times 57.0 \text{ cm}^3 \text{ mol}^{-1}$$

$$= 109.98 \text{ cm}^3$$

$$V_{unmixed} = n_{H_2O} \frac{M_{H_2O}}{\rho_{H_2O}} + n_{Et} \frac{M_{Et}}{\rho_{Et}}$$

$$= 2.00 \text{ mol} \times 18.02 \text{ g mol}^{-1} \times \frac{1 \text{ cm}^{-3}}{0.997 \text{ g}}$$

$$+ 1.333 \text{ mol} \times 46.07 \text{ g mol}^{-1} \times \frac{1 \text{ cm}^{-3}}{0.7893 \text{ g}}$$

$$= 36.15 \text{ cm}^3 + 77.63 \text{ cm}^3$$

$$= 113.78 \text{ cm}^3$$

$$\Delta V = V_{mixed} - V_{unmixed} = 109.98 \text{ cm}^3 - 113.78 \text{ cm}^3 = -3.8 \text{ cm}^3$$

P9.19) A solution is prepared by dissolving 32.5 g of a nonvolatile solute in 200 g of water. The vapor pressure above the solution is 21.85 Torr and the vapor pressure of pure water is 23.76 Torr at this temperature. What is the molecular weight of the solute?

$$x_{H_2O} = \frac{P_{H_2O}}{P_{H_2O}^*} = \frac{21.85 \text{ Torr}}{23.76 \text{ Torr}} = 0.9196$$

$$x_{\text{solute}} = 0.0804 = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{H_2O}};$$

$$n_{\text{solute}} = \frac{0.0804 n_{H_2O}}{0.9617} = \frac{0.0804 \times \frac{200 \text{ g}}{18.02 \text{ g mol}^{-1}}}{0.9196} = 0.970 \text{ mol}$$

$$M = \frac{32.5 \text{ g}}{0.970 \text{ mol}} = 33.5 \text{ g mol}^{-1}$$

P9.20) The heat of fusion of water is $6.008 \times 10^3 \text{ J mol}^{-1}$ at its normal melting point of 273.15 K. Calculate the freezing point depression constant K_f .

$$K_f = \frac{RM_{\text{solvent}} T_{\text{fusion}}^2}{\Delta H_{\text{fusion}}} = -\frac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 18.02 \times 10^3 \text{ kg mol}^{-1} \times (273.15 \text{ K})^2}{6.008 \times 10^3 \text{ J mol}^{-1}}$$

$$K_f = 1.86 \text{ K kg mol}^{-1}$$

P9.21) It is found that the dissolution of 5.25 g of a substance in 565 g of benzene at 298 K raises the boiling point by 0.625°C. Note that $K_f = 5.12 \text{ K kg mol}^{-1}$, $K_b = 2.53 \text{ K kg mol}^{-1}$, and the density of benzene is 876.6 kg m^{-3} . Calculate the freezing point depression, the ratio of the vapor pressure above the solution to that of the pure solvent, the osmotic pressure, and the molecular weight of the solute. $P_{\text{benzene}}^* = 103 \text{ Torr}$ at 298 K.

$$\Delta T_b = K_b m_{\text{solute}}; \quad m_{\text{solute}} = \frac{\Delta T_b}{K_b} = \frac{0.625 \text{ K}}{2.53 \text{ K kg mol}^{-1}} = 0.247 \text{ mol kg}^{-1}$$

$$M = \frac{5.25 \text{ g}}{0.247 \text{ mol kg}^{-1} \times 0.565 \text{ kg}} = 37.6 \text{ g mol}^{-1}$$

$$\Delta T_f = -K_f m_{\text{solute}} = -5.12 \text{ K kg mol}^{-1} \times 0.247 \text{ mol kg}^{-1} = -1.26 \text{ K}$$

$$\begin{aligned} \frac{P_{\text{benzene}}}{P_{\text{benzene}}^*} &= x_{\text{benzene}} = \frac{n_{\text{benzene}}}{n_{\text{benzene}} + n_{\text{solute}}} \\ &= \frac{\frac{565 \text{ g}}{78.11 \text{ g mol}^{-1}}}{\frac{565 \text{ g}}{78.11 \text{ g mol}^{-1}} + 0.247 \text{ mol kg}^{-1} \times 0.565 \text{ kg}} = 0.981 \end{aligned}$$

$$\pi = \frac{n_{\text{solute}} RT}{V} = \frac{\frac{5.25 \times 10^{-3} \text{ kg}}{37.6 \times 10^{-3} \text{ kg mol}^{-1}} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298 \text{ K}}{\frac{565 \times 10^{-3} \text{ kg}}{876.6 \text{ kg m}^{-3}}} = 5.37 \times 10^5 \text{ Pa}$$

P9.22) A sample of glucose ($C_6H_{12}O_6$) of mass 1.25 g is placed in a test tube of radius 1.00 cm. The bottom of the test tube is a membrane that is semipermeable to water. The tube is partially immersed in a beaker of water at 298 K so that the bottom of the test tube is only slightly below the level of the water in the beaker. The density of water at this temperature is 997 kg m^{-3} . After equilibrium is reached, how high is the water level of the water in the tube above that in the beaker? What is the value of the osmotic pressure?

You may find the approximation $\ln \frac{1}{1+x} \approx -x$ useful.

$$\pi V_m^* + RT \ln x_{\text{solvent}} = \pi V_m^* + RT \ln \frac{n_{\text{sucrose}}}{n_{\text{solvent}} + n_{\text{sucrose}}} = 0$$

$$\rho g h V_m^* + RT \ln \frac{\frac{\rho Ah}{M}}{\frac{\rho Ah}{M} + n_{\text{sucrose}}} = \rho g h V_m^* + RT \ln \frac{1}{1 + \frac{n_{\text{sucrose}} M}{\rho Ah}} = 0$$

Expanding the argument of the logarithmic term in a Taylor series, $\ln \frac{1}{1+x} \approx -x$

$$\rho g h V_m^* - RT \frac{n_{\text{sucrose}} M}{\rho Ah} = 0$$

$$h = \sqrt{\frac{RT n_{\text{sucrose}} M}{\rho^2 A g V_m^*}} = \sqrt{\frac{RT n_{\text{sucrose}}}{\rho A g}}$$

$$= \sqrt{\frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \frac{1.25 \times 10^{-3} \text{ kg}}{0.18016 \text{ kg mol}^{-1}}}{997 \text{ kg m}^{-3} \times 3.14 \times 10^{-4} \text{ m}^2 \times 9.81 \text{ m s}^{-2}}} = 2.37 \text{ m}$$

$$\pi = \rho g h = 997 \text{ kg m}^{-3} \times 9.81 \text{ m s}^{-2} \times 2.37 \text{ m} = 2.32 \times 10^4 \text{ Pa}$$

P9.23) The osmotic pressure of an unknown substance is measured at 298 K. Determine the molecular weight if the concentration of this substance is 25.5 kg m^{-3} , and the osmotic pressure is $4.50 \times 10^4 \text{ Pa}$. The density of the solution is 997 kg m^{-3} .

$$\pi = \frac{n_{\text{solute}} RT}{V} = \frac{c_{\text{solute}} \rho_{\text{solution}} RT}{M_{\text{solute}}}; \quad M_{\text{solute}} = \frac{\rho_{\text{solution}} c_{\text{solute}} / \text{kg}}{\pi} RT$$

$$M_{\text{solute}} = \frac{997 \text{ kg m}^{-3} \times 25.5 \text{ kg m}^{-3} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{4.50 \times 10^4 \text{ Pa}} = 1400 \text{ kg mol}^{-1}$$

P9.24) An ideal dilute solution is formed by dissolving the solute A in the solvent B. Write expressions equivalent to Equations (9.9) through (9.13) for this case.

We obtain the equations by replacing P_A^* by k_A^H .

$$P_{tot} = P_A + P_B = x_a k_H^A + (1 - x_A) P_B^*$$

$$y_A = \frac{P_A}{P_{tot}} = \frac{x_A k_H^A}{P_B^* (k_H^A - P_B^*) x_A}$$

$$x_A = \frac{y_A P_B^*}{k_H^A + (P_B^* - k_H^A) y_A}$$

$$P_{tot} = \frac{k_H^A P_B^*}{k_H^A + (P_B^* - k_H^A) y_A}$$

$$y_A = (k_H^A P_{tot} - k_H^A P_B^*) / [P_{tot} (k_H^A - P_B^*)]$$

P9.25) A solution is made up of 184.2 g of ethanol and 108.1 g of H₂O. If the volume of the solution is 333.4 cm³ and the partial molar volume of H₂O is 17.0 cm³, what is the partial molar volume of ethanol under these conditions?

$$V = n_{H_2O} \bar{V}_{H_2O} + n_{ethanol} \bar{V}_{ethanol}$$

$$\bar{V}_{ethanol} = \frac{V - n_{H_2O} \bar{V}_{H_2O}}{n_{ethanol}} = \frac{333.4 \text{ cm}^3 - \frac{108.1 \text{ g}}{18.02 \text{ g mol}^{-1}} \times 17.0 \text{ cm}^3 \text{ mol}^{-1}}{\frac{184.2 \text{ g}}{46.04 \text{ g mol}^{-1}}} = 57.8 \text{ cm}^3 \text{ mol}^{-1}$$

P9.26) Calculate the solubility of H₂S in 1 L of water if its pressure above the solution is 3.25 bar. The density of water at this temperature is 997 kg m⁻³.

$$x_{H_2S} = \frac{n_{H_2S}}{n_{H_2S} + n_{H_2O}} \approx \frac{n_{H_2S}}{n_{H_2O}} = \frac{P_{H_2S}}{k_{H_2S}^H} = \frac{3.25 \text{ bar}}{568 \text{ bar}} = 5.72 \times 10^{-3}$$

$$n_{H_2O} = \frac{\rho_{H_2O} V}{M_{H_2O}} = \frac{10^{-3} \text{ m}^3 \times 997 \text{ kg m}^{-3}}{18.02 \times 10^{-3} \text{ kg mol}^{-1}} = 55.4$$

$$n_{H_2S} = x_{H_2S} n_{H_2O} = 5.72 \times 10^{-3} \times 55.4 = 0.327 \text{ mol}$$

P9.27) The densities of pure water and ethanol are 997 and 789 kg m⁻³, respectively. The partial molar volumes of ethanol and water in a solution with $x_{ethanol} = 0.20$ are 55.2 and $17.8 \times 10^{-3} \text{ L mol}^{-1}$, respectively. Calculate the change in volume relative to the pure components when 1.00 L of a solution with $x_{ethanol} = 0.20$ is prepared.

$$V = n_{H_2O} \bar{V}_{H_2O} + n_{ethanol} \bar{V}_{ethanol}$$

$$\frac{V}{n_{total}} = x_{H_2O} \bar{V}_{H_2O} + x_{ethanol} \bar{V}_{ethanol} = 0.80 \times 17.8 \times 10^{-3} \text{ L mol}^{-1} + 0.20 \times 55.2 \times 10^{-3} \text{ L mol}^{-1}$$

$$\frac{V}{n_{total}} = 0.0253 \text{ L mol}^{-1}$$

$$n_{total} = \frac{1.00 \text{ L}}{0.0253 \text{ L mol}^{-1}} = 39.6 \text{ mol} = n_{H_2O} + n_{ethanol}$$

$$\frac{x_{ethanol}}{x_{H_2O}} = \frac{n_{ethanol}}{n_{H_2O}} = \frac{1}{4}; \quad n_{H_2O} = 31.7 \text{ mol} \quad n_{ethanol} = 7.90 \text{ mol}$$

$$V_{ideal} = n_{ethanol} \frac{M_{ethanol}}{\rho_{ethanol}} + n_{H_2O} \frac{M_{H_2O}}{\rho_{H_2O}}$$

$$= 7.90 \text{ mol} \times \frac{46.07 \times 10^{-3} \text{ kg mol}^{-1}}{789 \text{ kg m}^{-3}} + 31.7 \text{ mol} \times \frac{18.02 \times 10^{-3} \text{ kg mol}^{-1}}{998 \text{ kg m}^{-3}} = 1.034 \text{ L}$$

$$\Delta V = V - V_{ideal} = -0.034 \text{ L}$$

P9.28) At a given temperature, a nonideal solution of the volatile components A and B has a vapor pressure of 832 Torr. For this solution, $y_A = 0.404$. In addition, $x_A = 0.285$, $P_A^* = 591$ Torr, and $P_B^* = 503$ Torr. Calculate the activity and activity coefficient of A and B.

$$P_A = y_A P_{total} = 0.404 \times 832 \text{ Torr} = 336 \text{ Torr}$$

$$P_B = 832 \text{ Torr} - 336 \text{ Torr} = 496 \text{ Torr}$$

$$a_A = \frac{P_A}{P_A^*} = \frac{336 \text{ Torr}}{591 \text{ Torr}} = 0.569$$

$$\gamma_A = \frac{a_A}{x_A} = \frac{0.569}{0.285} = 2.00$$

$$a_B = \frac{P_B}{P_B^*} = \frac{496 \text{ Torr}}{503 \text{ Torr}} = 0.986$$

$$\gamma_B = \frac{a_B}{x_B} = \frac{0.986}{0.715} = 1.38$$

P9.29) Calculate the activity and activity coefficient for CS_2 at $x_{\text{CS}_2} = 0.7220$ using the data in Table 9.3 for both a Raoult's law and a Henry's law standard state.

$$a_{CS_2}^R = \frac{P_{CS_2}}{P_{CS_2}^*} = \frac{446.9 \text{ Torr}}{512.3 \text{ Torr}} = 0.8723$$

$$\gamma_{CS_2}^R = \frac{a_{CS_2}^R}{x_{CS_2}} = \frac{0.8723}{0.7220} = 1.208$$

$$a_{CS_2}^H = \frac{P_{CS_2}}{k_{H,CS_2}} = \frac{446.9 \text{ Torr}}{2010 \text{ Torr}} = 0.2223$$

$$\gamma_{CS_2}^H = \frac{a_{CS_2}^H}{x_{CS_2}} = \frac{0.2223}{0.7220} = 0.3079$$

P9.30) At high altitudes, mountain climbers are unable to absorb a sufficient amount of O₂ into their bloodstreams to maintain a high activity level. At a pressure of 1 bar, blood is typically 95% saturated with O₂, but near 18,000 feet where the pressure is 0.50 bar, the corresponding degree of saturation is 71%. Assuming that the Henry's law constant for blood is the same as for water, calculate the amount of O₂ dissolved in 1.00 L of blood for pressures of 1 bar and 0.500 bar. Air contains 20.99% O₂ by volume. Assume that the density of blood is 998 kg m⁻³.

By Dalton's law, P_{O₂} = 0.2099P. At sea level,

$$n = n_{H_2O} x_{O_2} = n_{H_2O} \frac{P_{O_2}}{k_H^{O_2}} = \frac{\rho_{H_2O} V P_{O_2} f_{sat}}{k_H^{O_2} M_{H_2O}}$$

$$n = \frac{998 \text{ kg m}^{-3} \times 10^{-3} \text{ m}^3 \times 0.2099 \text{ bar} \times 0.95}{4.95 \times 10^4 \text{ bar} \times 18.02 \times 10^{-3} \text{ kg mol}^{-1}} = 2.31 \times 10^{-4} \text{ mol}$$

$$\text{mass} = nM = 2.31 \times 10^{-4} \text{ mol} \times 32.0 \text{ g mol}^{-1} = 7.14 \times 10^{-3} \text{ g}$$

At 18,000 feet,

$$n = n_{H_2O} x_{O_2} = n_{H_2O} \frac{P_{O_2}}{k_H^{O_2}} = \frac{\rho_{H_2O} V P_{O_2} f_{sat}}{k_H^{O_2} M_{H_2O}}$$

$$n = \frac{998 \text{ kg m}^{-3} \times 10^{-3} \text{ m}^3 \times 0.2099 \times 0.500 \text{ bar} \times 0.71}{4.95 \text{ bar} \times 18.02 \times 10^{-3} \text{ kg mol}^{-1}} = 8.34 \times 10^{-5} \text{ mol}$$

$$\text{mass} = nM = 8.34 \times 10^{-5} \text{ mol} \times 32.0 \text{ g mol}^{-1} = 2.67 \times 10^{-3} \text{ g}$$

Questions on Concepts

Q10.1) Tabulated values of standard entropies of some aqueous ionic species are negative. Why is this statement consistent with the third law of thermodynamics?

This is possible due to the choice of standard state as $S_f^\circ(H^+, \text{aq}) \equiv 0$. Although absolute entropies of neutral species can be determined, this is not possible for ionic species because the solution must be electrically neutral. Therefore, it is necessary to choose a reference value, but as generally only differences in entropies (and other thermodynamic quantities) are desired, it is not necessary to know the absolute value.

Q10.2) Why is the value for the dielectric constant for water in the solvation shell around ions less than that for bulk water?

Water molecules immediately around the ion are ordered more than those in the bulk. Thus, they cannot respond to the electric field due to solvated ions. Therefore, they are less effective in screening the electric field due to solvated ions, leading to a smaller value of ϵ_r .

Q10.3) Why is it possible to formulate a theory for the activity coefficient for electrolyte solutions, but not for neutral solutes?

The dissolved species in electrolyte solutions have a universal form for their dominant interaction with the solvent – the Coulomb interaction. Non-electrolytes interact with much weaker, system specific potentials. The universality of the electrolyte- electrolyte interaction allows a general theory to be developed.

Q10.4) Why are activity coefficients calculated using the Debye–Hückel limiting law always less than one?

The activity coefficients are less than one because the charge on an electrolyte lowers the chemical potential of the electrolyte when compared with an analogous solution of uncharged solute molecules. This occurs because the charges interact attractively with the solvent, lowering the energy.

Q10.5) Why does an increase in the ionic strength in the range where the Debye–Hückel law is valid lead to an increase in the solubility of a weakly soluble salt?

In this regime, $\ln \gamma_\pm$ decreases with increasing I (as \sqrt{I}). The chemical potential of the electrolyte in solution becomes lower with increasing ionic strength, thus increasing solubility. Physically, increasing I leads to increased screening of repulsion between like-charged solute ions.

Q10.6) Discuss how the Debye–Hückel screening length changes as the (a) temperature, (b) dielectric constant, and (c) ionic strength of an electrolyte solution are increased.

- (a) Increasing T increases the screening length. The random thermal motion spreads out the cloud of screening ions.
- (b) Increasing ϵ_r increases screening length. Increased ϵ_r makes the potential attracting the counterion cloud weaker, causing it to spread out more.
- (c) Increasing ionic strength decreases the screening length. More counter ions available leads to more effective screening, decreasing $1/\kappa$.

Q10.7) What is the correct order of the following inert electrolytes in their ability to increase the degree of dissociation of acetic acid?

- a. 0.001m NaCl
- b. 0.001m KBr
- c. 0.10m CuCl_2

0.001 m NaCl and 0.001 m KBr will both increase dissociation of HOAc (salting in) – about the same (dilute solution, γ_{\pm} same according to Debye–Hückel). 0.1 m CuCl_2 will decrease dissociation because the solution is concentrated, leading to salting out.

Q10.8) Why is it not appropriate to use ionic radii from crystal structures to calculate $\Delta G_{\text{solvation}}^{\circ}$ of ions using the Born model?

The effective cavity that the ion occupies in the solvent medium will not have the same radius as the lattice-based radius. Better results can be obtained using the ion-water distance (to the center of charge), a more realistic estimate of the cavity radius r in the Born model.

Q10.9) Why is it not possible to measure the activity coefficient of $\text{Na}^+(aq)$?

It is impossible to create a solution of pure Na^+ in water. A counter ion is always required to give a solution that is electrically neutral, and this anion will always affect the measurement.

Q10.10) What can you conclude about the interaction between ions in an electrolyte solution if the mean ionic activity coefficient is greater than one?

Overall repulsive interactions must move than compensate any favorable attractive interactions between electrolyte solute and solvent.

Problems

P10.1) Calculate $\Delta H_{reaction}^\circ$ and $\Delta G_{reaction}^\circ$ for the reaction $\text{AgNO}_3(\text{aq}) + \text{KCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{KNO}_3(\text{aq})$.

$$\begin{aligned}\Delta G_{reaction}^\circ &= \Delta G_f^\circ(\text{AgCl}, \text{s}) + \Delta G_f^\circ(\text{K}^+, \text{aq}) + \Delta G_f^\circ(\text{NO}_3^-, \text{aq}) - \Delta G_f^\circ(\text{Ag}^+, \text{aq}) \\ &\quad - \Delta G_f^\circ(\text{NO}_3^-, \text{aq}) - \Delta G_f^\circ(\text{K}^+, \text{aq}) - \Delta G_f^\circ(\text{Cl}^-, \text{aq})\end{aligned}$$

$$\begin{aligned}\Delta G_{reaction}^\circ &= \Delta G_f^\circ(\text{AgCl}, \text{s}) - \Delta G_f^\circ(\text{Ag}^+, \text{aq}) - \Delta G_f^\circ(\text{Cl}^-, \text{aq}) = -109.8 \text{ kJ mol}^{-1} - 77.1 \text{ kJ} \\ &\quad \text{mol}^{-1} + 131.2 \text{ kJ mol}^{-1} = -55.7 \text{ kJ mol}^{-1}\end{aligned}$$

$$\Delta H_{reaction}^\circ = \Delta H_f^\circ(\text{AgCl}, \text{s}) - \Delta H_f^\circ(\text{Ag}^+, \text{aq}) - \Delta H_f^\circ(\text{Cl}^-, \text{aq})$$

$$\Delta H_{reaction}^\circ = -127.0 \text{ kJ mol}^{-1} - 105.6 \text{ kJ mol}^{-1} + 167.2 \text{ kJ mol}^{-1} = -65.4 \text{ kJ mol}^{-1}$$

P10.2) Calculate $\Delta H_{reaction}^\circ$ and $\Delta G_{reaction}^\circ$ for the reaction $\text{Ba}(\text{NO}_3)_2(\text{aq}) + 2 \text{ KCl}(\text{aq}) \rightarrow \text{BaCl}_2(\text{s}) + 2 \text{ KNO}_3(\text{aq})$.

$$\begin{aligned}\Delta G_{reaction}^\circ &= \Delta G_f^\circ(\text{BaCl}_2, \text{s}) + 2 \Delta G_f^\circ(\text{K}^+, \text{aq}) + 2 \Delta G_f^\circ(\text{NO}_3^-, \text{aq}) - \Delta G_f^\circ(\text{Ba}^{2+}, \text{aq}) \\ &\quad - 2 \Delta G_f^\circ(\text{NO}_3^-, \text{aq}) - 2 \Delta G_f^\circ(\text{K}^+, \text{aq}) - 2 \Delta G_f^\circ(\text{Cl}^-, \text{aq})\end{aligned}$$

$$\Delta G_{reaction}^\circ = \Delta G_f^\circ(\text{BaCl}_2, \text{s}) - \Delta G_f^\circ(\text{Ba}^{2+}, \text{aq}) - 2 \Delta G_f^\circ(\text{Cl}^-, \text{aq})$$

$$\Delta G_{reaction}^\circ = -806.7 \text{ kJ mol}^{-1} + 560.8 \text{ kJ mol}^{-1} + 2 \times 131.2 \text{ kJ mol}^{-1} = 16.5 \text{ kJ mol}^{-1}$$

$$\Delta H_{reaction}^\circ = \Delta H_f^\circ(\text{BaCl}_2, \text{s}) - \Delta H_f^\circ(\text{Ba}^{2+}, \text{aq}) - 2 \Delta H_f^\circ(\text{Cl}^-, \text{aq})$$

$$\Delta H_{reaction}^\circ = -855.0 \text{ kJ mol}^{-1} + 537.6 \text{ kJ mol}^{-1} + 2 \times 167.2 \text{ kJ mol}^{-1} = 17 \text{ kJ mol}^{-1}$$

P10.3) Calculate $\Delta S_{reaction}^\circ$ for the reaction $\text{AgNO}_3(\text{aq}) + \text{KCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{KNO}_3(\text{aq})$.

$$\Delta S_{reaction}^\circ = S^\circ(\text{AgCl}, \text{s}) - S^\circ(\text{Ag}^+, \text{aq}) - S^\circ(\text{Cl}^-, \text{aq})$$

$$\Delta S_{reaction}^\circ = 96.3 \text{ J K}^{-1} \text{ mol}^{-1} - 72.7 \text{ J K}^{-1} \text{ mol}^{-1} - 56.5 \text{ J K}^{-1} \text{ mol}^{-1} = -32.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

P10.4) Calculate $\Delta S_{reaction}^\circ$ for the reaction $\text{Ba}(\text{NO}_3)_2(\text{aq}) + 2 \text{ KCl}(\text{aq}) \rightarrow \text{BaCl}_2(\text{s}) + 2 \text{ KNO}_3(\text{aq})$.

$$\Delta S_{reaction}^\circ = S^\circ(\text{BaCl}_2, \text{s}) - S^\circ(\text{Ba}^{2+}, \text{aq}) - 2 \times S^\circ(\text{Cl}^-, \text{aq})$$

$$\Delta S_{reaction}^\circ = 123.7 \text{ J K}^{-1} \text{ mol}^{-1} - 9.6 \text{ J K}^{-1} \text{ mol}^{-1} - 2 \times 56.5 \text{ J K}^{-1} \text{ mol}^{-1} = 1.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

P10.5) Calculate $\Delta G_{solvation}^\circ$ in an aqueous solution for $\text{Cl}^-(\text{aq})$ using the Born model. The radius of the Cl^- ion is $1.81 \times 10^{-10} \text{ m}$.

$$\Delta G_{solvation}^{\circ} = \frac{Z^2 e^2 N_A}{8\pi \epsilon_0 r} \left(\frac{1}{\epsilon_r} - 1 \right)$$

ϵ_r for water at 298 K is 78.5

For water at 25°C

$$\Delta G_{solvation}^{\circ} = -\frac{z^2}{(r/\text{pm})} \times (6.86 \times 10^4 \text{ kJ mol}^{-1})$$

Cl⁻ radius is 181 pm

$$\begin{aligned}\Delta G_{solvation}^{\circ} &= -\frac{1}{181} \times 6.86 \times 10^4 \text{ kJ mol}^{-1} \\ &= -379 \text{ kJ mol}^{-1}\end{aligned}$$

P10.6) Calculate the value of m_{\pm} in 5.0×10^{-4} molal solutions of a) KCl, b) Ca(NO₃)₂, and c) ZnSO₄. Assume complete dissociation.

a) KCl

$$\begin{aligned}m_{\pm} &= (v_+^{v_+} v_-^{v_-})^{1/v} m \\ m_{\pm} &= \sqrt[1]{1} m = 5.0 \times 10^{-4} \text{ mol kg}^{-1}\end{aligned}$$

b) Ca(NO₃)₂

$$\begin{aligned}m_{\pm} &= (v_+^{v_+} v_-^{v_-})^{1/v} m \\ m_{\pm} &= (4)^{1/3} m = (4)^{1/3} \times 5.0 \times 10^{-4} \text{ mol kg}^{-1} = 7.9 \times 10^{-4} \text{ mol kg}^{-1}\end{aligned}$$

c) ZnSO₄

$$\begin{aligned}m_{\pm} &= (v_+^{v_+} v_-^{v_-})^{1/v} m \\ m_{\pm} &= (1)^{1/2} m = 5.0 \times 10^{-4} \text{ mol kg}^{-1}\end{aligned}$$

P10.7) Express μ_{\pm} in terms of μ_+ and μ_- for a) NaCl, b) MgBr₂, c) Li₃PO₄, and d) Ca(NO₃)₂. Assume complete dissociation.

$$\text{a) NaCl } \mu_{\pm} = \frac{\mu_{solute}}{v} = \frac{v_+ \mu_+ + v_- \mu_-}{v} = \frac{\mu_+ + \mu_-}{2}$$

$$\text{b) MgBr}_2 \quad \mu_{\pm} = \frac{\mu_{solute}}{v} = \frac{v_+ \mu_+ + v_- \mu_-}{v} = \frac{\mu_+ + 2\mu_-}{3}$$

c) $\text{Li}_3\text{PO}_4 \quad \mu_{\pm} = \frac{\mu_{\text{solute}}}{v} = \frac{v_+ \mu_+ + v_- \mu_-}{v} = \frac{3\mu_+ + \mu_-}{4}$

d) $\text{Ca}(\text{NO}_3)_2 \quad \mu_{\pm} = \frac{\mu_{\text{solute}}}{v} = \frac{v_+ \mu_+ + v_- \mu_-}{v} = \frac{\mu_+ + 2\mu_-}{3}$

P10.8) Express a_{\pm} in terms of a_+ and a_- for a) Li_2CO_3 , b) CaCl_2 , c) Na_3PO_4 , and d) $\text{K}_4\text{Fe}(\text{CN})_6$. Assume complete dissociation.

a) $\text{Li}_2\text{CO}_3 \quad a_{\pm} = (a_+^{v_+} a_-^{v_-})^{\frac{1}{v}} = (a_+^2 a_-)^{\frac{1}{3}}$

b) $\text{CaCl}_2 \quad a_{\pm} = (a_+^{v_+} a_-^{v_-})^{\frac{1}{v}} = (a_+ a_-^2)^{\frac{1}{3}}$

c) $\text{Na}_3\text{PO}_4 \quad a_{\pm} = (a_+^{v_+} a_-^{v_-})^{\frac{1}{v}} = (a_+^3 a_-)^{\frac{1}{4}}$

d) $\text{K}_4\text{Fe}(\text{CN})_6 \quad a_{\pm} = (a_+^{v_+} a_-^{v_-})^{\frac{1}{v}} = (a_+^4 a_-)^{\frac{1}{5}}$

P10.9) Express γ_{\pm} in terms of γ_+ and γ_- for a) SrSO_4 , b) MgBr_2 , c) K_3PO_4 , and d) $\text{Ca}(\text{NO}_3)_2$. Assume complete dissociation.

a) $\text{SrSO}_4 \quad \gamma_{\pm} = (\gamma_+ \gamma_-)^{\frac{1}{2}}$

b) $\text{MgBr}_2 \quad \gamma_{\pm} = (\gamma_+ \gamma_-^2)^{\frac{1}{3}}$

c) $\text{K}_3\text{PO}_4 \quad \gamma_{\pm} = (\gamma_+^3 \gamma_-)^{\frac{1}{4}}$

d) $\text{Ca}(\text{NO}_3)_2 \quad \gamma_{\pm} = (\gamma_+ \gamma_-^2)^{\frac{1}{3}}$

P10.10) Calculate the ionic strength in a solution that is 0.0050m in K_2SO_4 , 0.0010m in Na_3PO_4 , and 0.0025m in MgCl_2 .

$$\begin{aligned} I_{\text{K}_2\text{SO}_4} &= \frac{m}{2} (v_+ z_+^2 + v_- z_-^2) \\ &= \frac{0.0050}{2} (2 + 4) = 0.0150 \text{ mol kg}^{-1} \end{aligned}$$

$$\begin{aligned} I_{\text{Na}_3\text{PO}_4} &= \frac{m}{2} (v_+ z_+^2 + v_- z_-^2) \\ &= \frac{0.0010}{2} (3 + 9) = 0.0060 \text{ mol kg}^{-1} \end{aligned}$$

$$I_{MgCl_2} = \frac{m}{2} (v_+ z_+^2 + v_- z_-^2)$$

$$= \frac{0.0025}{2} (4 + 2) = 0.0075 \text{ mol kg}^{-1}$$

total ionic strength

$$I = (0.0150 + 0.0060 + 0.0075) \text{ mol kg}^{-1}$$

$$= 0.0285 \text{ mol kg}^{-1}$$

P10.11) Calculate the mean ionic activity of a 0.0150m K_2SO_4 solution for which the mean activity coefficient is 0.465.

$$a_{\pm} = \left(\frac{(v_+^{v_+} v_-^{v_-})^{\frac{1}{v}} m}{m^\circ} \right) \gamma_{\pm} = (2^2)^{\frac{1}{3}} 0.0150 \times 0.465 = 0.0111$$

P10.12) Calculate the mean ionic molality and mean ionic activity of a 0.150m $Ca(NO_3)_2$ solution for which the mean ionic activity coefficient is 0.165.

$$m_{\pm} = (v_+^{v_+} v_-^{v_-})^{\frac{1}{v}} m = (2^2)^{\frac{1}{3}} 0.150 \text{ mol kg}^{-1} = 0.238 \text{ mol kg}^{-1}$$

$$a_{\pm} = \left(\frac{m_{\pm}}{m^\circ} \right) \gamma_{\pm} = 0.238 \times 0.165 = 0.0393$$

P10.13) In the Debye-Hückel theory, the counter charge in a spherical shell of radius r and thickness dr around the central ion of charge $+q$ is given by $-q\kappa^2 r e^{-\kappa r} dr$. Calculate the most probable value of r , r_{mp} , from this expression. Evaluate r_{mp} for a 0.050m solution of NaCl at $298K$.

$$\frac{d(-q\kappa^2 r e^{-\kappa r})}{dr} = -q\kappa^2 e^{-\kappa r_{mp}} + q\kappa^3 r_{mp} e^{-\kappa r_{mp}} = 0$$

$$-1 + \kappa r_{mp} = 0; \quad r_{mp} = \frac{1}{\kappa}$$

$$\frac{1}{r_{mp}} = 9.211 \times 10^8 \sqrt{\frac{I \text{ mol kg}^{-1}}{\epsilon_r}} \text{ m}^{-1} = 9.211 \times 10^8 \sqrt{\frac{0.050}{78.54}} \text{ m}^{-1} = 2.32 \times 10^7 \text{ m}^{-1}$$

$$r_{mp} = 4.30 \times 10^{-8} \text{ m} = 43.0 \text{ nm}$$

P10.14) Calculate the Debye-Hückel screening length $\frac{1}{\kappa}$ at 298 K in a 0.00100m solution of NaCl.

$$\kappa = 9.211 \times 10^8 \sqrt{\frac{I \text{ mol kg}^{-1}}{\varepsilon_r}} \text{ m}^{-1} = 9.211 \times 10^8 \sqrt{\frac{0.00100}{78.54}} \text{ m}^{-1} = 3.29 \times 10^6 \text{ m}^{-1}$$

$$\frac{1}{\kappa} = 3.04 \times 10^{-7} \text{ m} = 304 \text{ nm}$$

P10.15) Calculate the probability of finding an ion at a distance greater than $\frac{1}{\kappa}$ from the central ion.

$$\int u dv = uv - \int v du$$

$$\text{Let } u = -q\kappa^2 r; \quad dv = e^{-\kappa r} \quad v = -\frac{1}{\kappa} e^{-\kappa r} \quad du = -q\kappa^2 dr$$

$$-\int q\kappa^2 r e^{-\kappa r} dr = q\kappa r e^{-\kappa r} - q\kappa \int e^{-\kappa r} dr = q\kappa r e^{-\kappa r} + qe^{-\kappa r}$$

$$P\left(r > \frac{1}{\kappa}\right) = \frac{\int_{\frac{1}{\kappa}}^{\infty} q\kappa^2 r e^{-\kappa r} dr}{\int_0^{\infty} q\kappa^2 r e^{-\kappa r} dr} = \frac{\left[q\kappa r e^{-\kappa r} + qe^{-\kappa r} \right]_{\frac{1}{\kappa}}^{\infty}}{\left[q\kappa r e^{-\kappa r} + qe^{-\kappa r} \right]_0^{\infty}} = \frac{0 - 2qe^{-1}}{0 - q} = \frac{2}{e} = 0.736$$

P10.16) Using the Debye–Hückel limiting law, calculate the value of γ_{\pm} in $5.0 \times 10^{-3} \text{ m}$ solutions of (a) KCl, (b) Ca(NO₃)₂, and (c) ZnSO₄. Assume complete dissociation.

a) KCl

$$I = \frac{m}{2} (v_+ z_+^2 + v_- z_-^2) = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2)$$

$$I = \frac{1}{2} (0.0050 \text{ mol kg}^{-1} + 0.0050 \text{ mol kg}^{-1}) = 0.0050 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 |z_+ z_-| \sqrt{\frac{I}{\text{mol kg}^{-1}}} = -1.173 \times \sqrt{0.0050} = -0.08294$$

$$\gamma_{\pm} = 0.92$$

b) Ca(NO₃)₂

$$I = \frac{m}{2} (v_+ z_+^2 + v_- z_-^2) = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2)$$

$$I = \frac{1}{2} (0.0050 \text{ mol kg}^{-1} + 2^2 \times 0.0050 \text{ mol kg}^{-1}) = 0.0125 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 |z_+ z_-| \sqrt{\frac{I}{\text{mol kg}^{-1}}} = -1.173 \times 2 \times \sqrt{0.0125} = -0.26229$$

$$\gamma_{\pm} = 0.77$$

c) ZnSO₄

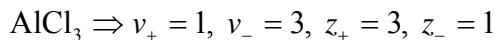
$$I = \frac{m}{2} (v_+ z_+^2 + v_- z_-^2) = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2)$$

$$I = \frac{1}{2} (4 \times 0.0050 \text{ mol kg}^{-1} + 4 \times 0.0050 \text{ mol kg}^{-1}) = 0.020 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 |z_+ z_-| \sqrt{\frac{I}{\text{mol kg}^{-1}}} = -1.173 \times 4 \times \sqrt{0.020} = -0.6635$$

$$\gamma_{\pm} = 0.52$$

P10.17) Calculate I , γ_{\pm} , and a_{\pm} for a 0.0250m solution of AlCl₃ at 298 K. Assume complete dissociation.



$$I = \frac{0.0250}{2} (9 + 3) = 0.1500 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 3 \times \sqrt{0.1500} = -1.3629$$

$$\gamma_{\pm} = 0.2559$$

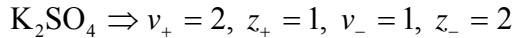
$$a_{\pm} = \left(\frac{m_{\pm}}{m^{\circ}} \right) \gamma_{\pm}$$

$$m_{\pm}^4 = (0.025) (0.025 \times 3)^3 = 1.0546875 \times 10^{-5}$$

$$m_{\pm} = 0.05699 \text{ mol kg}^{-1}$$

$$a_{\pm} = 0.05699 \times 0.2559 = 0.0146$$

P10.18) Calculate I , γ_{\pm} , and a_{\pm} for a 0.0250m solution of K₂SO₄ at 298 K. Assume complete dissociation. How confident are you that your calculated results will agree with experimental results?



$$I = \frac{0.0250}{2} (2 + 4) = 0.0750 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 2 \times \sqrt{0.0750} = -0.6425$$

$$\gamma_{\pm} = 0.523$$

$$a_{\pm} = \left(\frac{m_{\pm}}{m^{\circ}} \right) \gamma_{\pm}$$

$$m_{\pm}^3 = (0.050)^2 (0.0250) = 6.25 \times 10^{-5}$$

$$m_{\pm} = 0.03969 \text{ mol kg}^{-1}$$

$$a_{\pm} = 0.03969 \times 0.5260 = 0.0209$$

Not very confident. Figures 10.5 and 10.6 show significant deviations from predicted behavior for $I > 0.01 \text{ mol kg}^{-1}$.

P10.19) Calculate I , γ_{\pm} , and a_{\pm} for a $0.0325m$ solution of $\text{K}_4\text{Fe}(\text{CN})_6$ at 298 K.

$$I = \frac{m}{2} (v_+ z_+^2 + v_- z_-^2) = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2)$$

$$I = \frac{1}{2} (4 \times 0.0325 \text{ mol kg}^{-1} + 4^2 \times 0.0325 \text{ mol kg}^{-1}) = 0.325 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 |z_+ z_-| \sqrt{\frac{I}{\text{mol kg}^{-1}}} = -1.173 \times 4 \times \sqrt{0.325} = -2.6749$$

$$\gamma_{\pm} = 0.069$$

$$m_{\pm} = (v_+^{v_+} v_-^{v_-})^{\frac{1}{v}} m = (4^4)^{\frac{1}{5}} \times 0.0325 \text{ mol kg}^{-1} = 0.099 \text{ mol kg}^{-1}$$

$$a_{\pm} = \left(\frac{m_{\pm}}{m^{\circ}} \right) \gamma_{\pm} = 0.099 \times 0.069 = 0.0068$$

Not very confident. Figures 10.5 and 10.6 show significant deviations from predicted behavior for $I > 0.01 \text{ mol kg}^{-1}$.

P10.20) Calculate the solubility of BaSO_4 ($K_{sp} = 1.08 \times 10^{-10}$) (a) in pure H_2O and (b) in an aqueous solution with $I = 0.0010 \text{ mol kg}^{-1}$.



$$\nu_+ = 1, \quad \nu_- = 1$$

$$z_+ = 2, \quad z_- = 2$$

$$K_{sp} = \left(\frac{c_{\text{Ba}^{2+}}}{c^\circ} \right) \left(\frac{c_{\text{SO}_4^{2-}}}{c^\circ} \right) \gamma_\pm^2 = 1.08 \times 10^{-10}$$

$$c_{\text{Ba}^{2+}} = c_{\text{SO}_4^{2-}}$$

$$K_{sp} = \left(\frac{C_{\text{Ba}^{2+}}}{C^\circ} \right)^2 \gamma_\pm^2 = 1.08 \times 10^{-10}$$

$$\text{when } \gamma_\pm = 1 \quad c_{\text{Ba}^{2+}} = 1.039 \times 10^{-5} \text{ mol L}^{-1}$$

$$\begin{aligned} I &= \frac{m}{2} \sum (\nu_+ z_+^2 + \nu_- z_-^2) \\ &= \frac{1.039 \times 10^{-5}}{2} \times (4 + 4) = 4.157 \times 10^{-5} \text{ mol kg}^{-1} \end{aligned}$$

$$\ln \gamma_\pm = -1.173 \times 4 \times \sqrt{4.157 \times 10^{-5}} = -0.03025$$

$$\gamma_\pm = 0.97020$$

$$\text{when } \gamma_\pm = 0.970230 \quad c_{\text{Ba}^{2+}} = 1.0711 \times 10^{-5} \text{ mol L}^{-1}$$

$$I = \frac{1.0711 \times 10^{-5}}{2} \times (8) = 4.2846 \times 10^{-5} \text{ mol kg}^{-1}$$

$$\ln \gamma_\pm = -1.173 \times 4 \times \sqrt{4.2846 \times 10^{-5}} = -0.03071$$

$$\gamma_\pm = 0.9698$$

$$\text{when } \gamma_\pm = 0.9698 \quad c_{\text{Ba}^{2+}} = 1.0716 \times 10^{-5} \text{ mole L}^{-1}$$

$$I = \frac{1.0716 \times 10^{-5}}{2} \times (8) = 4.2866 \times 10^{-5} \text{ mol kg}^{-1}$$

$$\ln \gamma_\pm = -1.173 \times 4 \times \sqrt{4.2866 \times 10^{-5}} = -0.03072$$

$$\gamma_\pm = 0.9697$$

$$\text{solubility} = 1.07 \times 10^{-5} \text{ mol L}^{-1}$$

b) $I = 0.0010 \text{ mol kg}^{-1}$

$$\ln \gamma_{\pm} = 1.173 \times 4 \times \sqrt{0.0010} = -0.148374$$

$$\gamma_{\pm} = 0.8621$$

$$K_{sp} = \left(\frac{c_{Ba^{2+}}}{c^{\circ}} \right)^2 \times (0.8621)^2 = 1.08 \times 10^{-10}$$

$$c_{Ba^{2+}} = 1.21 \times 10^{-5} \text{ mol kg}^{-1}$$

The relative error is 20%. There is no need for a further iteration because the ionic strength in the solution is not influenced by the dissociation of the BaSO₄.

P10.21) Dichloroacetic acid has a dissociation constant of $K_a = 3.32 \times 10^{-2}$. Calculate the degree of dissociation for a 0.125*m* solution of this acid (a) using the Debye–Hückel limiting law and (b) assuming that the mean ionic activity coefficient is one.

a) We first consider the case when γ is given by the Debye–Hückel limiting law. The ionic strength is given by

$$I = \frac{m}{2}(2) = m = 0.04992 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.04992} = -0.2621$$

$$\gamma_{\pm} = 0.7694$$

We recalculate the ionic strength and iterate several times.

$$I = \frac{m}{2}(2) = m = 0.04992 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.04992} = -0.2621$$

$$\gamma_{\pm} = 0.7694$$

$$\text{when } \gamma_{\pm} = 0.7694, \frac{m^2 \gamma_{\pm}^2}{0.125 - m} = 3.32 \times 10^{-2}$$

$$m^2 = 7.0097 \times 10^{-3} - 0.05608 \text{ m}$$

$$m^2 + 0.05608 \text{ m} - 7.0097 \times 10^{-3} = 0$$

$$m = \frac{-0.05608 \pm \sqrt{(0.05608)^2 - 4(1)(-7.0097 \times 10^{-3})}}{2} = 0.06025 \text{ mol kg}^{-1}$$

$$I = 0.06025 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.06025} = -0.2879$$

$$\gamma_{\pm} = 0.7498$$

when $\gamma_{\pm} = 0.7498$

$$\frac{m^2}{0.125 - m} = 0.05905$$

$$m^2 + 0.05905 m - 7.3815 \times 10^{-3} = 0$$

$$m = \frac{-0.05905 \pm \sqrt{(0.05905)^2 - 4(1)(-7.3815 \times 10^{-3})}}{2} = 0.06132 \text{ mol kg}^{-1}$$

$$I = 0.06132 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = 0.7479$$

$$\gamma_{\pm} = 0.7479$$

when $\gamma_{\pm} = 0.7479$

$$\frac{m^2}{0.125 - m} = 0.05935$$

$$m^2 + 0.05935 m - 7.4191 \times 10^{-3} = 0$$

$$m = \frac{-0.05935 \pm \sqrt{(0.05935)^2 - 4(1)(-7.4191 \times 10^{-3})}}{2} = 0.06143 \text{ mol kg}^{-1}$$

$$I = 0.06143 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -0.2907$$

$$\gamma_{\pm} = 0.7477$$

when $\gamma_{\pm} = 0.7477$

$$\frac{m^2}{0.125 - m} = 0.05938$$

$$m^2 + 0.05938 m - 7.4228 \times 10^{-3} = 0$$

$$m = \frac{-0.05938 \pm \sqrt{(0.05938)^2 - 4(1)(-7.4228 \times 10^{-3})}}{2} = 0.06144 \text{ mol kg}^{-1}$$

This is a sufficiently good result, and we calculate the degree of dissociation to be

$$\frac{0.06144}{0.125} \times 100\% = 49\%$$

b) $\gamma_{\pm} = 1$

$$m^2 = 4.15 \times 10^{-3} - 3.32 \times 10^{-2} \text{ m}$$

$$m^2 + 3.32 \times 10^{-2} \text{ m} - 4.15 \times 10^{-3} = 0$$

$$m = \frac{-3.32 \times 10^{-2} \pm \sqrt{(3.32 \times 10^{-2})^2 - 4(1)(-4.15 \times 10^{-3})}}{2} = 0.04992 \text{ mol kg}^{-1}$$

$$\frac{0.04992}{0.125} \times 100\% = 40\%$$

This result is 20% smaller than that calculated using the Debye–Hückel limiting law.

P10.22) Chloroacetic acid has a dissociation constant of $K_a = 1.38 \times 10^{-3}$. a) Calculate the degree of dissociation for a 0.0825m solution of this acid using the Debye–Hückel limiting law. b) Calculate the degree of dissociation for a 0.0825m solution of this acid that is also 0.022m in KCl using the Debye–Hückel limiting law.

a) $K_a = 1.38 \times 10^{-3}$
 0.0825 m

$$K_a = \frac{(m_+ \gamma_+)(m_- \gamma_-)}{m} = \frac{m^2 \gamma_\pm^2}{0.0825 - m} = 1.38 \times 10^{-3}$$

when $\gamma_\pm = 1$

$$m^2 = 1.1385 \times 10^{-4} - 1.38 \times 10^{-3} \text{ m}$$

$$m^2 + 1.38 \times 10^{-3} \text{ m} - 1.1385 \times 10^{-4} = 0$$

$$m = \frac{-1.38 \times 10^{-3} \pm \sqrt{(1.38 \times 10^{-3})^2 - 4(1)(-1.1385 \times 10^{-4})}}{2} = 0.0100 \text{ mol kg}^{-1}$$

$$I = \frac{m}{2}(2) = m = 0.0100 \text{ mol kg}^{-1}$$

$$\ln \gamma_\pm = -1.173 \times 1 \times \sqrt{0.0100} = -0.1173$$

$$\gamma_\pm = 0.8893$$

when $\gamma_\pm = 0.8893$

$$m^2 = 1.43956 \times 10^{-4} - 1.7449 \times 10^{-3} \text{ m}$$

$$m^2 + 1.7449 \times 10^{-3} \text{ m} - 1.43956 \times 10^{-4} = 0$$

$$m = \frac{-1.7449 \times 10^{-3} \pm \sqrt{(1.7449 \times 10^{-3})^2 - 4(1)(-1.43956 \times 10^{-4})}}{2} = 0.0112 \text{ mol kg}^{-1}$$

$$I = \frac{m}{2}(2) = m = 0.0112 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.0112} = -0.1239$$

$$\gamma_{\pm} = 0.8835$$

when $\gamma_{\pm} = 0.8835$

$$m^2 = 1.4587 \times 10^{-4} - 1.7681 \times 10^{-3} \text{ m}$$

$$m^2 + 1.7681 \times 10^{-3} \text{ m} - 1.4587 \times 10^{-4} = 0$$

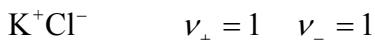
$$m = \frac{-1.7681 \times 10^{-3} \pm \sqrt{(1.7681 \times 10^{-3})^2 - 4(1)(-1.4587 \times 10^{-4})}}{2} = 0.0112 \text{ mol kg}^{-1}$$

$$I = 0.0112 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.0112} = -0.1239$$

$$\text{The degree of dissociation is } \frac{0.0112}{0.0825} \times 100\% = 13.6\%$$

b)



$$z_+ = 1 \quad z_- = 1$$

$I = 0.022 \text{ mol kg}^{-1}$ from the KCl alone.

We first calculate the activity coefficient using this value.

$$I = \frac{0.022}{2}(+1) = 0.022 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.022} = -0.1740$$

$$\gamma_{\pm} = 0.8403$$

We next calculate the concentration of the ions produced through the dissociation of the acid in the solution.

$$\frac{m^2 (0.8403)^2}{0.0825 - m} = 1.38 \times 10^{-3}$$

$$\frac{m^2}{0.0825 - m} = 1.9544 \times 10^{-3}$$

$$m^2 = 1.6124 \times 10^{-4} - 1.9544 \times 10^{-3} m$$

$$m^2 = 1.9544 \times 10^{-3} m - 1.6124 \times 10^{-4} = 0$$

$$m = \frac{-1.9544 \times 10^{-3} \pm \sqrt{(1.9544 \times 10^{-3})^2 - 4(1)(-1.6124 \times 10^{-4})}}{2} = 0.01176 \text{ mol kg}^{-1}$$

The ionic strength is the sum of that due to the chloroacetic acid and the KCl or
 $I = 0.022 + 0.012 = 0.034 \text{ mol kg}^{-1}$.

We recalculate γ_{\pm} using this value for the ionic strength.

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.034} = -0.2163$$

$$\gamma_{\pm} = 0.8055$$

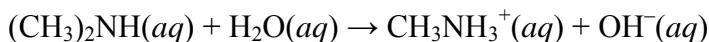
and recalculate m

$$\frac{m^2 (0.8055)^2}{0.0825 - m} = 1.38 \times 10^{-3} \text{ giving}$$

$$m = 0.01222 \text{ mol kg}^{-1}$$

Given the fact that the concentration of KCl is only known to 2 significant figures, this value of m is sufficiently close to the previous value that a further iteration is not necessary. The degree of dissociation is $\frac{0.01222}{0.0825} = 14.8\%$.

P10.23) The equilibrium constant for the hydrolysis of dimethylamine



is 5.12×10^{-4} . Calculate the extent of hydrolysis for (a) a $0.125m$ solution of $(CH_3)_2NH$ in water and (b) a solution that is also $0.045m$ in $NaNO_3$.



$$K = \frac{m^2 \gamma_{\pm}^2}{0.125 - m} = 5.12 \times 10^{-4}$$

if $\gamma_{\pm} = 1$,

$$m = 7.75 \times 10^{-3} \text{ mol kg}^{-1}$$

when $\gamma_{\pm} = 1$

$$I = \frac{m}{2}(2) = m = 7.75 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{7.75 \times 10^{-3}} = -0.1033$$

$$\gamma_{\pm} = 0.9019$$

when $\gamma_{\pm} = 0.9019$

$$m = 8.561 \times 10^{-3} \text{ mol kg}^{-1}$$

$$I = m = 8.561 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -0.1085$$

$$\gamma_{\pm} = 0.8971$$

when $\gamma_{\pm} = 0.8971$

$$m = 8.605 \times 10^{-3} \text{ mol kg}^{-1}$$

$$I = m = 8.605 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -0.1088$$

$$\gamma_{\pm} = 0.8969$$

when $\gamma_{\pm} = 0.8969$

$$m = 8.61 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\frac{8.61 \times 10^{-3}}{0.125} \times 100\% = 6.89\%$$

b) NaNO_3



$$I = \frac{0.045}{2}(1+1) = 0.045 \text{ mol kg}^{-1}$$

Add to this the ionic strength from part a).

$$I_{total} = 0.045 + 8.605 \times 10^{-3} = 0.0536 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.0536} = -0.2716$$

$$\gamma_{\pm} = 0.7622$$

$$K = \frac{(m)^2 (\gamma_{\pm})^2}{0.125} = \frac{(m)^2 (0.7622)^2}{0.125} = 5.12 \times 10^{-4}$$

$$m = 0.01006 \text{ mol kg}^{-1}$$

Carrying out another iteration

$$I_{total} = 0.045 + .01006 = 0.0551 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.0551} = -0.2753$$

$$\gamma_{\pm} = 0.7593$$

$$K = \frac{(m)^2 (\gamma_{\pm})^2}{0.125} = \frac{(m)^2 (0.7593)^2}{0.125} = 5.12 \times 10^{-4}$$

$$m = 0.01010 \text{ mol kg}^{-1}$$

The degree of dissociation is

$$\frac{0.01010}{0.125} \times 100\% = 8.08\%$$

P10.24) From the data in Table 10.3 (see Appendix A, Data Tables), calculate the activity of the electrolyte in 0.100*m* solutions of

- a. KCl b. H₂SO₄ c. MgCl₂

a) KCl 0.100 m $\gamma_{\pm} = 0.770$

$$a_{\pm} = \left(\frac{m_{\pm}}{m^{\circ}} \right) \gamma_{\pm} \quad m_{\pm}^{\nu} = m_{+}^{\nu} m_{-}^{\nu}$$

$$m_{\pm}^2 = (0.100)(0.100) \quad m_{\pm} = 0.100 \text{ mol kg}^{-1}$$

$$a_{\pm} = (0.100)(0.770) = 0.0770$$

b) H₂SO₄ 0.100 m $\gamma_{\pm} = 0.2655$

$$m_{\pm}^3 = (2 \times 0.100)^2 (0.100)^1 = 4.0 \times 10^{-3}$$

$$m_{\pm} = 0.15874 \text{ mol kg}^{-1}$$

$$a_{\pm} = (0.15874) \times (0.2655) = 0.0422$$

c) MgCl₂ 0.100 m $\gamma_{\pm} = 0.529$

$$m_{\pm}^3 = (0.100)(2 \times 0.100)^2 = 4.0 \times 10^{-3}$$

$$m_{\pm} = 0.15874 \text{ mol kg}^{-1}$$

$$a_{\pm} = (0.15874) \times (0.529) = 0.0840$$

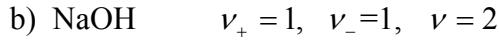
P10.25) Calculate the mean ionic molality, m_{\pm} , in 0.0500*m* solutions of (a) Ca(NO₃)₂, (b) NaOH, (c) MgSO₄, and (d) AlCl₃.

$$m_{\pm}^{\nu} = m_+^{\nu_+} m_-^{\nu_-}$$



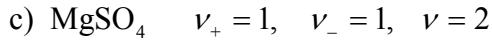
$$m_{\pm}^3 = (0.0500)(0.0500 \times 2)^2 = 5.00 \times 10^{-4}$$

$$m_{\pm} = 0.0794 \text{ mol kg}^{-1}$$



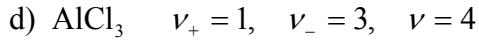
$$m_{\pm}^2 = (0.0500)(0.0500)$$

$$m_{\pm} = 0.0500 \text{ mol kg}^{-1}$$



$$m_{\pm}^2 = (0.0500)(0.0500)$$

$$m_{\pm} = 0.0500 \text{ mol kg}^{-1}$$



$$m_{\pm}^4 = (0.0500)(0.0500 \times 3)^3 = 1.6875 \times 10^{-4}$$

$$m_{\pm} = 0.1140 \text{ mol kg}^{-1}$$

P10.26) Calculate the ionic strength of each of the solutions in Problem P10.26.

$$I = \frac{m}{2} (\nu + z_+^2 + \nu_- z_-^2)$$

for $\text{Ca}(\text{NO}_3)_2$

$$I = \frac{0.0500}{2} (1 \times 2^2 + 2 \times 1^2) = 0.150 \text{ mol kg}^{-1}$$

for NaOH

$$I = \frac{0.0500}{2} (1 + 1) = 0.0500 \text{ mol kg}^{-1}$$

for MgSO_4

$$I = \frac{0.0500}{2} (1 \times 2^2 + 1 \times 2^2) = 0.200 \text{ mol kg}^{-1}$$

for AlCl_3

$$I = \frac{0.05}{2} (1 \times 3^2 + 3 \times 1^2) = 0.300 \text{ mol kg}^{-1}$$

P10.27) At 25°C, the equilibrium constant for the dissociation of acetic acid, K_a , is 1.75×10^{-5} . Using the Debye–Hückel limiting law, calculate the degree of dissociation in 0.100m and 1.00m solutions. Compare these values with what you would obtain if the ionic interactions had been ignored.



For 0.100 m

$$\frac{m^2 \gamma_{\pm}^2}{0.100 - m} = 1.75 \times 10^{-5}$$

when $\gamma_{\pm} = 1$

$$m = 1.314 \times 10^{-3} \text{ mol kg}^{-1}$$

$$I = \frac{m}{2} (2) = m = 1.314 \times 10^{-3}$$

$$\ln \gamma_{\pm} - 1.173 \times 1 \times \sqrt{1.314 \times 10^{-3}} = -0.04252$$

$$\gamma_{\pm} = 0.9584$$

when $\gamma_{\pm} = 0.9584$

$$m = 1.38056 \times 10^{-3} \text{ mol kg}^{-1}$$

$$I = m = 1.371 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -0.04343$$

$$\gamma_{\pm} = 0.9575$$

when $\gamma_{\pm} = 0.9575$

$$m = 1.372 \times 10^{-3} \text{ mol kg}^{-1}$$

$$I = m = 1.372 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -0.04345$$

$$\gamma_{\pm} = 0.9575$$

This result has converged sufficiently to calculate the degree of dissociation.

$$m = 1.372 \times 10^{-3}$$

$$\frac{1.372 \times 10^{-3}}{0.100} \times 100\% = 1.37\%$$

for 1.00 m

$$\frac{m^2 \gamma_{\pm}^2}{1.00} = 1.75 \times 10^{-5}$$

$$m^2 \gamma_{\pm}^2 = 1.75 \times 10^{-5}$$

$$m \gamma_{\pm} = 4.1833 \times 10^{-3}$$

when $\gamma_{\pm} = 1$

$$m = 4.1833 \times 10^{-3} \text{ mol kg}^{-1}$$

$$I = m = 4.1833 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -0.07587$$

$$\gamma_{\pm} = 0.9269$$

when $\gamma_{\pm} = 0.9269$

$$m = 4.5130 \times 10^{-3} \text{ mol kg}^{-1}$$

$$I = m = 4.5130 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -0.07880$$

$$\gamma_{\pm} = 0.9242$$

when $\gamma_{\pm} = 0.9242$

$$m = 4.5263 \times 10^{-3} \text{ mol kg}^{-1}$$

$$I = m = 4.5263 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -0.07892$$

$$\gamma_{\pm} = 0.9241$$

when $\gamma_{\pm} = 0.9241$

$$m = 4.5268 \times 10^{-3} \text{ mol kg}^{-1}$$

$$I = m = 4.5268 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -0.07892$$

$$\gamma_{\pm} = 0.9241$$

$$\frac{4.5268 \times 10^{-3}}{1.0} \times 100\% = 0.453\%$$

If ionic interactions are ignored

For 0.100 m

$$\frac{m^2}{0.100 - m} = 1.75 \times 10^{-5}$$

$$m = \sqrt{1.75 \times 10^{-5}} = 1.314 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\frac{1.314 \times 10^{-3}}{0.100} \times 100\% = 1.31\%$$

for 1.00 m

$$\frac{m^2}{0.10} = 1.75 \times 10^{-5}$$

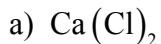
$$m = \sqrt{1.75 \times 10^{-5}} = 4.1833 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\frac{4.1833 \times 10^{-3}}{0.10} \times 100\% = 0.418\%$$

P10.28) Estimate the degree of dissociation of a 0.100*m* solution of acetic acid ($K_a = 1.75 \times 10^{-5}$), which is also 0.500*m* in the strong electrolyte given in parts a–c. Use the data tables to obtain γ_{\pm} , as the electrolyte concentration is too high to use the Debye–Hückel limiting law.



In each case, the activity of the ions produced in the dissociation of acetic acid is determined by the strong electrolyte.



From Table 10.3, $\gamma_{\pm} = 0.448$

$$1.75 \times 10^{-5} = \frac{\gamma_{\pm}^2 m^2}{0.100 - m} = \frac{(0.448)^2 m^2}{0.100 - m}$$

$$m = 0.002910 \text{ mol kg}^{-1}$$

$$\frac{0.002910}{0.100} \times 100\% = 2.91\%$$

b) KCl $\nu_+ = 1$, $\nu_- = 1$, $z_+ = 1$, $z_- = 1$

From Table 10.3, $\gamma_{\pm} = 0.649$

$$1.75 \times 10^{-5} = \frac{(0.649)^2 m^2}{0.100 - m}$$

$$m = 2.018 \times 10^{-3} \text{ mol kg}^{-1}$$

$$\frac{2.018 \times 10^{-3}}{0.100} \times 100\% = 2.02\%$$

c) MgSO₄ $\nu_+ = 1$, $\nu_- = 1$

$z_+ = 2$, $z_- = 2$

From Table 10.3, $\gamma_{\pm} = 0.0675$

$$1.75 \times 10^{-5} = \frac{\gamma_{\pm}^2 m^2}{0.100 - m} = \frac{(0.0675)^2 m^2}{0.100 - m}$$

$$m = 0.01777 \text{ mol kg}^{-1}$$

$$\frac{0.01777}{0.100} \times 100\% = 17.7\%$$

Questions on Concepts

Q11.1) What is the difference in the chemical potential and the electrochemical potential for an ion and for a neutral species in solution? Under what conditions is the electrochemical potential equal to the chemical potential for an ion?

$\tilde{\mu} = \mu + z\phi$. For a neutral species, the chemical potential and electrochemical potential have the same value. They differ by $z\phi$ for an ion. The electrochemical potential is equal to the chemical potential for an ion if $\phi = 0$.

Q11.2) Show that it follows from $\Delta G_f^\circ(H^+, aq) = 0$ for all T that the potential of the standard hydrogen electrode is zero.

$$\phi_{H^+/H_2}^\circ = \frac{\mu_{H^+}^\circ - \frac{1}{2}\mu_{H_2}^\circ}{F} = -\frac{\mu_{H^+}^\circ}{F} \text{ and } \mu_{H^+}^\circ = \Delta G_f^\circ(H^+, aq) = 0$$

Q11.3) To determine standard cell potentials, measurements are carried out in very dilute solutions rather than at unit activity. Why is this the case?

In order to determine the standard potential, the mean ionic activity must be known. It can be calculated in dilute solutions using the Debye-Hückel limiting law, but there is no reliable way to calculate the activity coefficient near unit activity.

Q11.4) Explain why it is possible that the magnitude of the maximum work available from a battery can be greater than the magnitude of the reaction enthalpy of the overall cell reaction.

$$|w_{electrical}| = |-ΔG| = \left| -ΔH \left(1 - \frac{TΔS}{ΔH} \right) \right| > |-ΔH| \text{ if } ΔS < 0$$

Q11.5) The temperature dependence of the potential of a cell is vanishingly small. What does this tell you about the thermodynamics of the cell reaction?

$$\text{Because } ΔS_R^\circ = - \left(\frac{\partial ΔG_R^\circ}{\partial T} \right)_P = nF \left(\frac{\partial E^\circ}{\partial T} \right)_P, ΔS_R^\circ \approx 0$$

Q11.6) Why is the capacitance of an electrolytic capacitor so high compared with conventional capacitors?

The positive and negative plates of an electrolytic capacitor are separated by an extremely small distance (the thickness of the electrical double layer, essentially). And so, the electric field is very strong and the capacitance large. $\left(\frac{\epsilon A}{d}, d \ll 30 \text{ \AA} \right)$

Q11.7) Can specifically adsorbed ions in the electrochemical double layer influence electrode reactions?

Yes, specifically adsorbed ions can play a central role in the atomic-scale processes occurring on an electrode surface (e.g. Cl^- on Cu electrode).

Q11.8) How can one conclude from Figure 11.18 that Cu atoms can diffuse rapidly over a well-ordered Au electrode in an electrochemical cell?

The copper atoms would be dispersed randomly over the Au surface if they could not diffuse laterally. Instead, they are seen only in islands and on edges, where they are tightly bound. They must have diffused there freely over the surface.

Q11.9) How is it possible to deposit Cu on a Au electrode at a potential lower than that corresponding to the reaction $\text{Cu}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Cu}(s)$?

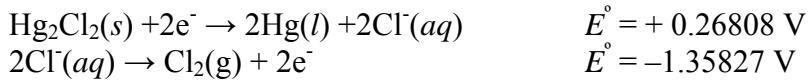
Cu^{2+} is more tightly bound to the Au surface than to Cu. Thus a lower potential is needed to reduce Cu^{2+} onto the Au surface.

Q11.10) Why is it possible to achieve high-resolution electrochemical machining by applying a voltage pulse rather than a dc voltage to the electrode being machined?

For a tool that is very close to a surface, the RC time constant for charging the double layer depends strongly on location. Thus, pulsed voltage charges will charge the layer in those locations where the tool is closest to the surface – allowing subsequent electrochemical reaction – but not in other locations. Therefore, the reactions are localized. This gives the high spatial selectivity needed for nanomachining.

Problems

P11.1) Calculate $\Delta G_{\text{reaction}}^\circ$ and the equilibrium constant at 298.15 K for the reaction $\text{Hg}_2\text{Cl}_2(s) \rightarrow 2\text{Hg}(l) + \text{Cl}_2(g)$.



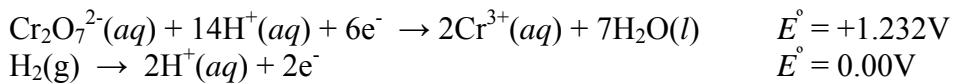
$$\Delta G_{reaction}^{\circ} = -nFE^{\circ} = -2 \times 96485 \text{ C mol}^{-1} \times 1.09019 \text{ V} = 210.4 \text{ kJ mol}^{-1}$$

$$\ln K = \frac{nF}{RT} E^{\circ} = -\frac{2 \times 96485 \text{ C mol}^{-1} \times 1.09019 \text{ V}}{8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298.15 \text{ K}}$$

$$= -85.002$$

$$K = 1.21 \times 10^{-37}$$

P11.2) Calculate ΔG_r° and the equilibrium constant at 298.15 K for the reaction $\text{Cr}_2\text{O}_7^{2-}(aq) + 3\text{H}_2(g) + 8\text{H}^+(aq) \rightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}(l)$.



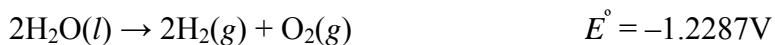
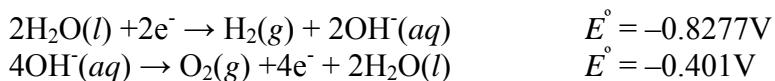
$$\Delta G_{reaction}^{\circ} = -nFE^{\circ} = -6 \times 96485 \text{ C mol}^{-1} \times 1.232 \text{ V} = -713.2 \text{ kJ mol}^{-1}$$

$$\ln K = \frac{nF}{RT} E^{\circ} = \frac{6 \times 96485 \text{ C mol}^{-1} \times 1.232 \text{ V}}{8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298.15 \text{ K}}$$

$$= 287.7$$

$$K = 9.06 \times 10^{124}$$

P11.3) Using half-cell potentials, calculate the equilibrium constant at 298.15 K for the reaction $2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g)$. Compare your answer with that calculated using the ΔG_f° in the data tables from Appendix A. What is the value of E° for the overall reaction that makes the two methods agree exactly?



$$\ln K = \frac{nF}{RT} E^\circ = -\frac{4 \times 96485 \text{ C mol}^{-1} \times 1.2287 \text{ V}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \\ = -191.303$$

$$K = 8.28 \times 10^{-84}$$

$$\ln K = -\frac{2\Delta G_f^\circ (\text{H}_2\text{O}, l)}{RT} = -\frac{2 \text{ mol} \times 237.1 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} = -191.301$$

$$K = 8.30 \times 10^{-84}$$

For the two results to agree, E° must be given by

$$E^\circ = -\frac{191.325 \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}}{4 \times 96485 \text{ C mol}^{-1}} = -1.22869 \text{ V}$$

This value lies within the error limits of the determination of E° .

P11.4) For the half-cell reaction $\text{AgBr}(s) + e^- \rightarrow \text{Ag}(s) + \text{Br}^-(aq)$, $E^\circ = +0.0713 \text{ V}$.

Using this result and $\Delta G_f^\circ(\text{AgBr}, s) = -96.9 \text{ kJ mol}^{-1}$, determine $\Delta G_f^\circ(\text{Br}^-, aq)$.

$$\Delta G_R^\circ = -nFE^\circ = \Delta G_f^\circ(\text{Br}^-, aq) - \Delta G_f^\circ(\text{AgBr}, s)$$

$$\Delta G_f^\circ(\text{Br}^-, aq) = \Delta G_f^\circ(\text{AgBr}, s) - nFE^\circ$$

$$\Delta G_f^\circ(\text{Br}^-, aq) = -96.9 \text{ kJ mol}^{-1} - 1 \text{ mol} \times 96485 \text{ C mol}^{-1} \times 0.0713 \text{ V} = -103.8 \text{ kJ mol}^{-1}$$

P11.5) For the half cell reaction $\text{Hg}_2\text{Cl}_2(s) + 2e^- \rightarrow 2\text{Hg}(l) + 2\text{Cl}^-(aq)$, $E^\circ = +0.26808 \text{ V}$.

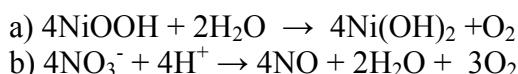
Using this result and the data tables from Appendix A, determine $\Delta G_f^\circ(\text{Cl}^-, aq)$.

$$\Delta G_R^\circ = -nFE^\circ = 2\Delta G_f^\circ(\text{Cl}^-, aq) - \Delta G_f^\circ(\text{Hg}_2\text{Cl}_2, s)$$

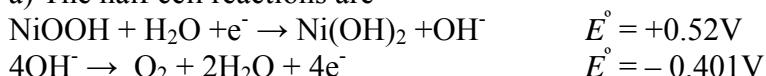
$$\Delta G_f^\circ(\text{Cl}^-, aq) = \frac{-\Delta G_f^\circ(\text{Hg}_2\text{Cl}_2, s) - nFE^\circ}{2}$$

$$\Delta G_f^\circ(\text{Cl}^-, aq) = \frac{-210.7 \text{ kJ mol}^{-1} - 2 \text{ mol} \times 96485 \text{ C mol}^{-1} \times 0.26808 \text{ V}}{2} = -131.2 \text{ kJ mol}^{-1}$$

P11.6) By finding appropriate half-cell reactions, calculate the equilibrium constant at 298.15 K for the following reactions:



a) The half cell reactions are

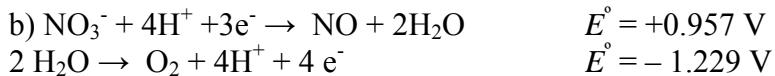


The overall reaction is

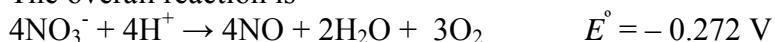


$$\ln K = \frac{nF}{RT} E^\circ = \frac{4 \times 96485 \text{ C mol}^{-1} \times 0.12 \text{ V}}{8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298.15 \text{ K}} \\ = 18.683$$

$$K = 1.30 \times 10^8$$



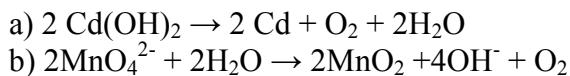
The overall reaction is



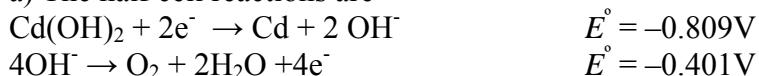
$$\ln K = \frac{nF}{RT} E^\circ = -\frac{12 \times 96485 \text{ C mol}^{-1} \times 0.272 \text{ V}}{8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298.15 \text{ K}} \\ = -127.047$$

$$K = 6.67 \times 10^{-56}$$

P11.7) By finding appropriate half-cell reactions, calculate the equilibrium constant at 298.15 K for the following reactions:



a) The half cell reactions are



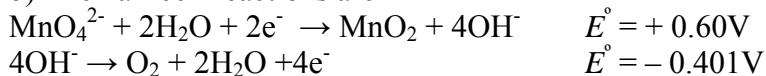
The overall reaction is



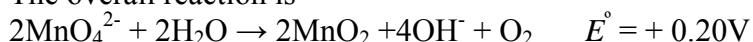
$$\ln K = \frac{nF}{RT} E^\circ = -\frac{4 \times 96485 \text{ C mol}^{-1} \times 1.21\text{V}}{8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298.15 \text{ K}} \\ = -188.391$$

$$K = 1.52 \times 10^{-82}$$

b) The half cell reactions are



The overall reaction is



$$\ln K = \frac{nF}{RT} E^\circ = \frac{4 \times 96485 \text{ C mol}^{-1} \times 0.20 \text{ V}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}$$

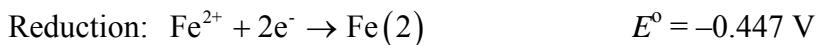
$$= 31.139$$

$$K = 3.34 \times 10^{13}$$

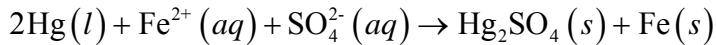
P11.8) Consider the cell $\text{Hg}(l) \mid \text{Hg}_2\text{SO}_4(s) \mid \text{FeSO}_4(aq, a = 0.01000) \mid \text{Fe}(s)$.

a. Write the cell reaction.

b. Calculate the cell potential, the equilibrium constant for the cell reaction, and $\Delta G_{reaction}^\circ$ at 25°C.



Cell reaction:



$$E_{cell}^\circ = -0.6125 + (-0.447) = -1.0595 \text{ V}$$

$$E_{cell} = E_{cell}^\circ - \frac{RT}{nF} \ln \left(\frac{1}{a_{\text{Fe}^{2+}} a_{\text{SO}_4^{2-}}} \right)$$

$$= -1.0595 - \frac{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298.15 \text{ K})}{2 \times (96,485 \text{ C mol}^{-1})} \ln \left(1 / (0.01)^2 \right)$$

$$= -1.178 \text{ V}$$

$$\Delta G_{reaction}^\circ = -nFE^\circ = (-2)(96,485 \text{ C mol}^{-1})(-1.0595 \text{ V})$$

$$= 204.5 \text{ kJ mol}^{-1}$$

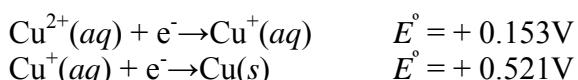
$$K = e^{-\Delta G_{reaction}^\circ / RT} = 1.49 \times 10^{-36}$$

P11.9) Determine the half-cell reactions and the overall cell reaction, calculate the cell potential, and determine the equilibrium constant at 298.15 K for the cell



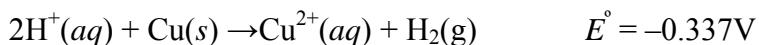
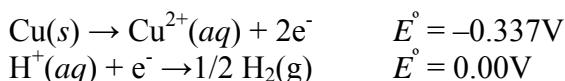
Is the cell reaction spontaneous as written?

We first calculate the E° for the reaction $\text{Cu}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Cu}(s)$ from the tabulated values for the reactions $\text{Cu}^{2+}(aq) + \text{e}^- \rightarrow \text{Cu}^+(aq)$ and $\text{Cu}^+(aq) + \text{e}^- \rightarrow \text{Cu}(s)$ in the data tables.



As in Example Problem 11.3, n_1 electrons are transferred in the reaction with the potential $E_{A/B}^\circ$, and n_2 electrons are transferred in the reaction with the potential $E_{B/C}^\circ$. If n_3 electrons are transferred in the reaction with the potential $E_{A/C}^\circ$, then
 $n_3 E_{A/C}^\circ = n_1 E_{A/B}^\circ + n_2 E_{B/C}^\circ$. Therefore

$$\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s) \quad E^\circ = \frac{0.153V + 0.521V}{2} = 0.337V$$



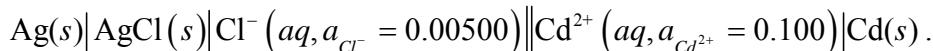
$$E = E^\circ - \frac{RT}{2F} \ln \frac{a_{H^+}^2}{a_{\text{Cu}^{2+}}} = -0.337V - \frac{0.05916}{2} \log_{10} \frac{0.0150}{(0.100)^2} V = -0.342V$$

$$\begin{aligned} \ln K &= \frac{nF}{RT} E^\circ = \frac{2 \times 96485 \text{ C mol}^{-1} \times (-0.337 \text{ V})}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \\ &= -26.235 \end{aligned}$$

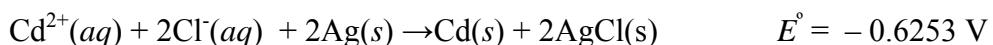
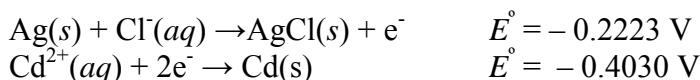
$$K = 4.04 \times 10^{-12}$$

The reaction is not spontaneous as written because $Q \gg K$ and $E < 0$.

P11.10) Determine the half-cell reactions and the overall cell reaction, calculate the cell potential and determine the equilibrium constant at 298.15 K for the cell



Is the cell reaction spontaneous as written?



$$\begin{aligned} E &= E^\circ - \frac{RT}{2F} \ln \frac{1}{a_{\text{Cd}^{2+}} a_{\text{Cl}^-}^2} = -0.6253 \text{ V} - \frac{0.05916}{2} \log_{10} \frac{1}{0.100 \times (0.00500)^2} \text{ V} \\ &= -0.7910 \text{ V} \end{aligned}$$

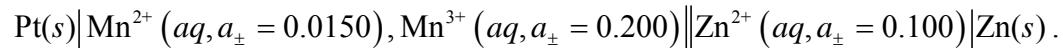
$$\begin{aligned} \ln K &= \frac{nF}{RT} E^\circ = \frac{2 \times 96485 \text{ C mol}^{-1} \times (-0.6253 \text{ V})}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \\ &= -48.678 \end{aligned}$$

$$K = 7.23 \times 10^{-22}$$

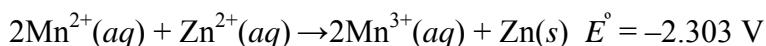
The reaction is not spontaneous as written because

$$Q = \frac{1}{(0.00500)^2 (0.100)} = 4 \times 10^5 \gg K . \text{ Another criterion is that } E < 0.$$

P11.11) Determine the half-cell reactions and the overall cell reaction, calculate the cell potential, and determine the equilibrium constant at 298.15 K for the cell



Is the cell reaction spontaneous as written?



$$E = E^\circ - \frac{RT}{2F} \ln \frac{a_{\text{Mn}^{3+}}^2}{a_{\text{Mn}^{2+}}^2 a_{\text{Zn}^{2+}}} = -2.303 \text{ V} - \frac{0.05916}{2} \log_{10} \frac{(0.200)^2}{(0.150)^2 0.100} \text{ V} = -2.340 \text{ V}$$

$$\begin{aligned} \ln K &= \frac{nF}{RT} E^\circ = \frac{2 \times 96485 \text{ C mol}^{-1} \times (-2.303 \text{ V})}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \\ &= -179.28 \end{aligned}$$

$$K = 1.38 \times 10^{-78}$$

The reaction is not spontaneous as written because $E < 0$.

P11.12) The half-cell potential for the reaction $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ is +1.03 V at 298.15 K when $a_{\text{O}_2} = 1$. Determine a_{H^+} .

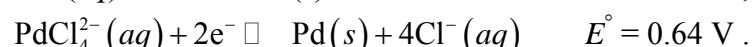
$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{a_{\text{O}_2} a_{\text{H}^+}^4}$$

$$1.03 \text{ V} = 1.23 \text{ V} - \frac{0.05916}{4} \log_{10} \frac{1}{a_{\text{H}^+}^4}$$

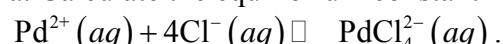
$$\log_{10} a_{\text{H}^+} = \frac{1.03 \text{ V} - 1.23 \text{ V}}{0.05916} = -3.381$$

$$a_{\text{H}^+} = 4.16 \times 10^{-4}$$

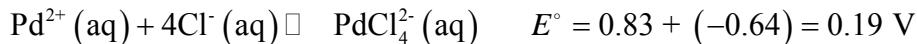
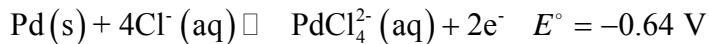
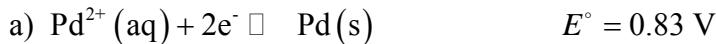
P11.13) You are given the following half-cell reactions:



a. Calculate the equilibrium constant for the reaction



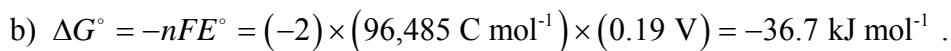
b. Calculate ΔG° for this reaction.



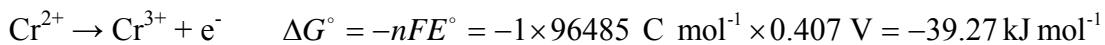
$$E^\circ = \frac{RT}{nF} \ln K$$

$$K = e^{nFE^\circ/RT}$$

$$K = \exp\left(\frac{2(96,485 \text{ C mol}^{-1}) \times (0.19 \text{ V})}{(8.3145 \text{ J mol}^{-1}\text{K}^{-1}) \times (298.15 \text{ K})}\right) = 2.65 \times 10^6$$

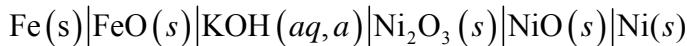


P11.14) Determine E° for the reaction $\text{Cr}^{2+} + 2\text{e}^- \rightarrow \text{Cr}$ from the one-electron reduction potential for Cr^{3+} and the three-electron reduction potential for Cr^{3+} given in Table 11.1 (see Appendix A).

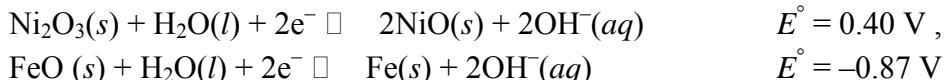


$$E^\circ_{\text{Cr}^{2+}/\text{Cr}} = -\frac{\Delta G^\circ}{nF} = \frac{-176.1 \times 10^3 \text{ J mol}^{-1}}{2 \times 96485 \text{ C mol}^{-1}} = -0.913 \text{ V}$$

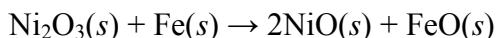
P11.15) The Edison storage cell is described by



and the half-cell reactions are as follows:



a. What is the overall cell reaction?



b. How does the cell potential depend on the activity of the KOH?

It doesn't because OH^- doesn't appear in the overall reaction.

c. How much electrical work can be obtained per kilogram of the active materials in the cell?

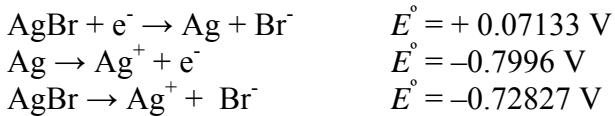
The mass of the reactants per mole of the overall reaction is $55.85\text{ g mol}^{-1} + 165.38\text{ g mol}^{-1} = 221.12\text{ g mol}^{-1}$. The number of mols of the reaction that includes 1 kg or reactants is $1000\text{ g}/221.12\text{ g mol}^{-1} = 4.52\text{ mol}$.

The maximum electrical work is given by

$$\begin{aligned} w &= \Delta G^\circ = 4.52\text{ mol} \times (-nFE^\circ) \\ &= 4.52\text{ mol} \times 2 \times 96,485\text{ C mol}^{-1} \times 1.27\text{ V} = -1108\text{ kJ} \end{aligned}$$

P11.16) Determine K_{sp} for AgBr at 298.15 K using the electrochemical cell described by $\text{Ag}(s) \parallel \text{AgBr}(s) \parallel \text{Br}^-(aq, a_{\text{Br}^-}) \parallel \text{Ag}^+(aq, a_{\text{Ag}^+}) \parallel \text{Ag}(s)$.

The half cell and overall reactions are



$$\begin{aligned} \log_{10} K_{sp} &= -\frac{nE^\circ}{0.05916} = -\frac{0.729\text{ V}}{0.05916\text{ V}} = -12.310 \\ K_{sp} &= 4.90 \times 10^{-13} \end{aligned}$$

P11.17) The standard potential E° for a given cell in which a two electron transfer takes place is 1.100 V at 298.15 K and $\left(\frac{\partial E^\circ}{\partial T}\right)_P = -6.50 \times 10^{-5}\text{ V K}^{-1}$. Calculate $\Delta G^\circ_{\text{reaction}}$, $\Delta S^\circ_{\text{reaction}}$, and $\Delta H^\circ_{\text{reaction}}$. Assume that $n = 2$.

$$\begin{aligned} \Delta G^\circ_{\text{reaction}} &= -nFE^\circ = -2 \times 96485\text{ C mol}^{-1} \times 1.100\text{ V} = -212.3\text{ kJ mol}^{-1} \\ \Delta S^\circ_{\text{reaction}} &= -\left(\frac{\partial \Delta G^\circ_{\text{reaction}}}{\partial T}\right)_P = nF\left(\frac{\partial E^\circ}{\partial T}\right)_P = -2 \times 96485\text{ C mol}^{-1} \times 6.50 \times 10^{-5}\text{ V K}^{-1} = -12.5\text{ J K}^{-1} \\ \Delta H^\circ_{\text{reaction}} &= \Delta G^\circ_{\text{reaction}} + T\Delta S^\circ_{\text{reaction}} = -212.3\text{ kJ K}^{-1}\text{mol}^{-1} - 298.15\text{ K} \times 12.5\text{ J K}^{-1} = -216.0\text{ kJ mol}^{-1} \end{aligned}$$

P11.18) For a given overall cell reaction in which a one electron transfer takes place,

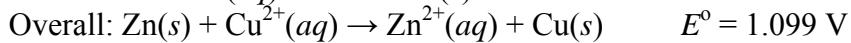
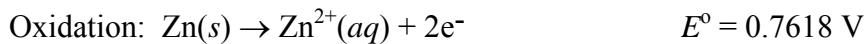
$$\Delta S_R^\circ = 17.5\text{ J mol}^{-1}\text{ K}^{-1} \text{ and } \Delta H_R^\circ = -225.0\text{ kJ mol}^{-1}. \text{ Calculate } E^\circ \text{ and } \left(\frac{\partial E^\circ}{\partial T}\right)_P. \text{ Assume that } n = 1.$$

$$E^\circ = -\frac{\Delta G_R^\circ}{nF} = -\frac{\Delta H_R^\circ - T\Delta S_R^\circ}{nF} = -\frac{-225.0 \text{ kJ mol}^{-1} - 298.15 \text{ K} \times 17.5 \text{ J K}^{-1}\text{mol}^{-1}}{1 \times 96485 \text{ C mol}^{-1}} = 2.38 \text{ V}$$

$$\left(\frac{\partial E^\circ}{\partial T}\right)_P = \frac{\Delta S_R^\circ}{nF} = \frac{17.5 \text{ J K}^{-1}\text{mol}^{-1}}{1 \times 96485 \text{ C mol}^{-1}} = 1.81 \times 10^{-4} \text{ V K}^{-1}$$

P11.19) Consider the Daniell cell for the indicated molalities:

$\text{Zn}(s) \parallel \text{ZnSO}_4(aq, 0.3000m) \parallel \text{CuSO}_4(aq, 0.2000m) \parallel \text{Cu}(s)$. The activity coefficient γ_\pm has the value 0.1040 for CuSO_4 and 0.08350 for ZnSO_4 at the indicated concentrations. Calculate E by a) setting the activity equal to the molality and b) by using the above values of the γ_\pm . How large is the relative error if the concentrations, rather than the activities, are used?



$$E_{cell}^\circ = E_{cell}^\circ - \frac{RT}{nF} \ln\left(\frac{a_{\text{Zn}}^{2+}}{a_{\text{Cu}}^{2+}}\right)$$

(1) Activities equal to molalities:

$$E_{cell}^\circ = 1.099 - \frac{(8.3145 \text{ J mol}^{-1}\text{K}^{-1}) \times (298.15 \text{ K})}{(2) \times (96,485 \text{ C mol}^{-1})} \ln\left(\frac{0.300}{0.200}\right) = 1.094 \text{ V}$$

(2) Using γ_\pm :

$$E_{cell}^\circ = 1.099 - \frac{(8.3145 \text{ J mol}^{-1}\text{K}^{-1}) \times (298.15 \text{ K})}{(2) \times (96,485 \text{ C mol}^{-1})} \ln\left(\frac{0.0835 \times 0.300}{0.104 \times 0.200}\right) = 1.097 \text{ V}$$

Relative error:

$$\frac{1.094 \text{ V} - 1.097 \text{ V}}{1.097 \text{ V}} \times 100\% = 0.27\%$$

P11.20) The standard half-cell potential for the reaction $\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}$ is +1.03 V at 298.15 K. Calculate E for a 0.500-molal solution of HCl for $a_{\text{O}_2} = 1$ (a) assuming that the a_{H^+} is equal to the molality and (b) using the measured mean ionic activity coefficient for this concentration, $\gamma_\pm = 0.757$. How large is the relative error if the concentrations, rather than the activities, are used?

$$E^\circ = 1.03 \text{ V} \quad a_{\text{O}_2} = 1 \quad E = E^\circ - \frac{RT}{nF} \ln \frac{1}{(a_{\text{H}^+})^4}$$

a) $a_{\text{H}^+} = 0.5$

$$E = 1.03 \text{ V} - \frac{(8.3145 \text{ J mol}^{-1}\text{K}^{-1}) \times (298.15 \text{ K})}{(2) \times (96,485 \text{ C mol}^{-1})} \ln(16) = 1.0122 \text{ V}$$

b) $a_{\text{H}^+} = (0.757) \times (0.5)$

$$E = 1.03 - \frac{(8.3145 \text{ J mol}^{-1}\text{K}^{-1}) \times (298.15 \text{ K})}{(2) \times (96,485 \text{ C mol}^{-1})} \ln[(0.757) \times (0.5)]^4 = 1.0050 \text{ V}$$

The relative error is given by

$$\frac{1.0122 \text{ V} - 1.0050 \text{ V}}{1.0050 \text{ V}} \times 100\% = 0.72\%$$

If rounding off to the correct number of significant figure were done at intermediate stages of the calculation, the relative error would be zero.

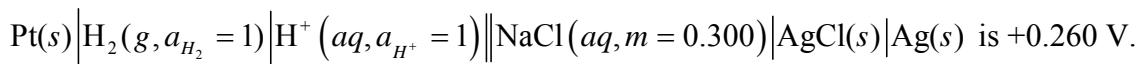
P11.21) Consider the half-cell reaction $\text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$. By what factor are n , Q , E , and E° changed if all the stoichiometric coefficients are multiplied by the factor two? Justify your answers.

n is proportional to the number of electrons transferred, and increases by the factor two. Q is squared if all stoichiometric factors are doubled. The factor by which it is increased depends on the activities of O_2 and H^+ .

$E^\circ = \frac{\Delta G^\circ}{nF}$ is unchanged because both ΔG° and n are doubled.

$E = E^\circ - \frac{RT}{nF} \ln Q$ is unchanged because the squaring of Q is offset exactly by the doubling of n .

P11.22) The cell potential E for the cell



Determine γ_{Cl^-} assuming that $\gamma_\pm = \gamma_{\text{Na}^+} = \gamma_{\text{Cl}^-}$.

The half cell and overall reactions are



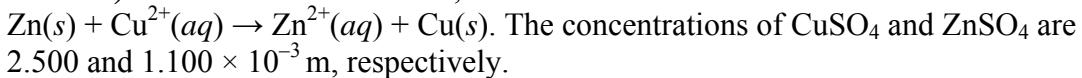
$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_{\text{H}^+} a_{\text{Cl}^-}}{\sqrt{a_{\text{H}_2}}} = E^\circ - \frac{RT}{nF} \ln a_{\text{Cl}^-} = E^\circ - \frac{RT}{nF} \ln \left(\gamma_\pm \frac{m_{\text{Cl}^-}}{m^\circ} \right)$$

$$\ln \gamma_\pm = \frac{nF(E^\circ - E)}{RT} - \ln \frac{m_{\text{Cl}^-}}{m^\circ}$$

$$\ln \gamma_\pm = \frac{1 \times 96,485 \text{ C mol}^{-1} (0.22233 \text{ V} - 0.260 \text{ V})}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} - \ln 0.30 = -0.2630$$

$$\gamma_\pm = 0.769$$

P11.23) Consider the Daniell cell, for which the overall cell reaction is



- Calculate E setting the activities of the ionic species equal to their molalities.
 - Calculate γ_\pm for each of the half-cell solutions using the Debye–Hückel limiting law.
 - Calculate E using the mean ionic activity coefficients determined in part (b).
- a) Calculate E setting the activities of the ionic species equal to their molalities. For this cell, $E^\circ = 1.099 \text{ V}$.

$$E = E^\circ - \frac{RT}{nF} \ln \frac{m_{\text{Zn}^{2+}}}{m_{\text{Cu}^{2+}}} = E^\circ - \frac{RT}{nF} \ln \frac{m_{\text{Zn}^{2+}}}{m_{\text{Cu}^{2+}}} \frac{m_{\text{SO}_4^{2-}}}{m_{\text{SO}_4^{2-}}}$$

$$E = 1.099 \text{ V} - \frac{0.05916}{2} \log_{10} \frac{1.10 \times 10^{-3} \text{ m}}{2.50 \times 10^{-3} \text{ m}}$$

$$E = 1.099 \text{ V} + 0.011 \text{ V} = 1.110 \text{ V.}$$

We next calculate the mean ionic activity coefficients

$$I_{\text{ZnSO}_4} = \frac{m}{2} (v_+ z_+^2 + v_- z_-^2) = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2)$$

$$I = \frac{1}{2} (4 \times 0.0011 \text{ mol kg}^{-1} + 4 \times 0.0011 \text{ mol kg}^{-1}) = 0.0044 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 |z_+ z_-| \sqrt{\frac{I}{\text{mol kg}^{-1}}} = -1.173 \times 4 \times \sqrt{0.0044} = -0.3112$$

$$\gamma_{\pm} = 0.733$$

$$I_{\text{CuSO}_4} = \frac{m}{2} (v_+ z_+^2 + v_- z_-^2) = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2)$$

$$I = \frac{1}{2} (4 \times 0.0025 \text{ mol kg}^{-1} + 4 \times 0.0025 \text{ mol kg}^{-1}) = 0.010 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 |z_+ z_-| \sqrt{\frac{I}{\text{mol kg}^{-1}}} = -1.173 \times 4 \times \sqrt{0.010} = -0.4692$$

$$\gamma_{\pm} = 0.626$$

We next calculate E using the activities

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} = E^\circ - \frac{RT}{nF} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \frac{a_{\text{SO}_4^{2-}}}{a_{\text{SO}_4^{2-}}}$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_{\pm}^2(\text{ZnSO}_4)}{a_{\pm}^2(\text{CuSO}_4)} = E^\circ - \frac{RT}{nF} \ln \frac{m_{\pm}^2 \gamma_{\pm}^2(\text{ZnSO}_4)}{m_{\pm}^2 \gamma_{\pm}^2(\text{CuSO}_4)}$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{m \gamma_{\pm}^2(\text{ZnSO}_4)}{m \gamma_{\pm}^2(\text{CuSO}_4)} = 1.10 \text{ V} - \frac{0.05916}{2} \log_{10} \frac{1.10 \times 10^{-3} m \times (0.733)^2}{2.50 \times 10^{-3} m \times (0.626)^2}$$

$$E = 1.099 \text{ V} + 0.007 = 1.106 \text{ V}$$

The relative error in this case is zero within the precision of the measurements.

P11.24) Consider the cell $\text{Pt}(s) \mid \text{H}_2(g, 1 \text{ atm}) \mid \text{H}^+(aq, a=1) \mid \text{Fe}^{3+}(aq), \text{Fe}^{2+}(aq) \mid \text{Pt}(s)$ given that $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$ and $E^\circ = 0.771 \text{ V}$.

- If the cell potential is 0.712 V, what is the ratio of $\text{Fe}^{2+}(aq)$ to $\text{Fe}^{3+}(aq)$?
- What is the ratio of these concentrations if the cell potential is 0.830 V?
- Calculate the fraction of the total iron present as $\text{Fe}^{3+}(aq)$ at cell potentials of 0.650, 0.700, 0.750, 0.771, 0.800, and 0.900 V. Graph the result as a function of the cell potential.

Overall reaction: $\text{H}_2 + 2\text{Fe}^{3+} \rightarrow 2\text{H}^+ + 2\text{Fe}^{2+}$ $E^\circ = 0.771 \text{ V}$

$$\begin{aligned} \text{a) } E &= E^\circ - \frac{RT}{2F} \ln \left(\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \right)^2 \\ &= E^\circ - \frac{RT}{F} \ln \left(\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \right) \end{aligned}$$

$$\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} = \exp \frac{(E^\circ - E) F}{RT}$$

If $E = 0.712 \text{ V}$

$$\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} = \exp \left(\frac{(0.771 \text{ V} - 0.712 \text{ V}) \times 96,485 \text{ C mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298.15 \text{ K}} \right) = 9.94$$

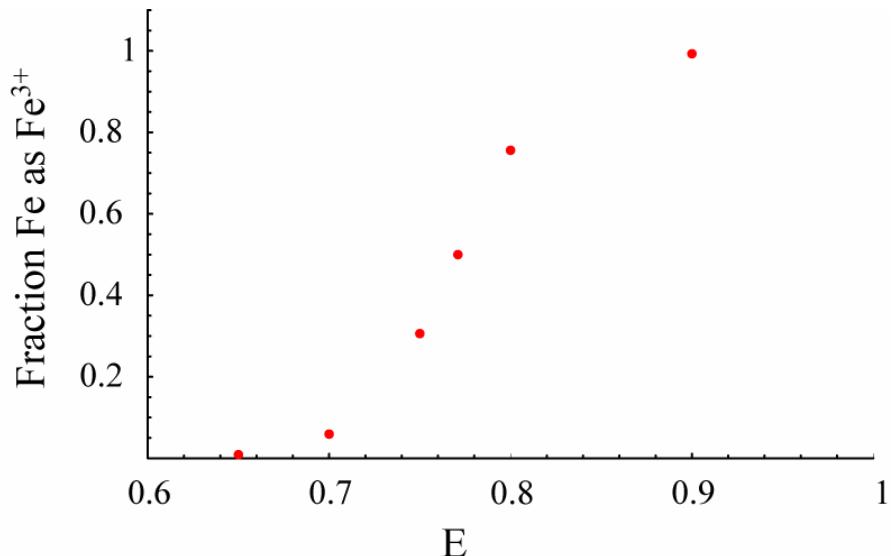
b) If $E = 0.830 \text{ V}$

$$\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} = \exp \left(\frac{(0.771 \text{ V} - 0.830 \text{ V}) \times 96,485 \text{ C mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298.15 \text{ K}} \right) = 0.101$$

$$\text{c) Fraction of Fe}^{3+}: \frac{a_{Fe^{3+}}}{a_{Fe^{3+}} + a_{Fe^{2+}}} = \frac{1}{1 + \left(\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \right)}$$

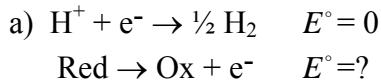
We use the method described above to find $a_{Fe^{2+}} / a_{Fe^{3+}}$. We find the following results:

$E(\text{V})$	$a_{Fe^{2+}} / a_{Fe^{3+}}$	Fraction of Fe ³⁺
0.650	111	8.93×10^{-3}
0.700	15.9	0.0593
0.750	2.26	0.306
0.771	1.0	0.5
0.800	0.323	0.756
0.900	6.60×10^{-3}	0.993



P11.25) Consider the couple Ox + e⁻ ⇌ Red with the oxidized and reduced species at unit activity. What must be the value of E° for this half-cell if the reductant Red is to liberate hydrogen at 1 atm from

- a. an acid solution with $a_{H^+} = 1$?
- b. water at pH = 7?
- c. Is hydrogen a better reducing agent in acid or basic solution?



Because the activities of H^+ and H_2 are one, $E = E^\circ = 0$ V. The same is true of the Ox-Red couple.

To liberate H_2 , E° for the reaction must be > 0 .

Therefore, E° for Ox + e⁻ → Red must be < 0 .

- b) For a pH of 7, $a_{H^+} = 10^{-7}$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{\sqrt{a_{H_2}}}{a_{H^+}} = -0.05916 \log_{10} (10^{-7}) = -0.414 \text{ V}$$

For the overall reaction to be spontaneous, E° for Red → Ox + e⁻ must be > 0.414 V.

- c) It is a better reducing agent in basic solution, because the oxidation potential for the reaction $\frac{1}{2} H_2 \rightarrow H^+ + e^-$ becomes more positive as the pH decreases .

P11.26) Consider the half-cell reaction $\text{AgCl}(s) + \text{e}^- \rightleftharpoons \text{Ag}(s) + \text{Cl}^-(aq)$. If $\Delta G_f^\circ(\text{AgCl}(s)) = -109.71 \text{ kJ mol}^{-1}$, and if $E^\circ = +0.222 \text{ V}$ for this half-cell, calculate the standard Gibbs energy of formation of $\text{Cl}^-(aq)$.

$$\Delta G_1^\circ = -109.71 \text{ kJ mol}^{-1}$$

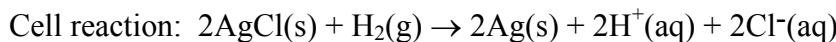
$$\Delta G_2^\circ = (-1) \times (96,485 \text{ C mol}^{-1}) \times (0.222 \text{ V}) = 21.4 \text{ kJ mol}^{-1}$$

$$\Delta G_3^\circ = \Delta G_f^\circ(\text{Cl}^-(aq)) = \Delta G_1^\circ + \Delta G_2^\circ = -131.1 \text{ kJ mol}^{-1}$$

P11.27) The data in the following table have been obtained for the potential of the cell $\text{Pt}(s)|\text{H}_2(g, f = 1 \text{ atm})|\text{HCl}(aq, m)|\text{AgCl}(s)|\text{Ag}(s)$ as a function of m at 25°C .

$m (\text{mol kg}^{-1})$	$E (\text{V})$	$m (\text{mol kg}^{-1})$	$E (\text{V})$	$m (\text{mol kg}^{-1})$	$E (\text{V})$
0.00100	0.59715	0.0200	0.43024	0.500	0.27231
0.00200	0.54425	0.0500	0.38588	1.000	0.23328
0.00500	0.49846	0.100	0.35241	1.500	0.20719
0.0100	0.46417	0.200	0.31874	2.000	0.18631

- a) Determine E° using a graphical method.
- b) Calculate γ_\pm for HCl at $m = 0.00100, 0.0100$, and 0.100 .



$$E = E^\circ - \frac{RT}{2F} \ln(a_{\text{H}^+} a_{\text{Cl}^-})^2 = E^\circ - \frac{RT}{F} \ln(a_{\text{H}^+} a_{\text{Cl}^-})$$

$$a_{\text{H}^+} a_{\text{Cl}^-} = a_\pm^2 = \gamma_\pm^2 m_\pm^2$$

$$E = E^\circ - \frac{2RT}{F} \left(\ln \frac{m}{m^\circ} \right) - \frac{2RT}{F} (\ln \gamma_\pm)$$

In the low concentration limit we can use the Debye-Hückel result

$$\ln \gamma_\pm = -0.50926 \log_{10} \sqrt{\frac{m}{m^\circ}} = -1.172614 \ln \sqrt{\frac{m}{m^\circ}}$$

Therefore, for dilute solutions

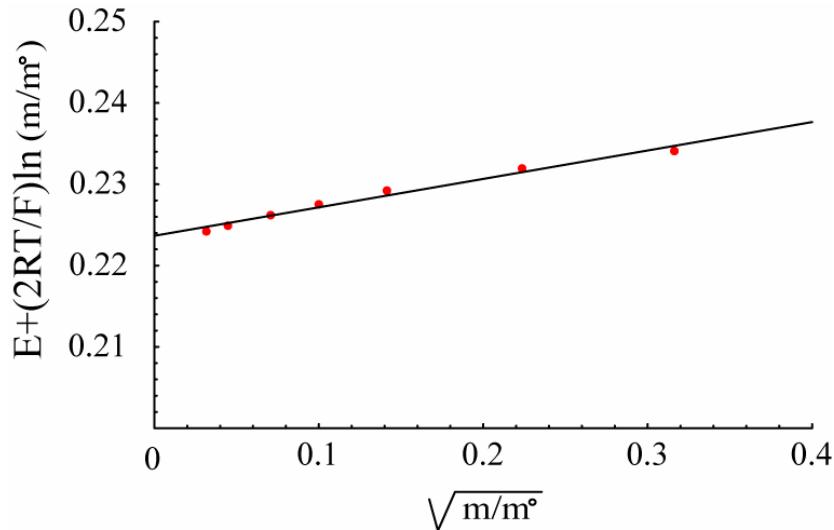
$$E + \frac{2RT}{F} \ln \left(\frac{m}{m^\circ} \right) = E^\circ + \frac{2RT}{F} \times 1.172614 \times \sqrt{\frac{m}{m^\circ}}$$

Using this result, a plot of $E + \frac{2RT}{F} \ln\left(\frac{m}{m^\circ}\right)$ (y axis) vs. $\sqrt{\frac{m}{m^\circ}}$ (x axis) will have an intercept of E° .

We use the data up to $m = 0.100$, as the Debye-Hückel model is not valid for more concentrated solutions.

$\frac{m}{m^\circ}$	$\sqrt{\frac{m}{m^\circ}}$	E	$E + \frac{2RT}{F} \ln\left(\frac{m}{m^\circ}\right)$
0.001	0.031623	0.57915	0.224212
0.002	0.044721	0.54425	0.224909
0.005	0.070711	0.49846	0.226203
0.010	0.1	0.46417	0.227531
0.020	0.141421	0.43024	0.229218
0.050	0.223607	0.38588	0.231943
0.100	0.316228	0.35241	0.234090

The data in the table is graphed below. The best fit line gives a value for E° of 0.223665 V.



Given E° we can now find γ_\pm from

$$\ln \gamma_\pm = \frac{F}{RT} (E^\circ - E) - \ln\left(\frac{m}{m^\circ}\right)$$

m/m°	$E^\circ = 0.223655 \text{ V}$	
	$\ln \gamma_\pm$	γ_\pm
0.001	-0.010654	0.989
0.010	-0.0755112	0.927
0.100	-0.203036	0.816

P11.28) Harnet and Hamer [*J. American Chemical Society* 57 (1935), 33] report values for the potential of the cell $\text{Pt}(s) \mid \text{PbSO}_4(s) \mid \text{H}_2\text{SO}_4(aq, a) \mid \text{PbSO}_4(s) \mid \text{PbO}_2(s) \mid \text{Pt}(s)$ over a wide range of temperature and H_2SO_4 concentrations. In 1m H_2SO_4 , their results were described by

$$E(\text{V}) = 1.91737 + 56.1 \times 10^{-6}t + 108 \times 10^{-8}t^2,$$

where t is the temperature on the Celsius scale. Calculate ΔG , ΔH , and ΔS for the cell reaction at 0° and 25°C .

$$E(\text{V}) = 1.91737 + (5.61 \times 10^{-6})t + (108 \times 10^{-8})t^2$$

$$\left(\frac{\partial E}{\partial T} \right)_P = (5.61 \times 10^{-6}) + 2(108 \times 10^{-8})t$$

$$\Delta G = -nFE \quad \Delta S = nF \left(\frac{\partial E}{\partial T} \right)_P \quad \Delta H = \Delta G + T\Delta S$$

a) 0°C

$$E = 1.91737 \text{ V}$$

$$\Delta G = -2(96,485 \text{ C mol}^{-1}) \times (1.91737 \text{ V}) = -369.99 \text{ kJ mol}^{-1}$$

$$\left(\frac{\partial E}{\partial T} \right)_P = 5.61 \times 10^{-6} \text{ V K}^{-1}$$

$$\Delta S = 2(96,485 \text{ C mol}^{-1}) \times (5.61 \times 10^{-6} \text{ V K}^{-1}) = 10.8 \text{ J mol}^{-1}\text{K}^{-1}$$

$$\Delta H = -369.99 \text{ kJ mol}^{-1} + \frac{(273.15 \text{ K})(10.8 \text{ J mol}^{-1}\text{K}^{-1})}{(1000 \text{ J kJ}^{-1})} = -367.0 \text{ kJ mol}^{-1}$$

b) 25°C

$$E = \left[1.91737 + (56.1 \times 10^{-6}) \times (25) + (108 \times 10^{-8}) \times (25)^2 \right] V = 1.91945 \text{ V}$$

$$\Delta G = -370.4 \text{ kJ mol}^{-1}$$

$$\left(\frac{\partial E}{\partial T} \right)_P = 5.61 \times 10^{-6} \text{ V K}^{-1} + 2(108 \times 10^{-8}) \times (25) \text{ V K}^{-1} = 1.101 \times 10^{-4} \text{ V K}^{-1}$$

$$\Delta S = 21.2 \text{ J mol}^{-1} \text{ K}^{-1}$$

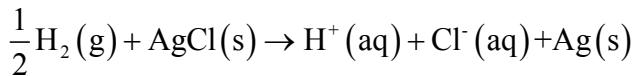
$$\Delta H = (-370.4 \text{ kJ mol}^{-1}) + \frac{(298.15 \text{ K})(21.2 \text{ J mol}^{-1} \text{ K}^{-1})}{(1000 \text{ J K}^{-1})} = -364.1 \text{ kJ mol}^{-1}$$

P11.29) Between 0° and 90°C, the potential of the cell

$\text{Pt}(s) \mid \text{H}_2(g, f=1 \text{ atm}) \mid \text{HCl}(aq, m=0.100) \mid \text{AgCl}(s) \mid \text{Ag}(s)$ is described by the equation

$E(V) = 0.35510 - 0.3422 \times 10^{-4}t - 3.2347 \times 10^{-6}t^2 + 6.314 \times 10^{-9}t^3$ where t is the temperature on the Celsius scale. Write the cell reaction and calculate ΔG , ΔH , and ΔS for the cell reaction at 50°C.

Cell reaction:



At 50°C

$$E = 0.35510 \text{ V} - (0.3422 \times 10^{-4} \text{ V } ^\circ\text{C}^{-1}) \times 50^\circ\text{C} - (3.2347 \times 10^{-6} \text{ V } ^\circ\text{C}^{-2})(50)^2 \text{ } ^\circ\text{C}^2 + (6.314 \times 10^{-9} \text{ V } ^\circ\text{C}^{-3})(50) \text{ } ^\circ\text{C}^3 = 0.3460915 \text{ V}$$

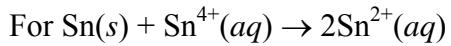
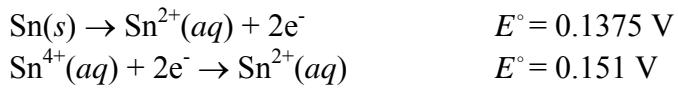
$$\Delta G = -nFE = (-1)(96,485 \text{ C mol}^{-1})(0.3460915 \text{ V}) = -33.4 \text{ kJ mol}^{-1}$$

$$\left(\frac{\partial E}{\partial T} \right)_P = -0.3422 \times 10^{-4} - 2(3.2347 \times 10^{-6})(50) + 3(6.314 \times 10^{-9})(50)^2 = -3.10335 \times 10^{-4} \text{ V K}^{-1}$$

$$\Delta S = nF \left(\frac{\partial E}{\partial T} \right)_P = -29.9 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta H = \Delta G + T\Delta S = -33.4 \text{ kJ mol}^{-1} + \frac{(323.15 \text{ K}) \times (-29.9 \text{ V K}^{-1})}{1000} = -43.1 \text{ kJ mol}^{-1}$$

P11.30) Consider the reaction $\text{Sn}(s) + \text{Sn}^{4+}(aq) \rightleftharpoons 2\text{Sn}^{2+}(aq)$. If metallic tin is in equilibrium with a solution of Sn^{2+} in which $a_{\text{Sn}^{2+}} = 0.100$, what is the activity of Sn^{4+} at equilibrium?



$$E^\circ = 0.1375 + 0.151 = 0.2885 \text{ V}$$

$$\Delta G^\circ = -nFE^\circ = -2(96,845 \text{ C mol}^{-1}) \times (0.2885 \text{ V}) = -55.7 \text{ kJ mol}^{-1}$$

$$K = e^{-\Delta G^\circ / RT} = 5.73 \times 10^9 \quad (298.15 \text{ K})$$

$$K = \frac{(a_{\text{Sn}^{2+}})^2}{a_{\text{Sn}^{4+}}}$$

$$a_{\text{Sn}^{4+}} = \frac{(a_{\text{Sn}^{2+}})^2}{K} = \frac{(0.100)^2}{5.73 \times 10^9} = 1.75 \times 10^{-12}$$

Chapter 12: From Classical to Quantum Mechanics

Problem numbers in italics indicate that the solution is included in the *Student's Solutions Manual*.

Questions on Concepts

Q12.1) How did Planck conclude that the discrepancy between experiments and classical theory for blackbody radiation was at high and not low frequencies?

The experimental results and the classical theory agree in the limit of low frequencies and diverge at high frequencies.

Q12.2) The inability of classical theory to explain the spectral density distribution of a blackbody was called the *ultraviolet catastrophe*. Why is this name appropriate?

The divergence between the classical theory and the experimental results is very pronounced in the UV region. In particular, because the classical theory predicts that the spectral density increases as ν^2 , the total energy radiated by a blackbody is predicted to be infinite. This prediction was clearly wrong, and the lack of agreement with the experimental results was viewed by scientists of the time as a catastrophe.

Q12.3) Why does the analysis of the photoelectric effect based on classical physics predict that the kinetic energy of electrons will increase with increasing light intensity?

In the classical theory, more light intensity leads to more energy absorption by the solid and the electrons. At equilibrium, as much energy must leave the surface as is absorbed. Therefore, the electrons will have a greater energy. Classical physicists thought that the greater energy would manifest as a higher speed. In fact, it appears as a larger number of electrons leaving the surface with a frequency determined by the photon energy and the work function of the surface.

Q12.4) What did Einstein postulate to explain that the kinetic energy of the emitted electrons in the photoelectric effect depends on the frequency? How does this postulate differ from the predictions of classical physics?

Einstein postulated that the energy of light depends on the frequency, whereas in classical theory, the energy depends only on the intensity and is independent of the frequency. He further postulated that the energy of light could only be an integral multiple of $h\nu$.

Q12.5) Which of the experimental results for the photoelectric effect suggests that light can display particle-like behavior?

The fact that at very low intensity the incident light is still able to eject electrons, if its frequency is above the threshold frequency, suggests that the energy of the light can be concentrated in a region of atomic dimensions at the surface of the solid. This suggests particle-like behavior.

Q12.6) In the diffraction of electrons by crystals, the volume sampled by the diffracting electrons is on the order of 3 to 10 atomic layers. If He atoms are incident on the surface, only the topmost atomic layer is sampled. Can you explain this difference?

Whereas electrons can penetrate through the topmost layer into the solid, He atoms are too large to allow penetration at thermal energies. Therefore electrons sample a number of atomic layers below the surface, and He atoms are only sensitive to the outermost layer.

Q12.7) In the double-slit experiment, researchers found that an equal amount of energy passes through each slit. Does this result allow you to distinguish between purely particle-like or purely wave-like behavior?

No. This result would be expected for both waves and particles. In the case of particles, the same number would pass through each slit for a large number of incident particles. For a wave, the fraction of the intensity of the wave that passes through each slit would be the same.

Q12.8) Is the intensity observed from the diffraction experiment depicted in Figure 12.6 the same for the angles shown in parts (b) and (c)?

Yes. For all minima in a graph of intensity versus frequency, the intensity is zero as seen in Figure 12.5.

Q12.9) What feature of the distribution depicted as Case 1 in Figure 12.7 tells you that the broad distribution arises from diffraction?

The intensity goes through a minimum and increases again on both sides of the maximum. This can only occur through wave interference.

Q12.10) Why were investigations at the atomic and subatomic levels required to detect the wave nature of particles?

The wavelength of particles with greater mass is so short that particle diffraction could not be observed experimentally. Therefore, the wave-particle duality present even in heavier particles was not observed.

Problems

P12.1) The distribution in wavelengths of the light emitted from a radiating blackbody is a sensitive function of the temperature. This dependence is used to measure the temperature of hot objects, without making physical contact with those objects, in a technique called *optical pyrometry*. In the limit $(hc/\lambda kT) \gg 1$, the maximum in a plot of $\rho(\lambda, T)$ versus λ is given by $\lambda_{\max} = hc/5kT$. At what wavelength does the maximum in $\rho(\lambda, T)$ occur for $T = 450$, 1500 , and 4500 K?

According to Example Problem 14.1, $\lambda_{\max} = \frac{hc}{5kT}$.

$$\lambda_{\max} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{5 \times 1.381 \times 10^{-23} \text{ J K}^{-1} \times 450 \text{ K}} = 6.40 \times 10^{-6} \text{ m at } 450 \text{ K. } \lambda_{\max} \text{ for } 1500 \text{ K and } 4500 \text{ K is } 1.92 \times 10^{-6} \text{ m and } 6.39 \times 10^{-7} \text{ m, respectively.}$$

P12.2) For a monatomic gas, one measure of the “average speed” of the atoms is the root mean square speed, $v_{rms} = \langle v^2 \rangle^{1/2} = \sqrt{\frac{3kT}{m}}$, in which m is the molecular mass and k is the Boltzmann constant. Using this formula, calculate the de Broglie wavelength for He and Ar atoms at 100 and at 500 K.

$$\begin{aligned} \lambda &= \frac{h}{mv_{rms}} = \frac{h}{\sqrt{3kTm}} = \frac{6.626 \times 10^{-34} \text{ J s}}{\sqrt{3 \times 1.381 \times 10^{-23} \text{ J K}^{-1} \times 100 \text{ K} \times 4.003 \text{ amu} \times 1.661 \times 10^{-27} \text{ kg amu}^{-1}}} \\ &= 1.26 \times 10^{-10} \text{ m} \end{aligned}$$

for He at 100 K. $\lambda = 5.65 \times 10^{-11} \text{ m}$ for He at 500 K. For Ar, $\lambda = 4.00 \times 10^{-11} \text{ m}$ and $1.79 \times 10^{-11} \text{ m}$ at 100 K and 500 K, respectively.

P12.3) Using the root mean square speed, $v_{rms} = \langle v^2 \rangle^{1/2} = \sqrt{\frac{3kT}{m}}$, calculate the gas temperatures of He and Ar for which $\lambda = 0.20$ nm, a typical value needed to resolve diffraction from the surface of a metal crystal. On the basis of your result, explain why Ar atomic beams are not suitable for atomic diffraction experiments.

For He,

$$\begin{aligned} T &= \frac{h^2}{3k m \lambda^2} \\ &= \frac{(6.626 \times 10^{-34} \text{ J s})^2}{3 \times 1.381 \times 10^{-23} \text{ J K}^{-1} \times 4.003 \text{ amu} \times 1.661 \times 10^{-27} \text{ kg amu}^{-1} \times (0.20 \times 10^{-9} \text{ m})^2} = 40 \text{ K} \end{aligned}$$

For Ar, $T = 4.0$ K.

The argon temperature is well below its liquifaction temperature at 4 K. It will not be possible to make an atomic beam of Ar atoms with this wavelength with conventional means.

P12.4) Electrons have been used to determine molecular structure by diffraction. Calculate the speed of an electron for which the wavelength is equal to a typical bond length, namely, 0.150 nm.

$$v = \frac{p}{m} = \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34} \text{ Js}}{9.109 \times 10^{-31} \text{ kg} \times 0.150 \times 10^{-9} \text{ m}} = 4.85 \times 10^6 \text{ m s}^{-1}$$

P12.5) Calculate the speed that a gas-phase oxygen molecule would have if it had the same energy as an infrared photon ($\lambda = 10^4$ nm), a visible photon ($\lambda = 500$ nm), an ultraviolet photon ($\lambda = 100$ nm), and an X-ray photon ($\lambda = 0.1$ nm). What temperature would the gas have if it had the same energy as each of these photons? Use the root mean

square speed, $v_{rms} = \sqrt{\langle v^2 \rangle^{1/2}} = \sqrt{\frac{3kT}{m}}$, for this calculation.

$$v = \sqrt{\frac{2E}{m}} = \sqrt{\frac{2hc}{m\lambda}} = \sqrt{\frac{2 \times 6.626 \times 10^{-34} \text{ Js} \times 2.998 \times 10^8 \text{ m s}^{-1}}{32.0 \text{ amu} \times 1.661 \times 10^{-27} \text{ kg} (\text{amu})^{-1} \times 10000 \times 10^{-9} \text{ m}}} = 864 \text{ m s}^{-1} \text{ for}$$

$\lambda = 10^4$ nm. The results for 500 nm, 100 nm and 0.1 nm are $3.87 \times 10^3 \text{ m s}^{-1}$, $8.65 \times 10^3 \text{ m s}^{-1}$, and $2.73 \times 10^5 \text{ m s}^{-1}$.

We calculate the temperature using the formula

$$T = \frac{M v_{rms}^2}{3R} = \frac{32.0 \text{ kg mol}^{-1} \times (864 \text{ m s}^{-1})^2}{3 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}} = 958 \text{ K}$$

$\lambda = 10^4$ nm. The results for 500 nm, 100 nm and 0.1 nm are 1.92×10^4 K, 9.60×10^4 K, and 9.56×10^7 K.

P12.6) Pulsed lasers are powerful sources of nearly monochromatic radiation. Lasers that emit photons in a pulse of 10-ns duration with a total energy in the pulse of 0.10 J at 1000 nm are commercially available.

a) What is the average power (energy per unit time) in units of watts (1 W = 1 J/s) associated with such a pulse?

b) How many 1000-nm photons are emitted in such a pulse?

$$\text{a) } P = \frac{\Delta E}{\Delta t} = \frac{0.10 \text{ J}}{1.0 \times 10^{-8} \text{ s}} = 1.0 \times 10^7 \text{ J s}^{-1}$$

$$\text{b) } N = \frac{E_{pulse}}{E_{photon}} = \frac{E_{pulse}}{h \frac{c}{\lambda}} = \frac{0.10 \text{ J}}{6.626 \times 10^{-34} \text{ J s}^{-1} \times \frac{2.998 \times 10^8 \text{ m s}^{-1}}{1.000 \times 10^6 \text{ m}}} = 5.0 \times 10^{17}$$

P12.7) Assume that water absorbs light of wavelength 3.00×10^{-6} m with 100% efficiency. How many photons are required to heat 1.00 g of water by 1.00 K? The heat capacity of water is $75.3 \text{ J mol}^{-1} \text{ K}^{-1}$.

$$E = Nhv = N \frac{hc}{\lambda} = n C_{p,m} \Delta T$$

$$N = \frac{m}{M} \frac{C_{p,m} \Delta T \lambda}{hc} = \frac{1.00 \text{ g}}{18.02 \text{ g mol}^{-1}} \frac{75.3 \text{ J K}^{-1} \text{ mol}^{-1} \times 1.00 \text{ K} \times 3.00 \times 10^{-6} \text{ m}}{6.626 \times 10^{-34} \text{ Js} \times 2.998 \times 10^8 \text{ ms}^{-1}} = 6.31 \times 10^{19}$$

P12.8) A 1000-W gas discharge lamp emits 3.00 W of ultraviolet radiation in a narrow range centered near 280 nm. How many photons of this wavelength are emitted per second?

$$n' = \frac{E_{total}}{E_{photon}} = \frac{3.00 \text{ W} \times 1 \text{ Js}^{-1} \text{ W}^{-1}}{\frac{hc}{\lambda}} = \frac{3.00 \text{ W} \times 1 \text{ Js}^{-1} \text{ W}^{-1}}{\frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ ms}^{-1}}{280 \times 10^{-9} \text{ m}}} = 4.23 \times 10^{18} \text{ s}^{-1}$$

P12.9) A newly developed substance that emits 225 W of photons with a wavelength of 225 nm is mounted in a small rocket such that all of the radiation is released in the same direction. Because momentum is conserved, the rocket will be accelerated in the opposite direction. If the total mass of the rocket is 5.25 kg, how fast will it be traveling at the end of 365 days in the absence of frictional forces?

The number of photons is given by

$$n' = \frac{E_{total}}{E_{photon}} = \frac{3.00 \text{ W} \times \frac{1 \text{ Js}^{-1}}{\text{W}}}{\frac{hc}{\lambda}} = \frac{225 \text{ W} \times \frac{1 \text{ Js}^{-1}}{\text{W}}}{\frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ ms}^{-1}}{225 \times 10^{-9} \text{ m}}} = 2.547 \times 10^{20} \text{ s}^{-1}$$

The momentum of one photon is

$$p = \frac{h}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s}}{225 \times 10^{-9} \text{ m}} = 2.945 \times 10^{-27} \text{ kg ms}^{-1}$$

The force is given by the rate of change of momentum.

$$F = \frac{d(n'p)}{dt} = 2.945 \times 10^{-27} \text{ kg ms}^{-1} \times 2.547 \times 10^{20} \text{ s}^{-1} = 7.501 \times 10^{-7} \text{ kg ms}^{-2}$$

The final speed is given by

$$v = v_0 + at = \frac{F}{m} t = \frac{7.501 \times 10^{-7} \text{ kg ms}^{-2}}{5.25 \text{ kg}} \times 365 \text{ days} \times \frac{86400 \text{ s}}{\text{day}} = 4.51 \text{ m s}^{-1}$$

P12.10) What speed does a H₂ molecule have if it has the same momentum as a photon of wavelength 280 nm?

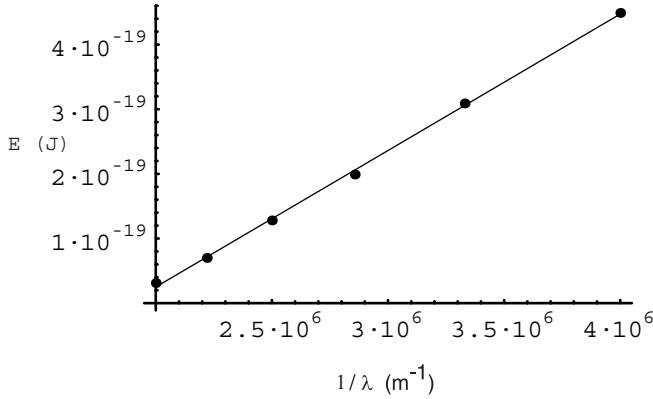
$$p = \frac{h}{\lambda} = m_{H_2} v_{H_2}$$

$$v_{H_2} = \frac{h}{m_{H_2} \lambda} = \frac{6.626 \times 10^{-34} \text{ J s}}{2.016 \text{ amu} \times 1.661 \times 10^{-27} \text{ kg} (\text{amu})^{-1} \times 280 \times 10^{-9} \text{ m}} = 0.707 \text{ m s}^{-1}$$

P12.11) The following data were observed in an experiment of the photoelectric effect from potassium:

10^{-19} Kinetic Energy (J)	4.49	3.09	1.89	1.34	7.00	3.11
Wavelength (nm)	250	300	350	400	450	500

Graphically evaluate these data to obtain values for the work function and Planck's constant.



The best-fit line is given by $E = -3.97362 \times 10^{-19} + 2.11171 \times 10^{-25} \frac{1}{\lambda}$.

Because the slope is hc , $h = \frac{2.11171 \times 10^{-25} \text{ J m}}{2.998 \times 10^8 \text{ m s}^{-1}} \approx 7.0 \times 10^{-34} \text{ J s}$. The work function is

given by the intercept of the line with the x axis at $y = 0$. $\phi = \frac{hc}{\lambda_0} - E$ where

$$\lambda_0 = \frac{2.1171 \times 10^{-25} \text{ J m}}{3.97362 \times 10^{-19} \text{ J}} = 5.30 \times 10^{-7} \text{ m}$$

This gives $\phi \approx 4.0 \times 10^{-19} \text{ J}$ or 2.5 eV.

P12.12) Show that the energy density radiated by a blackbody

$$\frac{E_{total}(T)}{V} = \int_0^{\infty} \rho(v, T) dv = \int_0^{\infty} \frac{8\pi h v^3}{c^3} \frac{1}{e^{hv/kT} - 1} dv \text{ depends on the temperature as } T^4.$$

(Hint: Make the substitution of variables $x = hv/kT$.) The definite integral

$$\int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}.$$

Using your result, calculate the energy density radiated by a blackbody

at 800 and 4000 K.

$$\frac{E_{total}}{V} = \int_0^{\infty} \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} d\nu. \text{ Let } x = \frac{h\nu}{kT}; \ dx = \frac{h}{kT} d\nu$$

$$\int_0^{\infty} \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} d\nu = \frac{8\pi k^4 T^4}{h^3 c^3} \int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{8\pi^5 k^4 T^4}{15 h^3 c^3}$$

$$\text{At 800 K, } \frac{E_{total}}{V} = \frac{8\pi^5 k^4 T^4}{15 h^3 c^3} = \frac{8\pi^5 (1.381 \times 10^{-23} \text{ J K}^{-1})^4 \times (800 \text{ K})^4}{15 \times (6.626 \times 10^{-34} \text{ J s})^3 \times (2.998 \times 10^8 \text{ m s}^{-1})^3} = 3.10 \times 10^{-4} \text{ J m}^{-3}$$

$$\text{At 4000, } \frac{E_{total}}{V} = \frac{8\pi^5 \times (1.381 \times 10^{-23} \text{ J K}^{-1})^4 \times (4000 \text{ K})^4}{15 \times (6.626 \times 10^{-34} \text{ J s})^3 \times (2.998 \times 10^8 \text{ m s}^{-1})^3} = 0.194 \text{ J m}^{-3}$$

P12.13) The power per unit area emitted by a blackbody is given by

$P = \sigma T^4$ with $\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$. Calculate the energy radiated by a spherical blackbody of radius 0.500 m at 1000 K per second. What would the radius of a blackbody at 2500 K be if it emitted the same energy as the spherical blackbody of radius 0.500 m at 1000 K?

$$E = A\sigma T^4 = 4\pi(0.500 \text{ m})^2 \times 5.67 \times 10^{-8} \text{ J s}^{-1} \text{ m}^{-2} \text{ K}^{-4} \times (1000 \text{ K})^4 = 1.78 \times 10^5 \text{ J s}^{-1}$$

Because the total energy radiated by the spheres must be equal,

$$4\pi r_1^2 \sigma T_1^4 = 4\pi r_2^2 \sigma T_2^4$$

$$r_2 = \sqrt{\frac{r_1^2 T_1^4}{T_2^4}} = \sqrt{\frac{(0.500 \text{ m})^2 (1000 \text{ K})^4}{(2500 \text{ K})^4}} = 0.0800 \text{ m}$$

P12.14) In our discussion of blackbody radiation, the average energy of an oscillator

$$\bar{E}_{osc} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \text{ was approximated as } \bar{E}_{osc} = \frac{h\nu}{(1 + \frac{h\nu}{kT}) - 1} = kT \text{ for } \frac{h\nu}{kT} \ll 1.$$

Calculate the relative error $= \frac{E - E_{approx}}{E}$ in making this approximation for

$\nu = 4 \times 10^{12} \text{ s}^{-1}$ at temperatures of 6000, 2000, and 500 K. Can you predict what the sign of the relative error will be without a detailed calculation?

$$\text{Relative Error} = \frac{E - E_{approx}}{E} = \frac{\left(\frac{h\nu}{\exp\left(\frac{h\nu}{kT}\right) - 1} \right) - kT}{\left(\frac{h\nu}{\exp\left(\frac{h\nu}{kT}\right) - 1} \right)}$$

$$= \frac{\left(\frac{h\nu}{\exp\left(\frac{h\nu}{kT}\right) - 1} \right) - kT}{\left(\frac{6.626 \times 10^{-34} \text{ J s} \times 4.00 \times 10^{12} \text{ s}^{-1}}{\exp\left(\frac{6.626 \times 10^{-34} \text{ J s} \times 4.00 \times 10^{12} \text{ s}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 6000 \text{ K}}\right) - 1} \right) - 1.381 \times 10^{-23} \text{ J K}^{-1} \times 6000 \text{ K}}$$

$$\text{Relative Error} = \frac{E - E_{approx}}{E} = -0.0162 \text{ for } T = 6000 \text{ K.}$$

The results for 2000 K, and 500 K are -0.0496 and -0.219.

Because $E_{approx} = kT > E$, the relative error $= \frac{E - E_{approx}}{E}$ is always a negative number.

P12.15) The power (energy per unit time) radiated by black body per unit area of surface expressed in units of W m^{-2} is given by $P = \sigma T^4$ with $\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$. The radius of the sun is $7.00 \times 10^5 \text{ km}$ and the surface temperature is 6000 K. Calculate the total energy radiated per second by the sun. Assume ideal blackbody behavior.

$$\begin{aligned} E &= PA = \sigma T^4 \times 4\pi r^2 \\ &= 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} \times (6000 \text{ K})^4 \times 4\pi \times (7.00 \times 10^8 \text{ m})^2 \\ &= 4.52 \times 10^{26} \text{ W} \end{aligned}$$

P12.16) A more accurate expression for \bar{E}_{osc} would be obtained by including additional terms in the Taylor-Mclaurin series. The Taylor-Mclaurin series expansion of $f(x)$ in the vicinity of x_0 is given by (see Math Supplement)

$$f(x) = f(x_0) + \left(\frac{df(x)}{dx} \right)_{x=x_0} (x - x_0) + \frac{1}{2!} \left(\frac{d^2 f(x)}{dx^2} \right)_{x=x_0} (x - x_0)^2 + \frac{1}{3!} \left(\frac{d^3 f(x)}{dx^3} \right)_{x=x_0} (x - x_0)^3 + \dots$$

Use this formalism to better approximate \bar{E}_{osc} by expanding $e^{\frac{h\nu}{kT}}$ in powers of $h\nu/kT$ out to $(h\nu/kT)^3$ in the vicinity of $h\nu/kT = 0$. Calculate the relative error, $\frac{\bar{E}_{osc} - kT}{\bar{E}_{osc}}$, if you

had not included the additional terms for $\nu = 1.00 \times 10^{12} \text{ s}^{-1}$ at temperatures of 800, 500, and 250 K.

The Taylor series expansion of $e^{\frac{h\nu}{kT}}$ is $1 + \frac{h\nu}{kT} + \frac{1}{2}\left(\frac{h\nu}{kT}\right)^2 + \frac{1}{6}\left(\frac{h\nu}{kT}\right)^3 + \dots$. Therefore

including terms up to $\left(\frac{h\nu}{kT}\right)^3$,

$$\bar{E}_{osc} = \frac{h\nu}{\frac{h\nu}{kT} + \frac{1}{2}\left(\frac{h\nu}{kT}\right)^2 + \frac{1}{6}\left(\frac{h\nu}{kT}\right)^3}$$

$$\frac{\bar{E}_{osc} - kT}{\bar{E}_{osc}} = \left[\frac{h\nu}{\frac{h\nu}{kT} + \frac{1}{2}\left(\frac{h\nu}{kT}\right)^2 + \frac{1}{6}\left(\frac{h\nu}{kT}\right)^3} - kT \right] \left/ \frac{h\nu}{\frac{h\nu}{kT} + \frac{1}{2}\left(\frac{h\nu}{kT}\right)^2 + \frac{1}{6}\left(\frac{h\nu}{kT}\right)^3} \right.$$

$$\frac{\bar{E}_{osc} - kT}{\bar{E}_{osc}} = \left[\frac{6.626 \times 10^{-34} \text{ J s} \times 1.00 \times 10^{12} \text{ s}^{-1}}{6.626 \times 10^{-34} \text{ J s} \times 1.00 \times 10^{12} \text{ s}^{-1}} \left/ \left\{ \begin{array}{l} \frac{6.626 \times 10^{-34} \text{ J s} \times 1.00 \times 10^{12} \text{ s}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 800 \text{ K}} + \frac{1}{2} \left(\frac{6.626 \times 10^{-34} \text{ J s} \times 1.00 \times 10^{12} \text{ s}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 800 \text{ K}} \right)^2 \\ + \frac{1}{6} \left(\frac{6.626 \times 10^{-34} \text{ J s} \times 1.00 \times 10^{12} \text{ s}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 800 \text{ K}} \right)^3 \end{array} \right\} \right] \right] \left/ -1.381 \times 10^{-23} \text{ J K}^{-1} \times 800 \text{ K} \right]$$

$$\left[\frac{6.626 \times 10^{-34} \text{ J s} \times 1.00 \times 10^{12} \text{ s}^{-1}}{6.626 \times 10^{-34} \text{ J s} \times 1.00 \times 10^{12} \text{ s}^{-1}} \left/ \left\{ \begin{array}{l} \frac{6.626 \times 10^{-34} \text{ J s} \times 1.00 \times 10^{12} \text{ s}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 800 \text{ K}} + \frac{1}{2} \left(\frac{6.626 \times 10^{-34} \text{ J s} \times 1.00 \times 10^{12} \text{ s}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 800 \text{ K}} \right)^2 \\ + \frac{1}{6} \left(\frac{6.626 \times 10^{-34} \text{ J s} \times 1.00 \times 10^{12} \text{ s}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 800 \text{ K}} \right)^3 \end{array} \right\} \right] \right]$$

$$\frac{\bar{E}_{osc} - kT}{\bar{E}_{osc}} = -0.0306 \text{ for } 800 \text{ K. The corresponding values for } 500 \text{ K and } 250 \text{ K are}$$

-0.0495 and -0.102.

P12.17) The observed lines in the emission spectrum of atomic hydrogen are given by

$$\tilde{\nu} (\text{cm}^{-1}) = R_H (\text{cm}^{-1}) \left(\frac{1}{n_1^2} - \frac{1}{n^2} \right) \text{cm}^{-1}, n > n_1. \text{ In the notation favored by spectroscopists,}$$

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{E}{hc} \text{ and } R_H = 109,677 \text{ cm}^{-1}. \text{ The Lyman, Balmer, and Paschen series refers to}$$

$n_1 = 1, 2, \text{ and } 3$, respectively, for emission from atomic hydrogen. What is the highest value of $\tilde{\nu}$ and E in each of these series?

The highest value for $\tilde{\nu}$ corresponds to $\frac{1}{n} \rightarrow 0$. Therefore

$$\tilde{\nu} = R_H \left(\frac{1}{1^2} \right) \text{cm}^{-1} = 109,677 \text{ cm}^{-1} \text{ or } E_{max} = 2.18 \times 10^{-18} \text{ J for the Lyman series.}$$

$$\tilde{\nu} = R_H \left(\frac{1}{2^2} \right) \text{cm}^{-1} = 27419 \text{ cm}^{-1} \text{ or } E_{max} = 5.45 \times 10^{-19} \text{ J for the Balmer series, and}$$

$$\tilde{\nu} = R_H \left(\frac{1}{3^2} \right) \text{cm}^{-1} = 12186 \text{ cm}^{-1} \text{ or } E_{max} = 2.42 \times 10^{-19} \text{ J for the Paschen series}$$

P12.18) A beam of electrons with a speed of $3.50 \times 10^4 \text{ m/s}$ is incident on a slit of width 200 nm. The distance to the detector plane is chosen such that the distance between the central maximum of the diffraction pattern and the first diffraction minimum is 0.500 cm. How far is the detector plane from the slit?

The diffraction minima satisfy the condition $\sin \theta = \frac{n\lambda}{a}$, $n = \pm 1, \pm 2, \dots$ and the first minimum is at $\sin \theta = \pm \frac{\lambda}{a}$. We choose the plus sign (the minus sign gives the distance from the slit in the opposite direction) giving

$$\sin \theta = \frac{\lambda}{a} = \frac{h}{mva} = \frac{6.626 \times 10^{-34} \text{ J s}}{9.109 \times 10^{-31} \text{ kg} \times 3.50 \times 10^4 \text{ m s}^{-1} \times 200 \times 10^{-9} \text{ m}} = 0.10392$$

$$\theta = 5.97 \text{ degrees}$$

The distance d from the screen and the position of the first minimum s are related by

$$d = \frac{s}{\tan \theta} = \frac{0.500 \text{ cm}}{0.1045} = 4.78 \text{ cm.}$$

P12.19) If an electron passes through an electrical potential difference of 1 V, it has an energy of 1 electron-volt. What potential difference must it pass through in order to have a wavelength of 0.100 nm?

$$E = \frac{1}{2} m_e v^2 = \frac{1}{2} m_e \times \left(\frac{h}{m_e \lambda} \right)^2 = \frac{h^2}{2m_e \lambda^2}$$

$$= \frac{(6.626 \times 10^{-34} \text{ J s})^2}{2 \times 9.109 \times 10^{-31} \text{ kg} \times (10^{-10} \text{ m})^2} = 2.41 \times 10^{-17} \text{ J} \times \frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} = 150.4 \text{ eV}$$

The electron must pass through an electrical potential of 150.4 V.

P12.20) What is the maximum number of electrons that can be emitted if a potassium surface of work function 2.40 eV absorbs $3.25 \times 10^{-3} \text{ J}$ of radiation at a wavelength of 300 nm? What is the kinetic energy and velocity of the electrons emitted?

$$E = h \frac{c}{\lambda} - \phi = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{300 \times 10^{-9} \text{ m}} - 2.40 \text{ eV} \times \frac{1.602 \times 10^{-19} \text{ J}}{\text{eV}} = 2.77 \times 10^{-19} \text{ J}$$

$$v = \sqrt{\frac{2E}{m}} = \sqrt{\frac{2 \times 2.77 \times 10^{-19} \text{ J}}{9.109 \times 10^{-31} \text{ kg}}} = 7.80 \times 10^5 \text{ m s}^{-1}$$

$$n = \frac{E_{total}}{E_{photon}} = \frac{E_{total}}{hc/\lambda} = \frac{3.25 \times 10^{-3} \text{ J}}{(6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}) / 300 \times 10^{-9} \text{ m}} = 4.91 \times 10^{15}$$

electrons.

P12.21) The work function of platinum is 5.65 eV. What is the minimum frequency of light required to observe the photoelectric effect on Pt? If light with a 150-nm wavelength is absorbed by the surface, what is the velocity of the emitted electrons?

- a) For electrons to be emitted, the photon energy must be greater than the work function of the surface.

$$E = h\nu \geq 5.65 \text{ eV} \times \frac{1.602 \times 10^{-19} \text{ J}}{\text{eV}} = 9.05 \times 10^{-19} \text{ J}$$

$$\nu \geq \frac{E}{h} \geq \frac{9.05 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} \geq 1.37 \times 10^{15} \text{ s}^{-1}$$

- b) The outgoing electron must first surmount the barrier arising from the work function, so not all the photon energy is converted to kinetic energy.

$$\begin{aligned} E_e &= h\nu - \phi = \frac{hc}{\lambda} - \phi \\ &= \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{150 \times 10^{-9} \text{ m}} - 9.05 \times 10^{-19} \text{ J} = 4.19 \times 10^{-19} \text{ J} \\ v &= \sqrt{\frac{2E_e}{m_e}} = \sqrt{\frac{2 \times 4.19 \times 10^{-19} \text{ J}}{9.11 \times 10^{-31} \text{ kg}}} = 9.59 \times 10^5 \text{ m s}^{-1} \end{aligned}$$

P12.22) X-rays can be generated by accelerating electrons in a vacuum and letting them impact on atoms in a metal surface. If the 1000-eV kinetic energy of the electrons is completely converted to the photon energy, what is the wavelength of the X-rays produced? If the electron current is $1.50 \times 10^{-5} \text{ A}$, how many photons are produced per second?

$$\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{1000 \text{ eV} \times \frac{1.602 \times 10^{-19} \text{ J}}{\text{eV}}} = 1.24 \text{ nm}$$

$$n = \frac{\text{current}}{\text{charge per electron}} = \frac{1.50 \times 10^{-5} \text{ C s}^{-1}}{1.602 \times 10^{-19} \text{ C}} = 9.36 \times 10^{13} \text{ s}^{-1}.$$

P12.23) When a molecule absorbs a photon, both the energy and momentum are conserved. If a H_2 molecule at 300 K absorbs an ultraviolet photon of wavelength 100 nm, what is the change in its velocity Δv ? Given that its average speed is

$$v_{rms} = \sqrt{3kT/m}, \text{ what is } \Delta v / v_{rms}?$$

Because momentum is conserved,

$$p_{photon} = \frac{h}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s}}{100 \times 10^{-9} \text{ m}} = 6.626 \times 10^{-27} \text{ kg m s}^{-1}$$

All this momentum is transferred to the H₂ molecule

$$\Delta p_{H_2} = 6.626 \times 10^{-27} \text{ kg m s}^{-1} = m \Delta v$$

$$\Delta v_{H_2} = \frac{6.626 \times 10^{-27} \text{ kg m s}^{-1}}{2.016 \text{ amu} \times 1.661 \times 10^{-27} \text{ kg/amu}} = 1.98 \text{ m s}^{-1}$$

$$\frac{\Delta v}{v} = \frac{1.98 \text{ m s}^{-1}}{\sqrt{\frac{3RT}{M}}} = \frac{1.98 \text{ m s}^{-1}}{\sqrt{\frac{3 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{2.016 \times 10^{-3} \text{ kg mol}^{-1}}}} = 1.03 \times 10^{-3}$$

Chapter 13: The Schrödinger Equation

Problem numbers in italics indicate that the solution is included in the *Student's Solutions Manual*.

Questions on Concepts

Q13.1) By discussing the diffraction of a beam of particles by a single slit, justify the statement that there is no sharp boundary between particle-like and wave-like behavior.

For a low particle energy, corresponding to a long wavelength, the diffraction pattern is clearly resolved. As the energy increases, the wavelength decreases, the diffraction peak moves closer to the central peak and its intensity decreases. The diffraction peak does not disappear with increasing energy; it simply becomes difficult to observe.

Q13.2) Why does a quantum mechanical system with discrete energy levels behave as if it has a continuous energy spectrum if the energy difference between energy levels ΔE satisfies the relationship $\Delta E \ll kT$?

If the difference in energy between levels becomes small compared to kT , the levels become “smeared out” and overlap. When this happens, the levels can no longer be distinguished, and from the viewpoint of the observer, the system has a continuous energy spectrum.

Q13.3) Why can we conclude that the wave function $\psi(x, t) = \psi(x)e^{-i(E/\hbar)t}$ represents a standing wave?

It represents a standing wave because it can be written as the product of a function that depends only on time with a function that depends only on the spatial coordinate. Therefore the nodes do not move with time.

Q13.4) Why is it true for any quantum mechanical problem that the set of wave functions is larger than the set of eigenfunctions?

The set of all wave functions must satisfy the boundary conditions as well as satisfy the conditions that allow us to interpret the square of the magnitude of the wave function in terms of probability. The set of eigenfunctions must satisfy an additional condition given by the eigenvalue equation. Because some wave functions won't satisfy the eigenvalue equation, the set of wave functions is larger than the set of eigenfunctions.

Q13.5) Is it correct to say that because the de Broglie wavelength of a H₂ molecule at 300 K is on the order of atomic dimensions that all properties of H₂ are quantized?

No. The system must be treated using quantum mechanics if the characteristic size is comparable to the wavelength. For a H₂ molecule moving in a one liter container, the wavelength is much smaller than the characteristic dimension of the container. In this case, the translational energy levels are so closely spaced that they can be described classically. Therefore, the pressure exerted by the H₂ molecules on the walls of the container can be described classically.

Q13.6) In Figure 13.6 the extent to which the approximate and true functions agree was judged visually. How could you quantify the quality of the fit?

You could use a function like $\int [f(x) - g(x)]^2 dx$, where $f(x)$ and $g(x)$ are the functions to be compared, as a quantitative measure of how alike the functions are. The value of the integral goes to zero as the two functions become identical.

Q13.7) If $\psi(x,t) = A \sin(kx - \omega t)$ describes a wave traveling in the plus x direction, how would you describe a wave moving in the minus x direction?

Consider the nodes in the function $\psi(x,t) = A \sin(kx + \omega t)$. The wave amplitude is zero for $2\pi\left(\frac{x}{\lambda} + \frac{t}{T}\right) = n\pi$ where n is an integer. Solving for x , we obtain the location of the nodes. $x = \lambda\left(\frac{n}{2} - \frac{t}{T}\right)$. We see that x decreases as t increases, showing that the wave is moving in the direction of negative x .

Q13.8) A traveling wave with arbitrary phase ϕ can be written as $\psi(x,t) = A \sin(kx - \omega t + \phi)$. What are the units of ϕ ? Show that ϕ could be used to represent a shift in the origin of time or distance.

The units of ϕ are radians. We can rewrite this equation either as $\psi(x,t) = A \sin(k\left[x + \frac{\phi}{k}\right] - \omega t)$ or $\psi(x,t) = A \sin(kx - \omega\left[t - \frac{\phi}{\omega}\right])$. The first of these equations suggests a shift in x , and the second suggests a shift in t .

Q13.9) One source emits spherical waves and another emits plane waves. For which source does the intensity measured by a detector of fixed size fall off more rapidly with distance? Why?

The intensity of the spherical source falls off more rapidly. The total intensity is the same for all spheres centered at the source. Larger spheres correspond to larger distances, and for a given detector area, the fraction of the intensity in the area A is $\frac{A}{4\pi r^2}$, where r is the radius of the sphere, which is equal to the distance

from the source to the detector. Therefore the measured intensity for the spherical source decreases as $1/r^2$. There is no decrease in intensity for the source emitting plane waves. A well collimated light source, such as a laser, is an approximation to a plane wave source.

Q13.10) Distinguish between the following terms applied to a set of functions: orthogonal, normalized, and complete.

Two functions $\phi_i(x)$ and $\phi_j(x)$ are orthogonal if $\int \phi_i^*(x) \phi_j(x) dx = 0$, normalized if $\int \phi_i^*(x) \phi_i(x) dx = \int \phi_j^*(x) \phi_j(x) dx = 1$, and complete if any well behaved function $\psi(x)$ can be expanded in terms of the $\phi_i(x)$, $\psi(x) = \sum_{m=1}^{\infty} b_m \phi_m(x)$.

Problems

P13.1) Assume that a system has a very large number of energy levels given by the formula $\varepsilon = \varepsilon_0 l^2$ with $\varepsilon_0 = 2.34 \times 10^{-22} \text{ J}$, where l takes on the integral values 1, 2, 3, Assume further that the degeneracy of a level is given by $g_l = 2l$. Calculate the ratios n_5/n_1 and n_{10}/n_1 for $T = 100 \text{ K}$ and $T = 650 \text{ K}$, respectively.

$$\frac{n_5}{n_1} = \frac{g_5}{g_1} \exp\left[\frac{-(\varepsilon_5 - \varepsilon_1)}{kT} \right] = \frac{2 \times 5}{2 \times 1} \exp\left[\frac{-(5^2 \varepsilon_0 - \varepsilon_0)}{kT} \right]$$

$$\frac{n_5}{n_1}(100 \text{ K}) = \frac{10}{2} \exp\left[\frac{-2.34 \times 10^{-22} \text{ J} \times (25-1)}{1.381 \times 10^{-23} \text{ JK}^{-1} \times 100 \text{ K}} \right] = 0.086$$

$$\frac{n_5}{n_1}(650 \text{ K}) = \frac{10}{2} \exp\left[\frac{-2.34 \times 10^{-22} \text{ J} \times (25-1)}{1.381 \times 10^{-23} \text{ JK}^{-1} \times 650 \text{ K}} \right] = 2.67$$

$$\frac{n_{10}}{n_1}(100 \text{ K}) = \frac{20}{2} \exp\left[\frac{-2.34 \times 10^{-22} \text{ J} \times (100-1)}{1.381 \times 10^{-23} \text{ JK}^{-1} \times 100 \text{ K}} \right] = 5.2 \times 10^{-7}$$

$$\frac{n_{10}}{n_1}(650 \text{ K}) = \frac{20}{2} \exp\left[\frac{-2.34 \times 10^{-22} \text{ J} \times (100-1)}{1.381 \times 10^{-23} \text{ JK}^{-1} \times 650 \text{ K}} \right] = 0.757$$

P13.2) Consider a two-level system with $\varepsilon_1 = 3.10 \times 10^{-21} \text{ J}$ and $\varepsilon_2 = 6.10 \times 10^{-21} \text{ J}$. If $g_2 = g_1$, what value of T is required to obtain $n_2/n_1 = 0.150$? What value of T is required to obtain $n_2/n_1 = 0.999$?

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \exp\left[\frac{-(\varepsilon_5 - \varepsilon_1)}{kT}\right]$$

$$\ln\left(\frac{n_2}{n_1}\right) = \ln\left(\frac{g_2}{g_1}\right) - \frac{(\varepsilon_5 - \varepsilon_1)}{kT}$$

$$\frac{1}{T} = \frac{k}{(\varepsilon_5 - \varepsilon_1)} \left[\ln\left(\frac{g_2}{g_1}\right) - \ln\left(\frac{n_2}{n_1}\right) \right]$$

$$T = \frac{(\varepsilon_5 - \varepsilon_1)}{k \left[\ln\left(\frac{g_2}{g_1}\right) - \ln\left(\frac{n_2}{n_1}\right) \right]}$$

$$\text{for } n_2/n_1 = 0.150 \quad T = \frac{3.00 \times 10^{-21} \text{J}}{1.381 \times 10^{-23} \text{J K}^{-1} \times [\ln(1) - \ln(0.150)]} = 115 \text{K}$$

$$\text{for } n_2/n_1 = 0.999 \quad T = \frac{3.00 \times 10^{-21} \text{J}}{1.381 \times 10^{-23} \text{J K}^{-1} \times [\ln(1) - \ln(0.999)]} = 2.17 \times 10^5 \text{K}$$

P13.3) To plot $\Psi(x, t) = A \sin(kx - \omega t)$ as a function of one of the variables x and t , the other variable needs to be set at a fixed value, x_0 or t_0 . If $\frac{\Psi(x_0, 0)}{\Psi_{\max}} = -0.280$, what is the constant value of x_0 in the upper panel of Figure 13.3? If $\frac{\Psi(0, t_0)}{\Psi_{\max}} = -0.309$, what is the constant value of t_0 in the lower panel of Figure 13.3? (Hint: The inverse sine function has two solutions within an interval of 2π . Make sure that you choose the correct one.)

$$\text{For the traveling wave } \Psi(x, t) = A \sin 2\pi \left(\frac{x}{\lambda} - \frac{t}{T} \right) = A \sin 2\pi \left(\frac{x}{1.46} - \frac{t}{1.00 \times 10^{-3}} \right)$$

$$\frac{\Psi(x_0, 0)}{\Psi_{\max}} = \sin 2\pi \left(\frac{x_0}{1.46 \text{m}} \right) = -0.284; \quad 2\pi \left(\frac{x_0}{1.46 \text{m}} \right)$$

$$= -0.28 \text{ radians or } \pi - (-0.28) = 3.43 \text{ radians}$$

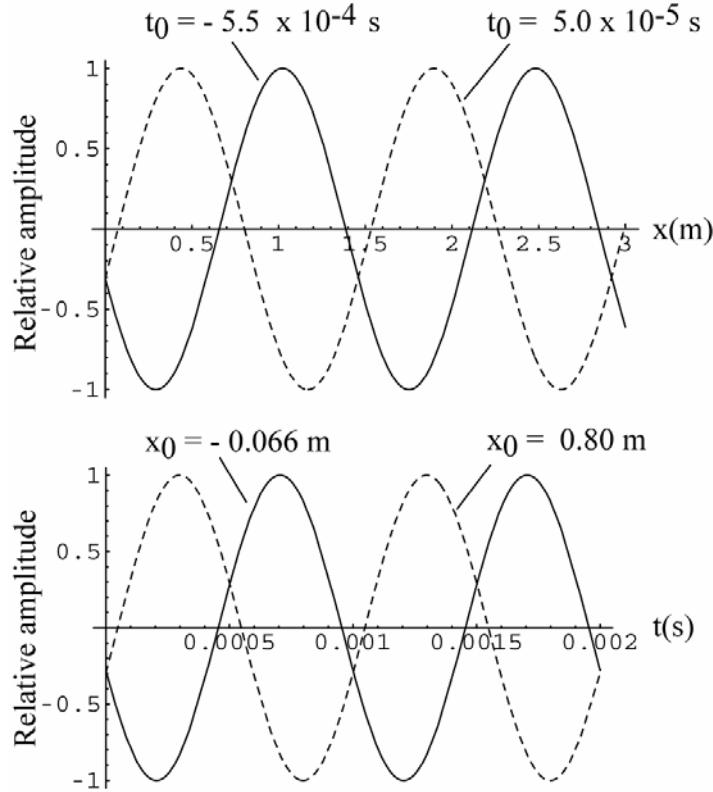
$$x = -6.4 \times 10^{-2} \text{ m or } 0.79 \text{ m}$$

$$\frac{\Psi(0, t_0)}{\Psi_{\max}} = A \sin 2\pi \left(\frac{-t_0}{1.00 \times 10^{-3} \text{s}} \right) = -0.309; \quad 2\pi \left(\frac{-t_0}{1.00 \times 10^{-3} \text{s}} \right)$$

$$= -0.31 \text{ radians or } \pi - (-0.31) = 3.45 \text{ radians}$$

$$t_0 = 5.0 \times 10^{-5} \text{s or } -5.5 \times 10^{-4} \text{s}$$

To decide which of the two values best fits the data in Figure 13.2, it is necessary to plot the data.



It is seen that the data are fit by $x_0 = 0.79$ m and $t_0 = -5.5 \times 10^{-4}$ s. Adding any positive or negative integral multiple of λ to x_0 or T to t_0 will give equally good agreement.

P13.4) A wave traveling in the z direction is described by the wave function

$$\Psi(z, t) = A_1 \mathbf{x} \sin(kz - \omega t + \phi_1) + A_2 \mathbf{y} \sin(kz - \omega t + \phi_2) \text{ where}$$

\mathbf{x} and \mathbf{y} are vectors of unit length along the x and y axes, respectively. Because the amplitude is perpendicular to the propagation direction, $\Psi(z, t)$ represents a transverse wave.

- a) What requirements must A_1 and A_2 satisfy for a plane polarized wave in the x - z plane?
- b) What requirements must A_1 and A_2 satisfy for a plane polarized wave in the y - z plane?
- c) What requirements must A_1 and A_2 and ϕ_1 and ϕ_2 satisfy for a plane polarized wave in a plane oriented at 45° to the x - z plane?
- d) What requirements must A_1 and A_2 and ϕ_1 and ϕ_2 satisfy for a circularly polarized wave?

- a) The amplitude along the x axis must oscillate, and the amplitude along the y axis must vanish. Therefore $A_1 \neq 0$ and $A_2 = 0$.

- b) The amplitude along the y axis must oscillate, and the amplitude along the x axis must vanish. Therefore $A_1 = 0$ and $A_2 \neq 0$.

- c) The amplitude along both the x and y axes must oscillate. Therefore $A_1 \neq 0$ and $A_2 \neq 0$. Because they must oscillate in phase, $\phi_1 = \phi_2$.
- d) The amplitude along both the x and y axes must oscillate with the same amplitude. Therefore $A_1 = A_2 \neq 0$. For circularly a polarized wave, the x and y components must be out of phase by $\pi/2$. Therefore $\phi_1 = \phi_2 \pm \frac{\pi}{2}$. This can be seen by comparing the x and y amplitudes for the positive sign.

$$\Psi(z, t) = A_1 \mathbf{x} \sin(kz - \omega t + \phi_1) + A_1 \mathbf{y} \sin(kz - \omega t + \phi_1 + \frac{\pi}{2})$$

$$\text{let } kz + \phi = kz'$$

$$\begin{aligned}\Psi(z, t) &= A_1 \mathbf{x} \sin(kz' - \omega t) + A_1 \mathbf{y} \sin(kz' - \omega t + \frac{\pi}{2}) \\ &= A_1 \mathbf{x} \sin(kz' - \omega t) + A_1 \mathbf{y} \left[\sin(kz' - \omega t) \cos \frac{\pi}{2} + \cos(kz' - \omega t) \sin \frac{\pi}{2} \right] \\ &= A_1 \mathbf{x} \sin(kz' - \omega t) + A_1 \mathbf{y} \cos(kz' - \omega t)\end{aligned}$$

The x and y amplitudes are $\pi/2$ out of phase and the sum of the squares of their amplitudes is a constant as required for a circle.

P13.5) Show that $\frac{a+ib}{c+id} = \frac{ac+bd+i(bc-ad)}{c^2+d^2}$

$$\frac{a+ib}{c+id} = \left(\frac{a+ib}{c+id} \right) \left(\frac{c-id}{c-id} \right) = \frac{ac+bd+ibc-iad}{c^2+d^2} = \frac{ac+bd+i(bc-ad)}{c^2+d^2}$$

- P13.6)** Does the superposition $\psi(x, t) = A \sin(kx - \omega t) + 2A \sin(kx + \omega t)$ generate a standing wave? Answer this question by using trigonometric identities to combine the two terms.

$$\psi(x, t) = A \sin(kx - \omega t) + 2A \sin(kx + \omega t)$$

Using the identities

$$\sin(\alpha \pm \beta) = \sin \alpha \cos \beta \pm \cos \alpha \sin \beta$$

$$\cos(\alpha \pm \beta) = \cos \alpha \cos \beta \mp \sin \alpha \sin \beta$$

the previous equation can be simplified to

$$\begin{aligned}\psi(x, t) &= A \sin kx \cos \omega t - A \cos kx \sin \omega t + 2A \sin kx \cos \omega t + 2A \cos kx \sin \omega t \\ &= 3A \sin kx \cos \omega t + A \cos kx \sin \omega t\end{aligned}$$

Because the wave function cannot be written as a single product of a function that is periodic in length with one that is periodic in time, the nodes will not be stationary. Therefore it is not a standing wave.

P13.7) Express the following complex numbers in the form $re^{i\theta}$.

a) $2 - 4i$ b) 6 c) $\frac{3+i}{4i}$ d) $\frac{8+i}{2-4i}$

In the notation $re^{i\theta}$, $r = |z| = \sqrt{a^2 + b^2}$ and $\theta = \cos^{-1}\left(\frac{\operatorname{Re} z}{|z|}\right)$.

a) $2 - 4i = 2\sqrt{5} \exp\left(i \cos^{-1} \frac{1}{\sqrt{5}}\right) = 2\sqrt{5} \exp(0.352i\pi)$
 b) $6 = 6 \exp(i \cos^{-1} 1) = 6 \exp(0)$
 c) $\frac{3+i}{4i} = \frac{1}{4} - \frac{3i}{4} = \frac{\sqrt{10}}{4} \exp\left(i \cos^{-1} \frac{1}{\sqrt{10}}\right) = \frac{\sqrt{10}}{4} \exp(0.398i\pi)$
 d) $\frac{8+i}{2-4i} = \frac{3}{5} + \frac{17i}{10} = \frac{\sqrt{13}}{2} \exp\left(i \cos^{-1} \frac{6}{5\sqrt{13}}\right) = \frac{\sqrt{13}}{2} \exp(0.392i\pi)$

P13.8) Express the following complex numbers in the form $a + ib$.

a) $2e^{i\pi/2}$ b) $2\sqrt{5} e^{-i\pi/2}$ c) $e^{i\pi}$ d) $\frac{3\sqrt{2}}{5+\sqrt{3}} e^{i\pi/4}$

To convert to the form $a + ib$, we use the equations $\operatorname{Re} z = z \cos \theta$ and $\operatorname{Im} z = z \sin \theta$

a) $2e^{i\pi/2} = 2 \cos \frac{\pi}{2} + \left(2 \sin \frac{\pi}{2}\right)i = 2i$
 b) $2\sqrt{5} e^{-i\pi/2} = 2\sqrt{5} \cos \frac{-\pi}{2} + \left(2\sqrt{5} \sin \frac{-\pi}{2}\right)i = -2\sqrt{5}i$
 c) $e^{i\pi} = \cos \pi + (\sin \pi)i = -1$
 d) $\frac{3\sqrt{2}}{5+\sqrt{3}} e^{i\pi/4} = \frac{3\sqrt{2}}{5+\sqrt{3}} \cos \frac{\pi}{4} + \left(\frac{3\sqrt{2}}{5+\sqrt{3}} \sin \frac{\pi}{4}\right)i = \frac{3\sqrt{2}}{5+\sqrt{3}} \frac{\sqrt{2}}{2} \cos \frac{\pi}{4} + \left(\frac{3\sqrt{2}}{5+\sqrt{3}} \frac{\sqrt{2}}{2}\right)i$
 $= \frac{3}{5+\sqrt{3}}(1+i)$

P13.9) Using the exponential representation of the sine and cosine functions

$$\cos \theta = \frac{1}{2}(e^{i\theta} + e^{-i\theta}) \quad \text{and} \quad \sin \theta = \frac{1}{2i}(e^{i\theta} - e^{-i\theta}), \text{ show that}$$

a) $\cos^2 \theta + \sin^2 \theta = 1$

b) $\frac{d(\cos \theta)}{d \theta} = -\sin \theta$

Chapter 13/The Schrödinger Equation

c) $\sin\left(\theta + \frac{\pi}{2}\right) = \cos \theta$

a)

$$\begin{aligned} \cos^2 \theta + \sin^2 \theta &= \left[\frac{1}{2} (e^{i\theta} + e^{-i\theta}) \right]^2 + \left[\frac{1}{2i} (e^{i\theta} - e^{-i\theta}) \right]^2 \\ &= \frac{1}{4} (2 + e^{2i\theta} + e^{-2i\theta}) - \frac{1}{4} (-2 + e^{2i\theta} + e^{-2i\theta}) = 1 \end{aligned}$$

b)

$$\frac{d(\cos \theta)}{d\theta} = \frac{d\left[\frac{1}{2}(e^{i\theta} + e^{-i\theta})\right]}{d\theta} = \frac{1}{2}(ie^{i\theta} - ie^{-i\theta}) = -\frac{1}{2}(e^{i\theta} - e^{-i\theta}) = -\sin \theta$$

c)

$$\sin\left(\theta + \frac{\pi}{2}\right) = \frac{1}{2i} \left(e^{i\left[\theta + \frac{\pi}{2}\right]} - e^{-i\left[\theta + \frac{\pi}{2}\right]} \right) = \frac{1}{2i} \left(e^{i\frac{\pi}{2}} e^{i\theta} - e^{-i\frac{\pi}{2}} e^{-i\theta} \right) = \frac{i}{2i} (e^{i\theta} + e^{-i\theta}) = \cos \theta$$

P13.10) Determine in each of the following cases if the function in the first column is an eigenfunction of the operator in the second column. If so, what is the eigenvalue?

a) $\sin \theta \cos \phi$	$\frac{\partial}{\partial \phi}$
b) $e^{-x^2/2}$	$\frac{1}{x} \frac{d}{dx}$
c) $\sin \theta$	$\frac{\sin \theta}{\cos \theta} \frac{d}{d\theta}$

a) $\sin \theta \cos \phi \quad \frac{\partial}{\partial \phi}$

$$\frac{\partial}{\partial \phi} \sin \theta \cos \phi = -\sin \theta \sin \phi. \quad \text{Not an eigenfunction}$$

b) $e^{-x^2/2} \quad \frac{1}{x} \frac{d}{dx}$

$$\frac{1}{x} \frac{d}{dx} e^{-x^2/2} = -e^{-x^2/2} \quad \text{Eigenfunction with eigenvalue } -1$$

c) $\sin \theta \quad \frac{\sin \theta}{\cos \theta} \frac{d}{d\theta}$

$$\frac{\sin \theta}{\cos \theta} \frac{d}{d\theta} \sin \theta = \sin \theta \quad \text{Eigenfunction with eigenvalue } +1$$

P13.11) Determine in each of the following cases if the function in the first column is an eigenfunction of the operator in the second column. If so, what is the eigenvalue?

a) $x^3 \quad \frac{d^3}{dx^3}$

b) $x y \quad x \frac{\partial}{\partial x} + y \frac{\partial}{\partial y}$

c) $\sin \theta \cos \phi \quad \frac{\partial^2}{\partial \theta^2}$

a) $x^3 \quad \frac{d}{dx^3}$

$$\frac{d x^3}{d x^3} = 6 \quad \text{Not an eigenfunction}$$

b) $x y \quad x \frac{\partial}{\partial x} + y \frac{\partial}{\partial y}$

$$x \frac{\partial xy}{\partial x} + y \frac{\partial xy}{\partial y} = 2xy \quad \text{Eigenfunction with eigenvalue } +2$$

c) $\sin \theta \cos \phi \quad \frac{\partial^2}{\partial \theta^2}$

$$\frac{\partial^2}{\partial \theta^2} (\sin \theta \cos \phi) = -\sin \theta \cos \phi \quad \text{Eigenfunction with eigenvalue } -1$$

P13.12) Determine in each of the following cases if the function in the first column is an eigenfunction of the operator in the second column. If so, what is the eigenvalue?

a) $3 \cos^2 \theta - 1 \quad \frac{1}{\sin \theta} \frac{d}{d \theta} \left(\sin \theta \frac{d}{d \theta} \right)$

b) $e^{-x^2/2} \quad \frac{d^2}{dx^2} - x^2$

c) $e^{-4i\phi} \quad \frac{d^2}{d\phi^2}$

a) $3 \cos^2 \theta - 1 \quad \frac{1}{\sin \theta} \frac{d}{d \theta} \left(\sin \theta \frac{d}{d \theta} \right)$

$$\frac{1}{\sin \theta} \frac{d}{d \theta} \left(\sin \theta \frac{d(3 \cos^2 \theta - 1)}{d \theta} \right) = \frac{1}{\sin \theta} \frac{d}{d \theta} (-6 \cos \theta \sin^2 \theta)$$

$$= \frac{1}{\sin \theta} (6 \sin^3 \theta - 12 \cos^2 \theta \sin \theta) = 6 \sin^2 \theta - 12 \cos^2 \theta$$

$$= 6 - 18 \cos^2 \theta = -6(3 \cos^2 \theta - 1)$$

Chapter 13/The Schrödinger Equation

Eigenfunction with eigenvalue -6.

b) $e^{-\frac{1}{2}x^2}$ $\frac{d^2}{dx^2} - x^2$

$$\frac{d^2 e^{-\frac{1}{2}x^2}}{dx^2} - x^2 e^{-\frac{1}{2}x^2} = -e^{-\frac{1}{2}x^2}$$

Eigenfunction with eigenvalue -1.

c) $e^{-4i\phi}$ $\frac{d^2}{d\phi^2}$

$$\frac{d^2 e^{-4i\phi}}{d\phi^2} = -16e^{-4i\phi}$$

Eigenfunction with eigenvalue -16.

P13.13) Determine in each of the following cases if the function in the first column is an eigenfunction of the operator in the second column. If so, what is the eigenvalue?

a) $e^{-i(3x+2y)}$ $\frac{\partial^2}{\partial x^2}$

b) $\sqrt{x^2 + y^2}$ $\frac{1}{x}(x^2 + y^2) \frac{\partial}{\partial x}$

c) $\sin \theta \cos \theta \sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) + 6 \sin^2 \theta$

a) $e^{-i(3x+2y)}$ $\frac{\partial^2}{\partial x^2}$

$$\frac{\partial^2 e^{-i(3x+2y)}}{\partial x^2} = -9e^{-i(3x+2y)} \quad \text{Eigenfunction with eigenvalue -9.}$$

b) $\sqrt{x^2 + y^2}$ $\frac{1}{x}(x^2 + y^2) \frac{\partial}{\partial x}$

$$\frac{1}{x}(x^2 + y^2) \frac{\partial \sqrt{x^2 + y^2}}{\partial x} = \sqrt{x^2 + y^2} \quad \text{Eigenfunction with eigenvalue +1.}$$

c) $\sin \theta \cos \theta \sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) + 6 \sin^2 \theta$

$$\begin{aligned} \sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d \sin \theta \cos \theta}{d\theta} \right) + 6 \sin^3 \theta \cos \theta &= \sin \theta \frac{d}{d\theta} \left(\sin \theta [1 - 2 \sin^2 \theta] \right) + 6 \sin^3 \theta \cos \theta \\ &= \sin \theta (\cos \theta - 6 \sin^2 \theta \cos \theta) + 6 \sin^3 \theta \cos \theta = \sin \theta \cos \theta \end{aligned}$$

Eigenfunction with eigenvalue +1.

P13.14) Which of the following wave functions are eigenfunctions of the operator d/dx ? If they are eigenfunctions, what is the eigenvalue?

a) $a e^{-3x} + b e^{-3ix}$ b) $\sin^2 x$ c) e^{-ix} d) $\cos a x$ e) e^{-ix^2}

a) $\frac{d(a e^{-3x} + b e^{-3ix})}{d x} = -3a e^{-3x} - 3i b e^{-3ix}$ Not an eigenfunction

b) $\frac{d \sin^2 x}{d x} = 2 \sin x \cos x$ Not an eigenfunction

c) $\frac{d e^{-ix}}{d x} = -i e^{-ix}$ Eigenfunction with eigenvalue $-i$

d) $\frac{d \cos a x}{d x} = -a \sin a x$ Not an eigenfunction

e) $\frac{d e^{-ix^2}}{d x} = -2i x e^{-ix^2}$ Not an eigenfunction

P13.15) Which of the following wave functions are eigenfunctions of the operator d^2/dx^2 ? If they are eigenfunctions, what is the eigenvalue?

a) $a e^{-3x} + b e^{-3ix}$ b) $\sin^2 x$ c) e^{-ix} d) $\cos a x$ e) e^{-ix^2}

a) $\frac{d^2(a e^{-3x} + b e^{-3ix})}{d x^2} = 9a e^{-3x} - 9b e^{-3ix}$ Not an eigenfunction

b) $\frac{d^2 \sin^2 x}{d x^2} = -2 \sin^2 x + 2 \cos^2 x$ Not an eigenfunction

c) $\frac{d^2 e^{-ix}}{d x^2} = -e^{-ix}$ Eigenfunction with eigenvalue -1

d) $\frac{d^2 \cos a x}{d x^2} = -a^2 \cos a x$ Eigenfunction with eigenvalue $-a^2$

e) $\frac{d^2 e^{-ix^2}}{d x^2} = -2i e^{-ix^2} - 4x^2 e^{-ix^2}$ Not an eigenfunction

P13.16) If two operators act on a wave function as indicated by $\hat{A}\hat{B} f(x)$, it is important to carry out the operations in succession with the first operation being that nearest to the

Chapter 13/The Schrödinger Equation

function. Mathematically, $\hat{A}\hat{B} f(x) = \hat{A}(\hat{B} f(x))$ and $\hat{A}^2 f(x) = \hat{A}(\hat{A} f(x))$. Evaluate the following successive operations $\hat{A}\hat{B} f(x)$. The operators \hat{A} and \hat{B} are listed in the first and second columns and $f(x)$ is listed in the third column.

a) $\frac{d}{dx}$ $\frac{d}{dx}$ $x^2 + e^{ax^2}$

b) $\frac{\partial^2}{\partial y^2}$ $\frac{\partial}{\partial x}$ $(\cos 3y) \sin^2$

c) $\frac{\partial}{\partial \theta}$ $\frac{\partial^2}{\partial \phi^2}$ $\frac{\cos \phi}{\sin \theta}$

$$\text{a)} \frac{d}{dx} \left[\frac{d(x^2 + e^{ax^2})}{dx} \right] = \frac{d}{dx} [2x + 2a x e^{ax^2}] = 2 + 4a^2 x^2 e^{ax^2} + 2a e^{ax^2}$$

$$\text{b)} \frac{\partial^2}{\partial y^2} \left[\frac{\partial(\cos 3y \sin^2 x)}{\partial x} \right] = \frac{\partial^2}{\partial y^2} [2 \cos 3y \sin x \cos x] = -18 \cos 3y \sin x \cos x$$

$$\text{c)} \frac{\partial}{\partial \theta} \left[\frac{\partial^2 \left(\frac{\cos \phi}{\sin \theta} \right)}{\partial \phi^2} \right] = \frac{\partial}{\partial \theta} \left[-\frac{\cos \phi}{\sin \theta} \right] = \frac{\cos \phi \cos \theta}{\sin^2 \theta}$$

P13.17) If two operators act on a wave function as indicated by $\hat{A}\hat{B} f(x)$, it is important to carry out the operations in succession with the first operation being that nearest to the function. Mathematically, $\hat{A}\hat{B} f(x) = \hat{A}(\hat{B} f(x))$ and $\hat{A}^2 f(x) = \hat{A}(\hat{A} f(x))$. Evaluate the following successive operations $\hat{A}\hat{B} f(x)$. The operators \hat{A} and \hat{B} are listed in the first two columns and $f(x)$ is listed in the third column.

a) $\frac{d}{dx}$ x $x e^{-ax^2}$

b) x $\frac{d}{dx}$ $x e^{-ax^2}$

c) $y \frac{\partial}{\partial x}$ $x \frac{\partial}{\partial y}$ $e^{-a(x^2+y^2)}$

Note that your answers to parts (a) and (b) are not identical. As we will learn in Chapter 18, the fact that switching the order of the operators x and d/dx changes the outcome of the operation $\hat{A}\hat{B} f(x)$ is the basis for the Heisenberg uncertainty principle.

a) $\frac{d}{dx} \left[x(x e^{-ax^2}) \right] = 2x e^{-ax^2} - 2a x^3 e^{-ax^2}$

b) $x \left[\frac{d}{dx} (x e^{-ax^2}) \right] = x e^{-ax^2} - 2a x^3 e^{-ax^2}$

c) $y \frac{\partial}{\partial x} \left[x \frac{\partial (e^{-a(x^2+y^2)})}{\partial y} \right] = y \frac{\partial}{\partial x} \left[-2a x y e^{-a(x^2+y^2)} \right] =$
 $= -2a y^2 e^{-a(x^2+y^2)} + 4a^2 x^2 y^2 e^{-a(x^2+y^2)}$

P13.18) Find the result of operating with $\frac{d^2}{dx^2} - 4x^2$ on the function e^{-ax^2} . What must the value of a be to make this function an eigenfunction of the operator?

$$\frac{d^2 e^{-ax^2}}{dx^2} - 4x^2 e^{-ax^2} = -2ae^{-ax^2} - 4x^2 e^{-ax^2} + 4a^2 x^2 e^{-ax^2} = -2ae^{-ax^2} + 4(a^2 - 1)x^2 e^{-ax^2}$$

For the function to be an eigenfunction of the operator, the terms containing $x^2 e^{-ax^2}$ must vanish. This is the case if $a = \pm 1$.

P13.19) Find the result of operating with $(1/r^2)(d/dr)(r^2 d/dr) + 2/r$ on the function Ae^{-br} . What must the values of A and b be to make this function an eigenfunction of the operator?

$$\begin{aligned} \frac{1}{r^2} \frac{d}{dr} r^2 \frac{dAe^{-br}}{dr} + \frac{2Ae^{-br}}{r} &= \frac{1}{r^2} \frac{d}{dr} (-bAr^2 e^{-br}) + \frac{2Ae^{-br}}{r} \\ &= \frac{1}{r^2} (-2brAe^{-br} + b^2 r^2 A e^{-br}) + \frac{2Ae^{-br}}{r} \\ &= \frac{2Ae^{-br}}{r} (2 - 2b) + b^2 A e^{-br} \end{aligned}$$

To be an eigenfunction of the operator, the terms in $\frac{Ae^{-br}}{r}$ must vanish. This requires that $b = 1$. There are no restrictions on the value of A .

P13.20) Find the result of operating with $\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$ on the function $x^2 + y^2 + z^2$.

Is this function an eigenfunction of the operator?

$\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right) (x^2 + y^2 + z^2) = 6$. Therefore, the function is not an eigenfunction of the operator.

P13.21) Show that the set of functions $\phi_n(\theta) = e^{in\theta}$, $0 \leq \theta \leq 2\pi$, are orthogonal if n and m are integers. To do so, you need to show that the integral

$$\int_0^{2\pi} \phi_m^*(\theta) \phi_n(\theta) d\theta = 0 \text{ for } m \neq n \text{ if } n \text{ and } m \text{ are integers.}$$

$$\begin{aligned} \int_0^{2\pi} \phi_m^*(\theta) \phi_n(\theta) d\theta &= \int_0^{2\pi} e^{-im\theta} e^{in\theta} d\theta = \int_0^{2\pi} e^{i(n-m)\theta} d\theta = \left[\frac{1}{i(n-m)} e^{i(n-m)\theta} \right]_0^{2\pi} \\ &= \frac{1}{i(n-m)} [e^{i(n-m)2\pi} - e^0] = \frac{1}{i(n-m)} [\cos(n-m)2\pi + \sin(n-m)2\pi - 1] \end{aligned}$$

Because n and m are integers, $(n-m)$ is an integer and the arguments of the sine and cosine functions are integral multiples of 2π .

$$\int_0^{2\pi} \phi_m^*(\theta) \phi_n(\theta) d\theta = \frac{1}{i(n-m)} [1 + 0 - 1] = 0$$

P13.22) Show by carrying out the integration that $\sin(m\pi x/a)$ and $\cos(m\pi x/a)$, where m is an integer, are orthogonal over the interval $0 \leq x \leq a$. Would you get the same result if you used the interval $0 \leq x \leq 3a/4$? Explain your result.

$$\begin{aligned} \int_0^a \cos\left(\frac{m\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx &= \left[\frac{a}{2m\pi} \sin^2\left(\frac{m\pi x}{a}\right) \right]_0^a = \frac{a}{2m\pi} [\sin^2(m\pi) - 0] = 0 \\ \int_0^{\frac{3a}{4}} \cos\left(\frac{m\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx &= \int_0^{\frac{3a}{4}} \cos\left(\frac{m\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx \\ &= \left[\frac{a}{2m\pi} \sin^2\left(\frac{m\pi x}{a}\right) \right]_0^{\frac{3a}{4}} = \frac{a}{2m\pi} \left[\sin^2\left(\frac{3m\pi}{4}\right) - 0 \right] \neq 0 \end{aligned}$$

except for the special case $\frac{3m}{4} = n$ where n is an integer. The length of the integration interval must be n periods (for n an integer) to make the integral zero.

P13.23) Normalize the set of functions $\phi_n(\theta) = e^{in\theta}$, $0 \leq \theta \leq 2\pi$. To do so, you need to multiply the functions by a so-called normalization constant N so that the integral

$$N N^* \int_0^{2\pi} \phi_m^*(\theta) \phi_n(\theta) d\theta = 1 \text{ for } m = n$$

$$N N^* \int_0^{2\pi} e^{-in\theta} e^{in\theta} d\theta = N N^* \int_0^{2\pi} d\theta = 2\pi N N^* = 1 \text{ This is satisfied for } N = \frac{1}{\sqrt{2\pi}}$$

normalized functions are $\phi_n(\theta) = \frac{1}{\sqrt{2\pi}} e^{in\theta}$, $0 \leq \theta \leq 2\pi$.

P13.24) In normalizing wave functions, the integration is over all space in which the wave function is defined. The following examples allow you to practice your skills in two- and three-dimensional integration.

a) Normalize the wave function $\sin\left(\frac{n\pi x}{a}\right)\sin\left(\frac{m\pi y}{b}\right)$ over the range

$0 \leq x \leq a$, $0 \leq y \leq b$. The element of area in two-dimensional Cartesian coordinates is $dx dy$; n and m are integers and a and b are constants.

b) Normalize the wave function $e^{-r/a} \cos\theta \sin\phi$ over the interval

$0 \leq r < \infty$, $0 \leq \theta \leq \pi$, $0 \leq \phi \leq 2\pi$. The volume element in three-dimensional spherical coordinates is $r^2 \sin\theta dr d\theta d\phi$.

a)

$$1 = N^2 \int_0^a \int_0^b \sin^2\left(\frac{n\pi x}{a}\right) \sin^2\left(\frac{m\pi y}{b}\right) dx dy$$

$$\text{Let } u = \frac{n\pi x}{a}, w = \frac{m\pi y}{b}; \text{ then } dx = \frac{adu}{n\pi} \text{ and } dy = \frac{bdw}{m\pi}$$

$$1 = N^2 \frac{a}{n\pi} \frac{b}{m\pi} \int_0^{m\pi} \int_0^{n\pi} \sin^2 u \sin^2 w du dw$$

$$= N^2 \frac{a}{n\pi} \frac{b}{m\pi} \left[\int_0^{m\pi} \sin^2 u du \right] \left[\int_0^{n\pi} \sin^2 w dw \right]$$

$$\text{Using the standard integral } \int (\sin^2 ax) dx = \frac{1}{2}x - \frac{1}{4a} \sin 2ax$$

$$1 = N^2 \frac{a}{n\pi} \frac{b}{m\pi} \left[\left(\frac{m\pi}{2} - \frac{1}{4} \sin 2m\pi - 0 - \frac{1}{4} \sin 0 \right) \right] \times \left[\left(\frac{n\pi}{2} - \frac{1}{4} \sin 2n\pi - 0 - \frac{1}{4} \sin 0 \right) \right]$$

$$= N^2 \frac{a}{n\pi} \frac{b}{m\pi} \frac{n\pi}{2} \frac{m\pi}{2} = N^2 \frac{ab}{4}$$

$$N = \frac{2}{\sqrt{ab}}$$

b)

$$1 = N^2 \int_0^{2\pi} d\phi \int_0^\pi d\theta \int_0^\infty e^{-2r/a} \cos^2 \theta \sin^2 \phi r^2 \sin \theta dr = N^2 \int_0^{2\pi} \sin^2 \phi d\phi \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^\infty r^2 e^{-2r/a} dr$$

Using the standard integral $\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$ ($a > 0$, n positive integer)

$$1 = N^2 \left(\frac{2\pi}{2} - \frac{1}{4} \sin 2\pi - 0 - \frac{1}{4} \sin 0 \right) \times \frac{1}{3} (\cos^3 0 - \cos \pi) \times \left(\frac{2! a^3}{2^3} \right) = N^2 a^3 \frac{\pi}{6}$$

$$N = \sqrt{\frac{6}{\pi a^3}}$$

P13.25) Show that the following pairs of wave functions are orthogonal over the indicated range.

a) $e^{-\frac{1}{2}\alpha x^2}$ and $(2\alpha x^2 - 1)e^{-\frac{1}{2}\alpha x^2}$, $-\infty \leq x < \infty$ where α is a constant that is greater than zero.

b) $\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$ and $\frac{r}{a_0} e^{-r/2a_0} \cos \theta$ over the interval $0 \leq r < \infty$, $0 \leq \theta \leq \pi$, $0 \leq \phi \leq 2\pi$

a)

$$\begin{aligned} \int_{-\infty}^{\infty} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} e^{-\frac{1}{2}\alpha x^2} dx &= \int_{-\infty}^{\infty} (2\alpha x^2 - 1) e^{-\alpha x^2} dx = 2\alpha \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx - \int_{-\infty}^{\infty} e^{-\alpha x^2} dx \\ &= 4\alpha \int_0^{\infty} x^2 e^{-\alpha x^2} dx - 2 \int_0^{\infty} e^{-\alpha x^2} dx \text{ because the integrand is an even function of } x. \end{aligned}$$

Using the standard integrals $\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$ ($a > 0$, n positive integer)

$$\text{and } \int_0^\infty e^{-ax^2} dx = \left(\frac{\pi}{4a} \right)^{1/2}$$

$$\int_{-\infty}^{\infty} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} e^{-\frac{1}{2}\alpha x^2} dx = 4\alpha \frac{1}{2^2 \alpha} \sqrt{\frac{\pi}{\alpha}} - \sqrt{\frac{\pi}{\alpha}} = 0$$

b)

$$\begin{aligned}
& \int_0^{2\pi} d\phi \int_0^\pi \cos \theta \sin \theta d\theta \int_0^\infty \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} \frac{r}{a_0} e^{-r/2a_0} r^2 dr \\
&= 2\pi \left(\int_0^\pi \cos \theta \sin \theta d\theta \right) \left(\int_0^\infty \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} \frac{r}{a_0} e^{-r/2a_0} r^2 dr \right) \\
&= 2\pi \left(\int_0^\infty \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} \frac{r}{a_0} e^{-r/2a_0} r^2 dr \right) \left(\frac{1}{2} \cos^2 0 - \frac{1}{2} \cos^2 \pi \right) = 0
\end{aligned}$$

P13.26) Because $\int_0^d \cos\left(\frac{n\pi x}{d}\right) \cos\left(\frac{m\pi x}{d}\right) dx = 0$, $m \neq n$, the functions

$\cos(n\pi x/d)$ for $n = 1, 2, 3, \dots$ form an orthogonal set. What constant must these functions be multiplied by to form an orthonormal set?

$$1 = N^2 \int_0^d \cos\left(\frac{m\pi x}{d}\right) \cos\left(\frac{m\pi x}{d}\right) dx = N^2 \left[\frac{x}{2} + \frac{d}{4m\pi} \sin\left(\frac{2m\pi x}{d}\right) \right]_0^d$$

where we have used the standard integral $\int (\cos^2 ax) dx = \frac{1}{2}x + \frac{1}{4a} \sin 2ax$

$$1 = N^2 \left[\frac{d}{2} + \frac{d}{4m\pi} \sin(2m\pi) - \frac{0}{2} - \frac{d}{4m\pi} \sin(0) \right] = \frac{d}{2} N^2 = 1$$

$$N = \sqrt{\frac{2}{d}}$$

P13.27) Use a Fourier series expansion to express the function $f(x) = x$, $-b \leq x \leq b$ in the form $f(x) = d_0 + \sum_{n=1}^m c_n \sin\left(\frac{n\pi x}{b}\right) + d_n \cos\left(\frac{n\pi x}{b}\right)$. Obtain d_0 and the first five coefficients c_n and d_n .

Chapter 13/The Schrödinger Equation

$$d_0 = \frac{1}{2b} \int_{-b}^b f(x) dx = \frac{1}{2b} \int_{-b}^b x dx = 0$$

$$d_n = \frac{1}{b} \int_{-b}^b f(x) \cos\left(\frac{n\pi x}{b}\right) dx = \frac{1}{b} \int_{-b}^b x \cos\left(\frac{n\pi x}{b}\right) dx$$

Using the standard integral $\int x \cos ax = \frac{\cos ax}{a^2} + \frac{x \sin ax}{a}$

$$d_n = \frac{1}{b} \left[\left(\frac{b}{n\pi} \right)^2 \cos\left(\frac{n\pi b}{b}\right) + \left(\frac{b}{n\pi} \right) b \sin\left(\frac{n\pi b}{b}\right) - \left(\frac{b}{n\pi} \right)^2 \cos\left(\frac{n\pi(-b)}{b}\right) - \left(\frac{b}{n\pi} \right)(-b) \sin\left(\frac{n\pi(-b)}{b}\right) \right] = 0$$

All the $d_n = 0$ because $f(x)$ is an odd function of x .

$$c_n = \frac{1}{b} \int_{-b}^b f(x) \sin\left(\frac{n\pi x}{b}\right) dx = \frac{1}{b} \int_{-b}^b x \sin\left(\frac{n\pi x}{b}\right) dx$$

Using the standard integral $\int x \sin ax = -\frac{x \cos ax}{a} + \frac{\sin ax}{a^2}$

$$c_n = \frac{1}{b} \left[\left(\frac{b}{n\pi} \right)^2 \sin\left(\frac{n\pi x}{b}\right) - \left(\frac{b}{n\pi} \right) x \cos\left(\frac{n\pi x}{b}\right) \right]_{-b}^b$$

$$c_n = \frac{1}{b} \left[\left(\frac{b}{n\pi} \right)^2 \sin\left(\frac{n\pi b}{b}\right) - \left(\frac{b}{n\pi} \right) b \cos\left(\frac{n\pi b}{b}\right) - \left(\frac{b}{n\pi} \right)^2 \sin\left(\frac{n\pi(-b)}{b}\right) + \left(\frac{b}{n\pi} \right)(-b) \cos\left(\frac{n\pi(-b)}{b}\right) \right]$$

$$c_n = \frac{2}{b} \left[\left(\frac{b}{n\pi} \right)^2 \sin(n\pi) - \frac{b^2}{n\pi} \cos(n\pi) \right]$$

$$c_n = \left(\frac{2b}{n\pi} \right) \cos n\pi = \frac{2b}{n\pi} (-1)^{n+1}$$

Therefore, $d_0 = 0$ and $d_1 - d_5 = 0$. $c_1 = \frac{2b}{\pi}$, $c_2 = -\frac{b}{\pi}$, $c_3 = \frac{2b}{3\pi}$, $c_4 = -\frac{b}{2\pi}$, and $c_5 = \frac{2b}{5\pi}$

P13.28) Carry out the following coordinate transformations.

a) Express the point $x = 3$, $y = 2$, and $z = 1$ in spherical coordinates.

b) Express the point $r = 5$, $\theta = \frac{\pi}{4}$, and $\phi = \frac{3\pi}{4}$ in Cartesian coordinates.

$$\text{a) } r = \sqrt{x^2 + y^2 + z^2} = \sqrt{3^2 + 2^2 + 1} = \sqrt{14}$$

$$\theta = \cos^{-1} \frac{z}{\sqrt{x^2 + y^2 + z^2}} = \cos^{-1} \frac{1}{\sqrt{14}} = 1.30 \text{ radians}$$

$$\phi = \tan^{-1} \frac{y}{x} = \tan^{-1} \frac{2}{3} = 0.588 \text{ radians}$$

$$\text{b) } x = r \sin \theta \cos \phi = 5 \sin \frac{\pi}{4} \cos \frac{3\pi}{4} = -2.5$$

$$y = r \sin \theta \sin \phi = 5 \sin \frac{\pi}{4} \sin \frac{3\pi}{4} = 2.5$$

$$z = r \cos \theta = 5 \cos \frac{\pi}{4} = \frac{5}{\sqrt{2}}$$

P13.29) Operators can also be expressed as matrices and wave functions as column vectors. The operator matrix $\begin{pmatrix} \alpha & \beta \\ \delta & \varepsilon \end{pmatrix}$ acts on the wave function $\begin{pmatrix} a \\ b \end{pmatrix}$ according to the rule $\begin{pmatrix} \alpha & \beta \\ \delta & \varepsilon \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} \alpha a + \beta b \\ \delta a + \varepsilon b \end{pmatrix}$. In words, the 2×2 matrix operator acting on the two-element column wave function generates another two-element column wave function. If the wave function generated by the operation is the original wave function multiplied by a constant, the wave function is an eigenfunction of the operator. What is the effect of the operator $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ on the column vectors $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$, $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ and $\begin{pmatrix} -1 \\ 1 \end{pmatrix}$? Are these wave functions eigenfunctions of the operator? See the Math Supplement for a discussion of matrices.

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} -1 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix} = (-1) \begin{pmatrix} -1 \\ 1 \end{pmatrix}$$

Only $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ are eigenfunctions with the eigenvalues 1 and -1 , respectively.

P13.30) Let $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ represent the unit vectors along the x and y directions, respectively. The operator $\begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix}$ effects a rotation in the x - y plane. Show that the length of an arbitrary vector $\begin{pmatrix} a \\ b \end{pmatrix} = a \begin{pmatrix} 1 \\ 0 \end{pmatrix} + b \begin{pmatrix} 0 \\ 1 \end{pmatrix}$, which is defined as $\sqrt{a^2 + b^2}$, is unchanged by this rotation. See the Math Supplement for a discussion of matrices.

$$\begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} a \cos \theta - b \sin \theta \\ a \sin \theta + b \cos \theta \end{pmatrix}$$

The length of the vector is given by

$$\begin{aligned} \sqrt{(a \cos \theta - b \sin \theta)^2 + (a \sin \theta + b \cos \theta)^2} &= (a^2 \cos^2 \theta + b^2 \sin^2 \theta - 2ab \sin \theta \cos \theta \\ &\quad + a^2 \sin^2 \theta + b^2 \cos^2 \theta + 2ab \sin \theta \cos \theta)^{1/2} \\ &= \sqrt{a^2 (\cos^2 \theta + \sin^2 \theta) + b^2 (\cos^2 \theta + \sin^2 \theta)} = \sqrt{a^2 + b^2} \end{aligned}$$

This result shows that the length of the vector is not changed.

Chapter 15: Using Quantum Mechanics on Simple Systems

Problem numbers in italics indicate that the solution is included in the *Student's Solutions Manual*.

Questions on Concepts

Q15.1) Why are standing-wave solutions for the free particle not compatible with the classical result $x = x_0 + v_0 t$?

Because the particle is moving, we must represent it by a traveling wave, for which the nodes move with time. This is not possible using a standing wave, because the nodes do not move with time.

Q15.2) Why is it not possible to normalize the free-particle wave functions over the whole range of motion of the particle?

This is the case because $\int_{-L}^L \psi^*(x)\psi(x)dx = A_+A_+\int_{-L}^L e^{-ikx}e^{+ikx}dx = A_+A_+2L$ diverges as $L\rightarrow\infty$.

Q15.3) Show that for the particle in the box total energy eigenfunctions,

$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$, $\psi(x)$ is a continuous function at the edges of the box. Is $\frac{d\psi(x)}{dx}$ a continuous function of x at the edges of the box?

$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) = 0$ at $x = 0$ and $x = a$. Because the wave function is zero everywhere outside the box, it has the value zero at $x = 0$ and $x = a$. Therefore, $\psi(x)$ is a continuous function of x because there is no abrupt change in the function at $x = 0$ or $x = a$.

$$\frac{d\psi(x)}{dx} = \frac{d}{dx} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) = \sqrt{\frac{2}{a}} \frac{n\pi}{a} \cos\left(\frac{n\pi x}{a}\right) = 1 \text{ at } x = 0$$

$\cos n\pi = 1$ for n zero or even and -1 for n odd at $x = a$.

$\frac{d\psi(x)}{dx} = 0$ everywhere outside the box because $\psi(x) = 0$ outside the box.

Because $\frac{d\psi(x)}{dx}$ can be one when approaching $x = a$ from inside the box, and is always

equal to zero outside of the box, $\frac{d\psi(x)}{dx}$ is not a continuous function at $x = a$.

Q15.4) Can the particles in a one-dimensional box, a square two-dimensional box, and a cubic three-dimensional box all have degenerate energy levels?

The two and three dimensional boxes can have degenerate energy levels if the lengths along the x and y or x, y , and z directions are the same or if any of the quantities

$\frac{n_x^2}{a^2}, \frac{n_y^2}{b^2},$ or $\frac{n_z^2}{c^2}$ are equal. The one dimensional box levels have only one state per level.

Q15.5) We set the potential energy in the particle in the box equal to zero and justified it by saying that there is no absolute scale for potential energy. Is this also true for kinetic energy?

Yes. $E_{kinetic} = \frac{1}{2}mv^2$, and the velocity is measured relative to the frame of reference. The

same is true if we express the kinetic energy as $E_{kinetic} = \frac{\hbar^2 k^2}{2m}$, because the value of $p = \hbar k$ depends on the frame of reference if the observer is moving relative to the source.

Q15.6) Why are traveling-wave solutions for the particle in the box not compatible with the boundary conditions?

The nodes in traveling waves move with time. This is incompatible with the boundary conditions for the particle in the box.

Q15.7) Why is the zero point energy lower for a He atom in a box than for an electron?

The zero point energy $E = \frac{\hbar^2}{8ma^2}$ varies inversely with the mass, and the mass of a He atom is much greater than the mass of an electron.

Q15.8) Invoke wave-particle duality to address the following question: How does a particle get through a node in a wave function to get to the other side of the box?

The question poses a problem only if we try to see the “particle” as a pure particle rather than as a wave-particle. The essence of particle-wave particle duality is that some properties are more easily addressed in a wave picture, and some properties are more

easily addressed in a particle picture. Address this question by looking at the “particle” as a wave. We can easily make a guitar string vibrate over its whole length and still have nodes by holding a finger at the fifth fret. The wave-like properties of the “particle” allow it to have a nonzero probability of being found within any interval dx throughout the box, even if the amplitude of the wave function is zero at a number of special points.

Q15.9) What is the difference between probability and probability density?

Probability is expressed as $\psi^*(\tau)\psi(\tau)d\tau$ and is the probability density $\psi^*(\tau)\psi(\tau)$ integrated over the interval $d\tau$.

Q15.10) Explain using words, rather than equations, why if

$V(x, y, z) \neq V_x(x) + V_y(y) + V_z(z)$, the total energy eigenfunctions cannot be written in the form $\psi(x, y, z) = X(x)Y(y)Z(z)$.

If the potential has the form $V(x, y, z) = V_x(x) + V_y(y) + V_z(z)$, then the total energy can be written in the form $E = E_x + E_y + E_z$. This allows the Schrödinger equation to be separated into separate equations for x , y and z and the wave functions to be written in the form $\psi(x, y, z) = X(x)Y(y)Z(z)$. However, if $V(x, y, z) \neq V_x(x) + V_y(y) + V_z(z)$, this separation into three separate Schrödinger equations is not possible, and $\psi(x, y, z)$ cannot be factored into three terms, each of which depends only on one variable.

Problems

P15.1) Show by examining the position of the nodes that $\text{Re}[A_+ e^{i(kx-\omega t)}]$ and $\text{Re}[A_- e^{i(-kx-\omega t)}]$ represent plane waves moving in the positive and negative x directions, respectively. The notation $\text{Re}[\cdot]$ refers to the real part of the function in the brackets.

$\text{Re}[A_+ e^{i(kx-\omega t)}] = \cos(kx - \omega t)$. The nodes of this function occur at

$$kx - \omega t = (2n+1)\frac{\pi}{2}$$

$$x = (2n+1)\frac{\pi}{2} + \omega t$$

Because the position of the nodes is increasing as t increases, this function represents a plane wave moving in the positive x direction.

$\text{Re}[A_- e^{i(-kx-\omega t)}] = \cos(-kx - \omega t) = \cos(kx + \omega t)$. The nodes of this function occur at

$$kx + \omega t = (2n+1)\frac{\pi}{2}$$

$$x = (2n+1)\frac{\pi}{2} - \omega t$$

Because the position of the nodes is decreasing as t increases, this function represents a plane wave moving in the negative x direction.

P15.2) Show that the energy eigenvalues for the free particle, $E = \frac{\hbar^2 k^2}{2m}$, are consistent with

the classical result $E = \frac{1}{2}mv^2$.

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

From the de Broglie relation, $p = \frac{\hbar}{\lambda}$

$$E = \frac{1}{2m} \left(\frac{\hbar}{\lambda} \right)^2 = \frac{\hbar^2 k^2}{2m}, \text{ showing consistency between the classical and quantum result.}$$

P15.3) Are the total energy eigenfunctions for the free particle in one dimension,

$\psi^+(x) = A_+ e^{+i\sqrt{\frac{2mE}{\hbar^2}}x}$ and $\psi^-(x) = A_- e^{-i\sqrt{\frac{2mE}{\hbar^2}}x}$, eigenfunctions of the one-dimensional linear momentum operator? If so, what are the eigenvalues?

$$-i\hbar \frac{d}{dx} A_+ e^{+i\sqrt{\frac{2mE}{\hbar^2}}x} = -(i)^2 \hbar \sqrt{\frac{2mE}{\hbar^2}} A_+ e^{+i\sqrt{\frac{2mE}{\hbar^2}}x} = \hbar k A_+ e^{+ikx}$$

Eigenfunction with eigenvalue $+\hbar k$

$$-i\hbar \frac{d}{dx} A_- e^{-i\sqrt{\frac{2mE}{\hbar^2}}x} = -(i)^2 \hbar \sqrt{\frac{2mE}{\hbar^2}} A_- e^{-i\sqrt{\frac{2mE}{\hbar^2}}x} = -\hbar k A_- e^{-ikx}$$

Eigenfunction with eigenvalue $-\hbar k$

P15.4) Is the superposition wave function for the free particle

$\psi^+(x) = A_+ e^{+i\sqrt{\frac{2mE}{\hbar^2}}x} + A_- e^{-i\sqrt{\frac{2mE}{\hbar^2}}x}$ an eigenfunction of the momentum operator? Is it an eigenfunction of the total energy operator? Explain your result.

$$\begin{aligned} -i\hbar \frac{d}{dx} \left(A_+ e^{+i\sqrt{\frac{2mE}{\hbar^2}}x} + A_- e^{-i\sqrt{\frac{2mE}{\hbar^2}}x} \right) &= -(i)^2 \hbar \sqrt{\frac{2mE}{\hbar^2}} A_+ e^{+i\sqrt{\frac{2mE}{\hbar^2}}x} + (i)^2 \hbar \sqrt{\frac{2mE}{\hbar^2}} A_- e^{-i\sqrt{\frac{2mE}{\hbar^2}}x} \\ &= \hbar k A_+ e^{+i\sqrt{\frac{2mE}{\hbar^2}}x} - \hbar k A_- e^{-i\sqrt{\frac{2mE}{\hbar^2}}x} \end{aligned}$$

This function is not an eigenfunction of the momentum operator, because the operation does not return the original function multiplied by a constant.

$$\begin{aligned}
 -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \left(A_+ e^{+i\sqrt{\frac{2mE}{\hbar^2}}x} + A_- e^{-i\sqrt{\frac{2mE}{\hbar^2}}x} \right) &= -(i)^2 \frac{\hbar^2}{2m} \frac{2mE}{\hbar^2} A_+ e^{+i\sqrt{\frac{2mE}{\hbar^2}}x} - (-i)^2 \frac{\hbar^2}{2m} \frac{2mE}{\hbar^2} A_- e^{-i\sqrt{\frac{2mE}{\hbar^2}}x} \\
 &= E \left(A_+ e^{+i\sqrt{\frac{2mE}{\hbar^2}}x} + A_- e^{-i\sqrt{\frac{2mE}{\hbar^2}}x} \right)
 \end{aligned}$$

This function is an eigenfunction of the total energy operator. Because the energy is proportional to p^2 , the difference in sign of the momentum of these two components does not affect the energy.

P15.5) Consider a particle in a one-dimensional box defined by

$V(x) = 0, a > x > 0$ and $V(x) = \infty, x \geq a, x \leq 0$. Explain why each of the following unnormalized functions is or is not an acceptable wave function based on criteria such as being consistent with the boundary conditions, and with the association of $\psi^*(x)\psi(x)dx$ with probability.

- a) $A \cos \frac{n\pi x}{a}$
- b) $B(x+x^2)$
- c) $Cx^3(x-a)$
- d) $\frac{D}{\sin \frac{n\pi x}{a}}$

a) $A \cos \frac{n\pi x}{a}$ is not an acceptable wave function because it does not satisfy the boundary condition that $\psi(0)=0$.

b) $B(x+x^2)$ is not an acceptable wave function because it does not satisfy the boundary condition that $\psi(a)=0$.

c) $Cx^3(x-a)$ is an acceptable wave function. It satisfies both boundary conditions and can be normalized.

d) $\frac{D}{\sin \frac{n\pi x}{a}}$ is not an acceptable wave function. It goes to infinity at $x=0$ and cannot be normalized in the desired interval.

P15.6) Evaluate the normalization integral for the eigenfunctions of \hat{H} for the particle in the box $\psi_n(x) = A \sin \left(\frac{n\pi x}{a} \right)$ using the trigonometric identity $\sin^2 y = \frac{1-\cos 2y}{2}$.

$$1 = \int_0^a A^2 \sin^2 \left(\frac{n\pi x}{a} \right) dx$$

$$\text{let } y = \frac{n\pi x}{a}; dx = \frac{a}{n\pi} dy$$

$$1 = A^2 \frac{a}{n\pi} \int_0^{n\pi} \sin^2 y dy = A^2 \frac{a}{n\pi} \int_0^{n\pi} \frac{1 - \cos 2y}{2} dy = A^2 \frac{a}{n\pi} \left[\frac{y}{2} - \frac{\sin 2y}{4} \right]_0^{n\pi}$$

$$= \frac{A^2}{2} \frac{a}{n\pi} n\pi - \frac{A^2}{2} \frac{a}{n\pi} (\sin 2n\pi - \sin 0) = \frac{A^2 a}{2}$$

$$A = \sqrt{\frac{2}{a}}$$

P15.7) Use the eigenfunction $\psi(x) = A'e^{+ikx} + B'e^{-ikx}$ rather than $\psi(x) = A \sin kx + B \cos kx$ to apply the boundary conditions for the particle in the box.

- a) How do the boundary conditions restrict the acceptable choices for A' and B' and for k ?
- b) Do these two functions give different probability densities if each is normalized?

a)

$$\begin{aligned} \psi(x) &= A'e^{+ikx} + B'e^{-ikx} = A' \cos kx + B' \cos(-kx) + i(A' \sin kx + B' \sin(-kx)) \\ &= A' \cos kx + B' \cos kx + i(A' \sin kx - B' \sin kx) \end{aligned}$$

$$\psi(0) = A' + B' = 0, \text{ giving } A' = -B'. \text{ Therefore}$$

$$\psi(x) = A' \cos kx - A' \cos kx + i(A' \sin kx + A' \sin kx) = 2iA' \sin kx$$

$$\psi(a) = 2iA' \sin ka = 0$$

This leads to the same condition on k , namely $ka = n\pi$. The amplitude is now $2iA'$ rather than A .

b) The wave function after the imposition of the boundary conditions is

$$\psi(x) = A'(e^{+ikx} - e^{-ikx}) = 2iA' \sin kx. \text{ After the normalization condition is imposed,}$$

$(2iA')(-2iA') = \frac{2}{a}$. Therefore functions are indistinguishable, because both will give the same probability densities when normalized.

P15.8) Calculate the probability that a particle in a one-dimensional box of length a is found between $0.31a$ and $0.35a$ when it is described by the following wave functions:

a) $\sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$

b) $\sqrt{\frac{2}{a}} \sin\left(\frac{3\pi x}{a}\right)$

What would you expect for a classical particle? Compare your results in the two cases with the classical result.

a)

Using the standard integral $\int \sin^2(by) dy = \frac{y}{2} - \frac{1}{4b} \sin(2by)$

$$\begin{aligned} P &= \frac{2}{a} \int_{0.31a}^{0.35a} \sin^2\left(\frac{\pi x}{a}\right) dx = \left[\frac{x}{2} - \frac{a}{4\pi} \sin\left(\frac{2\pi x}{a}\right) \right]_{0.31a}^{0.35a} \\ &= \frac{2}{a} \left[\frac{0.35a}{2} - \frac{a}{4\pi} \sin(0.70\pi) - \frac{0.31a}{2} + \frac{a}{4\pi} \sin(0.62\pi) \right] \\ &= 0.04 + \frac{1}{2\pi} [\sin(0.62\pi) - \sin(0.70\pi)] = 0.059 \end{aligned}$$

b)

Using the standard integral $\int \sin^2(by) dy = \frac{y}{2} - \frac{1}{4b} \sin(2by)$

$$\begin{aligned} P &= \frac{2}{a} \int_{0.31a}^{0.35a} \sin^2\left(\frac{3\pi x}{a}\right) dx = \frac{2}{a} \left[\frac{0.35a}{2} - \frac{a}{12\pi} \sin(2.10\pi) - \frac{0.31a}{2} + \frac{a}{12\pi} \sin(1.86\pi) \right] \\ &= 0.04 + \frac{1}{6\pi} [\sin(1.86\pi) - \sin(2.10\pi)] = 0.0010 \end{aligned}$$

Because a classical particle is equally likely to be in any given interval, the probability will be 0.04 independent of the energy. In the ground state, the interval chosen is near the maximum of the wave function so that the quantum mechanical probability is greater than the classical probability. For the $n = 3$ state, the interval chosen is near a node of the wave function so that the quantum mechanical probability is much less than the classical probability.

P15.9) Are the eigenfunctions of \hat{H} for the particle in the one-dimensional box also eigenfunctions of the position operator \hat{x} ? Calculate the average value of x for the case where $n = 3$. Explain your result by comparing it with what you would expect for a classical particle. Repeat your calculation for $n = 5$ and, from these two results, suggest an expression valid for all values of n . How does your result compare with the prediction based on classical physics?

No, they are not eigenfunctions because multiplying the function by x does not return the function multiplied by a constant.

For $n = 3$,

$$\langle x \rangle = \int_0^a \psi^*(x) x \psi(x) dx = \frac{2}{a} \int_0^a x \sin^2\left(\frac{3\pi x}{a}\right) dx$$

Using the standard integral $\int x \sin^2(bx) dx = \frac{x^2}{4} - \frac{\cos(2bx)}{8b^2} - \frac{x \sin(2bx)}{4b}$

$$\langle x \rangle = \frac{2}{a} \left[\frac{x^2}{4} - \frac{\cos\left(\frac{6\pi x}{a}\right)}{8\left(\frac{3\pi x}{a}\right)^2} - \frac{x \sin\left(\frac{6\pi x}{a}\right)}{4\left(\frac{3\pi x}{a}\right)} \right]_0^a$$

$$\langle x \rangle = \frac{2}{a} \left[\frac{a^2}{4} - \frac{\cos(6\pi)}{72\pi^2} - \frac{a \sin(6\pi)}{12\pi} + \frac{\cos(0)}{72\pi^2} - \frac{0 \sin(0)}{12\pi} \right] = \frac{2}{a} \left[\frac{a^2}{4} - \frac{1}{72\pi^2} - 0 + \frac{1}{72\pi^2} - 0 \right] = \frac{a}{2}$$

For $n = 5$,

$$\langle x \rangle = \int_0^a \psi^*(x) x \psi(x) dx = \frac{2}{a} \int_0^a x \sin^2\left(\frac{5\pi x}{a}\right) dx$$

Using the standard integral $\int x \sin^2(bx) dx = \frac{x^2}{4} - \frac{\cos(2bx)}{8b^2} - \frac{x \sin(2bx)}{4b}$

$$\langle x \rangle = \frac{2}{a} \left[\frac{x^2}{4} - \frac{\cos\left(\frac{10\pi x}{a}\right)}{8\left(\frac{5\pi x}{a}\right)^2} - \frac{x \sin\left(\frac{10\pi x}{a}\right)}{4\left(\frac{5\pi x}{a}\right)} \right]_0^a$$

$$\begin{aligned} \langle x \rangle &= \frac{2}{a} \left[\frac{a^2}{4} - \frac{\cos(10\pi)}{200\pi^2} - \frac{a \sin(10\pi)}{20\pi} + \frac{\cos(0)}{200\pi^2} - \frac{0 \sin(0)}{20\pi} \right] = \frac{2}{a} \left[\frac{a^2}{4} - \frac{1}{200\pi^2} - 0 + \frac{1}{200\pi^2} - 0 \right] \\ &= \frac{a}{2} \end{aligned}$$

The general expression valid for all states is $\langle x \rangle = \frac{a}{2}$. Classical physics gives the same result because the particle is equally likely to be at any position. The average of all these values is the midpoint of the box.

P15.10) Are the eigenfunctions of \hat{H} for the particle in the one-dimensional box also eigenfunctions of the momentum operator \hat{p}_x ? Calculate the average value of p_x for the case $n = 3$. Repeat your calculation for $n = 5$ and, from these two results, suggest an expression valid for all values of n . How does your result compare with the prediction based on classical physics?

For $n = 3$,

$$\langle p \rangle = \int_0^a \psi^*(x) \left(-i\hbar \frac{d}{dx} \right) \psi(x) dx = \frac{-2i\hbar}{a} \frac{3\pi}{a} \int_0^a \sin\left(\frac{3\pi x}{a}\right) \cos\left(\frac{3\pi x}{a}\right) dx$$

Using the standard integral $\int \sin(bx)\cos(bx)dx = \frac{\cos^2(bx)}{2b}$

$$\langle p \rangle = \frac{-2i\hbar}{a} \frac{3\pi}{a} \left[\frac{\cos^2(3\pi)}{2b} - \frac{\cos^2(0)}{2b} \right] = \frac{-2i\hbar}{a} \frac{3\pi}{a} \left[\frac{1}{2b} - \frac{1}{2b} \right] = 0$$

For $n = 5$,

$$\langle p \rangle = \int_0^a \psi^*(x) \left(-i\hbar \frac{d}{dx} \right) \psi(x) dx = \frac{-2i\hbar}{a} \frac{5\pi}{a} \int_0^a \sin\left(\frac{5\pi x}{a}\right) \cos\left(\frac{3\pi x}{a}\right) dx$$

Using the standard integral $\int \sin(bx)\cos(bx)dx = \frac{\cos^2(bx)}{2b}$

$$\langle p \rangle = \frac{-2i\hbar}{a} \frac{5\pi}{a} \left[\frac{\cos^2(5\pi)}{2b} - \frac{\cos^2(0)}{2b} \right] = \frac{-2i\hbar}{a} \frac{5\pi}{a} \left[\frac{1}{2b} - \frac{1}{2b} \right] = 0$$

This is the same result that would be obtained using classical physics. The classical particle is equally likely to be moving in the positive and negative x directions. Therefore the average of a large number of measurements of the momentum is zero for the classical particle moving in a constant potential.

P15.11) It is useful to consider the result for the energy eigenvalues for the one-dimensional

$$E_n = \frac{\hbar^2 n^2}{8ma^2}, n = 1, 2, 3, \dots \text{as a function of } n, m, \text{ and } a.$$

- a) By what factor do you need to change the box length to decrease the zero point energy by a factor of 400 for a fixed value of m ?
- b) By what factor would you have to change n for fixed values of a and m to increase the energy by a factor of 400?
- c) By what factor would you have to increase a at constant n to have the zero point energies of an electron be equal to the zero point energy of a proton in the box?

$$\text{a) } \frac{E_n}{E_{n'}} = \frac{(a')^2}{a^2}, = 400; \quad \frac{a'}{a} = 20$$

$$\text{b) } \frac{E_n}{E_{n'}} = \frac{n^2}{(n')^2}, = 400; \quad \frac{n}{n'} = 20$$

c)

$$\frac{1}{m_e a_e^2} = \frac{1}{m_p a_p^2}$$

$$\frac{a_e}{a_p} = \sqrt{\frac{m_p}{m_e}} = \sqrt{\frac{1.673 \times 10^{-27} \text{ kg}}{9.109 \times 10^{-31} \text{ kg}}} = 42.9$$

P15.12) Is the superposition wave function $\psi(x) = \sqrt{\frac{2}{a}} \left[\sin\left(\frac{n\pi x}{a}\right) + \sin\left(\frac{m\pi x}{a}\right) \right]$ an eigenfunction of the total energy operator for the particle in the box?

$$\begin{aligned} \hat{H}\psi(x) &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \left[\sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) + \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi x}{a}\right) \right] \\ &= \frac{\hbar^2 n^2}{8ma^2} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) + \frac{\hbar^2 m^2}{8ma^2} \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi x}{a}\right) \end{aligned}$$

Because the result is not the wave function multiplied by a constant, the superposition wave function is not an eigenfunction of the total energy operator.

P15.13) The function $\psi(x) = Ax\left(1 - \frac{x}{a}\right)$ is an acceptable wave function for the particle in the one dimensional infinite depth box of length a . Calculate the normalization constant A and the expectation values $\langle x \rangle$ and $\langle x^2 \rangle$.

$$\begin{aligned} 1 &= A^2 \int_0^a \left[x \left(1 - \frac{x}{a}\right) \right]^2 dx = A^2 \int_0^a \left[\frac{x^4}{a^2} - 2\frac{x^3}{a} + x^2 \right] dx \\ 1 &= A^2 \left[\frac{x^5}{5a^2} - \frac{x^4}{2a} + \frac{x^3}{3} \right]_0^a = A^2 \left[\frac{a^3}{5} - \frac{a^3}{2} + \frac{a^3}{3} \right]_0^a = A^2 \frac{a^3}{30} \\ A &= \sqrt{\frac{30}{a^3}} \\ \langle x \rangle &= \int_0^a \psi^*(x) x \psi(x) dx = \frac{30}{a^3} \int_0^a x \left[x \left(1 - \frac{x}{a}\right) \right]^2 dx \\ &= \frac{30}{a^3} \left[\frac{x^4}{4} - \frac{2x^5}{5a} + \frac{x^6}{6a^2} \right]_0^a = \frac{30}{a^3} \left[\frac{a^4}{6} - \frac{2a^4}{5} + \frac{a^4}{4} \right] = \frac{30}{a^3} \frac{a^4}{60} = \frac{a}{2} \\ \langle x^2 \rangle &= \int_0^a \psi^*(x) x^2 \psi(x) dx = \frac{30}{a^3} \int_0^a x^2 \left[x \left(1 - \frac{x}{a}\right) \right]^2 dx \\ &= \frac{30}{a^3} \left[\frac{x^5}{5} - \frac{x^6}{3a} + \frac{x^7}{7a^2} \right]_0^a = \frac{30}{a^3} \left[\frac{a^5}{5} - \frac{a^5}{3} + \frac{a^5}{7} \right] = \frac{30}{a^3} \frac{a^5}{105} = \frac{2a^2}{7} \end{aligned}$$

P15.14) Derive an equation for the probability that a particle characterized by the quantum number n is in the first quarter ($0 \leq x \leq \frac{a}{4}$) of an infinite depth box. Show that this probability approaches the classical limit as $n \rightarrow \infty$.

Using the standard integral $\int \sin^2(b y) dy = \frac{y}{2} - \frac{1}{4b} \sin(2b y)$

$$\begin{aligned} P &= \frac{2}{a} \int_0^{0.25a} \sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{2}{a} \left[\frac{x}{2} - \frac{1}{4n\pi} \sin\left(\frac{2n\pi x}{a}\right) \right]_0^{0.25a} \\ &= \frac{2}{a} \left[\frac{a}{8} - \frac{a}{4n\pi} \sin\left(\frac{n\pi}{2}\right) - \frac{0}{2} + \frac{a}{4n\pi} \sin(0) \right] = \frac{1}{4} - \frac{1}{2n\pi} \sin\left(\frac{n\pi}{2}\right) \end{aligned}$$

As $n \rightarrow \infty$, the second term goes to zero, and the probability approaches $\frac{1}{4}$.

This is the classical value, because the particle is equally likely to be found anywhere in the box.

P15.15) What is the solution of the time-dependent Schrödinger equation $\Psi(x, t)$ for the total energy eigenfunction $\psi_4(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{4\pi x}{a}\right)$ in the particle in the box model? Write $\omega = \frac{E}{\hbar}$ explicitly in terms of the parameters of the problem.

$$\psi(x, t) = \psi(x) e^{-i\omega t} = \psi(x) e^{-i\frac{Et}{\hbar}}$$

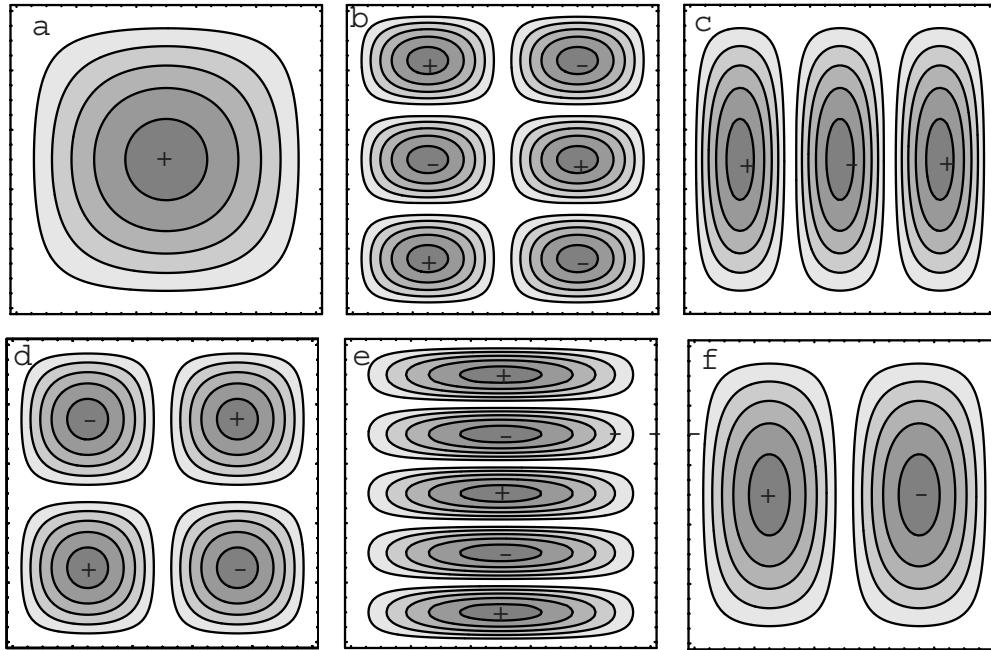
$$\text{Because } E = \frac{n^2 \hbar^2}{8ma^2} = \frac{16\hbar^2}{8ma^2},$$

$$\psi(x, t) = \sqrt{\frac{2}{a}} \sin\left(\frac{4\pi x}{a}\right) e^{-i\frac{4\pi\hbar t}{ma^2}}$$

P15.16) For a particle in a two-dimensional box, the total energy eigenfunctions are

$$\psi_{n_x n_y}(x, y) = N \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{b}.$$

- a) Obtain an expression for $E_{n_x n_y}$ in terms of n_x , n_y , a , and b by substituting this wave function into the two-dimensional analog of Equation (15.19).
- b) Contour plots of several eigenfunctions are shown here. The x and y directions of the box lie along the horizontal and vertical directions, respectively. The amplitude has been displayed as a gradation in colors. Regions of positive and negative amplitude are indicated. Identify the values of the quantum numbers n_x and n_y for plots a–f.



a)

$$\begin{aligned}
 & -\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial x^2} \left[\sqrt{\frac{4}{a^2}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \right] + \frac{\partial^2}{\partial y^2} \left[\sqrt{\frac{4}{a^2}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \right] \right] \\
 &= \frac{\hbar^2}{2m} \left(\frac{n_x \pi x}{a} \right)^2 \left[\sqrt{\frac{4}{a^2}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \right] + \frac{\hbar^2}{2m} \left(\frac{n_y \pi y}{a} \right)^2 \left[\sqrt{\frac{4}{a^2}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \right] \\
 &= \frac{\hbar^2 (n_x^2 + n_y^2)}{8 m a^2} \left[\sqrt{\frac{4}{a^2}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \right]
 \end{aligned}$$

Because application of the total energy operator returns the wave function multiplied by a

constant, $\psi_{n_x, n_y}(x, y) = N \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{b}$ is an eigenfunction of the total energy operator.

b) From the result of part (a), $E_{n_x, n_y} = \frac{\hbar^2 (n_x^2 + n_y^2)}{8 m a^2}$

a: $n_x = 1 \quad n_y = 1$

b: $n_x = 2 \quad n_y = 3$

c: $n_x = 3 \quad n_y = 1$

d: $n_x = 2 \quad n_y = 2$

e: $n_x = 1 \quad n_y = 5$

f: $n_x = 2 \quad n_y = 1$

P15.17) Normalize the total energy eigenfunction for the rectangular two-dimensional box,

$$\psi_{n_x, n_y}(x, y) = N \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right)$$

in the interval $0 \leq x \leq a$, $0 \leq y \leq b$.

$$1 = \int_0^a \int_0^b \psi^*(x, y) \psi(x, y) dx dy = N^2 \int_0^a \sin^2\left(\frac{n_x \pi x}{a}\right) dx \int_0^b \sin^2\left(\frac{n_y \pi y}{b}\right) dy$$

Using the standard integral $\int \sin^2 \alpha x dx = \frac{x}{2} - \frac{\sin(2\alpha x)}{4\alpha}$

$$\begin{aligned} & N^2 \int_0^a \sin^2\left(\frac{n_x \pi x}{a}\right) dx \int_0^b \sin^2\left(\frac{n_y \pi y}{b}\right) dy \\ &= N^2 \left[\frac{a}{2} - \frac{a}{4n_x \pi} (\sin n_x \pi - \sin 0) \right] \times \left[\frac{b}{2} - \frac{b}{4n_y \pi} (\sin n_y \pi - \sin 0) \right] = N^2 \frac{ab}{4} \\ & N = \sqrt{\frac{4}{ab}} \text{ and } \psi(x, y) = \sqrt{\frac{4}{ab}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \end{aligned}$$

P15.18) Consider the contour plots of Problem P15.16.

- a) What are the most likely area or areas $dxdy$ to find the particle for each of the eigenfunctions of \hat{H} depicted in plots a–f?
- b) For the one-dimensional box, the nodes are points. What form do the nodes take for the two-dimensional box? Where are the nodes located in plots a–f? How many nodes are there in each contour plot?
- a) What is the most likely point to find the particle for each of the eigenfunctions of \hat{H} depicted in plots a–e?

The most likely location of the particle is the set of points at which the wave function has its largest positive or negative value as indicated by the gray scale. There are 1, 6, 3, 4, 5, and 2 equivalent points in plots a–e respectively.

- b) For the one-dimensional box, the nodes are points. What form do the nodes take for the two-dimensional box? Where are the nodes located in plots a–e? How many nodes are there in each contour plot?

The nodes are lines that lie between values at which the absolute magnitude of the wave function reaches its maximum value. There are 0, 3, 2, 2, 4, and 1 nodes in plots a–e, respectively.

P15.19) Show by substitution into Equation (15.19) that the eigenfunctions of \hat{H} for a box with lengths along the x , y , and z directions of a , b , and c , respectively, are

$$\psi_{n_x, n_y, n_z}(x, y, z) = N \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

- b) Obtain an expression for E_{n_x, n_y, n_z} in terms of n_x , n_y , n_z and a , b , and c .

a)

$$\begin{aligned}
 & -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \left[N \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right) \right] - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} \left[N \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right) \right] \\
 & - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} \left[N \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right) \right] \\
 & = \frac{\hbar^2}{2m} \left(\frac{n_x \pi x}{a} \right)^2 N \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right) + \frac{\hbar^2}{2m} \left(\frac{n_y \pi y}{b} \right)^2 N \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right) \\
 & + \frac{\hbar^2}{2m} \left(\frac{n_z \pi z}{c} \right)^2 N \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right) \\
 & = \frac{\hbar^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) N \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)
 \end{aligned}$$

Because application of the total energy operator returns the wave function multiplied by a constant, $\psi_{n_x, n_y, n_z}(x, y, z) = N \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$ is an eigenfunction of the total energy operator.

b) Based on the result from part (a), $E_{n_x, n_y, n_z} = \frac{\hbar^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$

P15.20) Normalize the total energy eigenfunctions for the three-dimensional box in the interval $0 \leq x \leq a$, $0 \leq y \leq b$, $0 \leq z \leq c$.

$$\begin{aligned}
 1 &= \int_0^a \int_0^b \int_0^c \psi^*(x, y, z) \psi(x, y, z) dxdydz \\
 &= N^2 \int_0^a \sin^2\left(\frac{n_x \pi x}{a}\right) dx \int_0^b \sin^2\left(\frac{n_y \pi y}{b}\right) dy \int_0^c \sin^2\left(\frac{n_z \pi z}{c}\right) dz
 \end{aligned}$$

Using the standard integral $\int \sin^2 \alpha x dx = \frac{x}{2} - \frac{\sin(2\alpha x)}{4\alpha}$

$$\begin{aligned}
 1 &= N^2 \int_0^a \sin^2\left(\frac{n_x \pi x}{a}\right) dx \int_0^b \sin^2\left(\frac{n_y \pi y}{b}\right) dy \int_0^c \sin^2\left(\frac{n_z \pi z}{c}\right) dz \\
 1 &= N^2 \left[\frac{a}{2} - \frac{a}{4n_x \pi} (\sin n_x \pi - \sin 0) \right] \times \left[\frac{b}{2} - \frac{b}{4n_y \pi} (\sin n_y \pi - \sin 0) \right] \times \left[\frac{c}{2} - \frac{c}{4r\pi} (\sin n_z \pi - \sin 0) \right] = N^2 \frac{abc}{8}
 \end{aligned}$$

$$N = \sqrt{\frac{8}{abc}} \text{ and } \psi(x, y) = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

P15.21) In discussing the Boltzmann distribution in Chapter 13, we used the symbols g_i and g_j to indicate the degeneracies of the energy levels i and j . By degeneracy, we mean the

number of distinct quantum states (different quantum numbers) all of which have the same energy.

a) Using your answer to Problem P15.16a, what is the degeneracy of the energy level $\frac{5h^2}{8ma^2}$ for

the square two-dimensional box of edge length a ?

b) Using your answer to Problem P15.19b, what is the degeneracy of the energy level

$\frac{9h^2}{8ma^2}$ for a three-dimensional cubic box of edge length a ?

a) What is the degeneracy of the energy level $\frac{5h^2}{8ma^2}$ for the square two-dimensional box?

The only pairs n_x, n_y that satisfy the equation $n_x^2 + n_y^2 = 5$ are 2, 1 and 1, 2. Therefore the degeneracy of this energy level is 2.

b) What is the degeneracy of the energy level $\frac{9h^2}{8ma^2}$ for a three-dimensional cubic box of edge length a ?

The only trios of nonzero numbers n, q, r that satisfy the equation $n_x^2 + n_y^2 + n_z^2 = 9$ are 2, 2, 1; 2, 1, 2; and 1, 2, 2. Therefore the degeneracy of this energy level is 3.

P15.22) This problem explores under what conditions the classical limit is reached for a macroscopic cubic box of edge length a . An argon atom of average translational energy $3/2 kT$ is confined in a cubic box of volume $V = 0.500 \text{ m}^3$ at 298 K. Use the result from Equation (15.25) for the dependence of the energy levels on a and on the quantum numbers n_x, n_y , and n_z .

a) What is the value of the “reduced quantum number” $\alpha = \sqrt{n_x^2 + n_y^2 + n_z^2}$ for $T = 298 \text{ K}$?

b) What is the energy separation between the levels a and $a + 1$? (Hint: Subtract E_{a+1} from E_a before plugging in numbers.)

c) Calculate the ratio $\frac{E_{\alpha+1} - E_\alpha}{k T}$ and use your result to conclude whether a classical or quantum mechanical description is appropriate for the particle.

$$E_{n_x, n_y, n_z} = \frac{\hbar^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

$$(n_x^2 + n_y^2 + n_z^2) = \frac{8ma^2 E_{n_x, n_y, n_z}}{\hbar^2}$$

$$\alpha = \sqrt{(n_x^2 + n_y^2 + n_z^2)} = \sqrt{\frac{8ma^2 E_{n_x, n_y, n_z}}{\hbar^2}}$$

$$\alpha = \sqrt{\frac{8 \times 39.95 \text{ amu} \times 1.661 \times 10^{-27} \text{ kg(amu)}^{-1} \times (0.500 \text{ m}^3)^{2/3} \times 1.5 \times 1.381 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2}}$$

$$\alpha = 6.86 \times 10^{10}$$

b) What is the energy separation between the levels α and $\alpha+1$? (Hint: Subtract $E_{\alpha+1}$ from E_α before plugging in numbers.)

$$E_{\alpha+1} - E_\alpha = \frac{\hbar^2}{8ma^2} ([\alpha+1]^2 - \alpha^2) = \frac{\hbar^2 (2\alpha+1)}{8ma^2}$$

$$= \frac{(6.626 \times 10^{-34} \text{ Js})^2 (2 \times 6.86 \times 10^{10} + 1)}{8 \times 39.95 \text{ amu} \times 1.661 \times 10^{-27} \text{ kg(amu)}^{-1} \times (0.500 \text{ m}^3)^{2/3}} = 1.80 \times 10^{-31} \text{ J}$$

c) Calculate the ratio $\frac{E_{\alpha+1} - E_\alpha}{kT}$ and use your result to conclude whether a classical or quantum mechanical description is appropriate for the particle.

$$\frac{E_{\alpha+1} - E_\alpha}{kT} = \frac{1.80 \times 10^{-31} \text{ J}}{1.361 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K}} = 4.44 \times 10^{-7}$$

Because $\Delta E \ll kT$, a classical description is appropriate.

P15.23) Generally, the quantization of translational motion is not significant for atoms because of their mass. However, this conclusion depends on the dimensions of the space to which they are confined. Zeolites are structures with small pores that we describe by a cube with edge length 1 nm. Calculate the energy of a H₂ molecule with $n_x = n_y = n_z = 10$. Compare this energy to kT at $T = 300$ K. Is a classical or a quantum description appropriate?

$$E_{n_x, n_y, n_z} = \frac{\hbar^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

$$= \frac{(6.626 \times 10^{-34} \text{ Js})^2 (10^2 + 10^2 + 10^2)}{8 \times 2.016 \text{ amu} \times 1.661 \times 10^{-27} \text{ kg(amu)}^{-1} \times (10^{-9} \text{ m})^2} = 4.92 \times 10^{-21} \text{ J}$$

Using the results of P15.22, the ratio of the energy spacing between levels and kT determines if a classical or quantum description is appropriate.

$$E_{\alpha+1} - E_\alpha = \frac{h^2}{8ma^2} ([\alpha+1]^2 - \alpha^2) = \frac{h^2(2\alpha+1)}{8ma^2} \text{ where } \alpha = \sqrt{(n_x^2 + n_y^2 + n_z^2)}$$

$$= \frac{(6.626 \times 10^{-34} \text{ Js})^2 (\sqrt{300} + 1)}{8 \times 2.016 \text{ amu} \times 1.661 \times 10^{-27} \text{ kg(amu)}^{-1} \times (10^{-9} \text{ m})^2} = 3.00 \times 10^{-22} \text{ J}$$

$$\frac{E_{\alpha+1} - E_\alpha}{kT} = \frac{3.00 \times 10^{-22} \text{ J}}{1.361 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K}} = 0.073$$

Because this ratio is not much smaller than one, a quantum description is appropriate.

P15.24) Two wave functions are distinguishable if they lead to a different probability density. Which of the following wave functions are distinguishable from $\sin \theta + i \cos \theta$?

a) $(\sin \theta + i \cos \theta) \left(\frac{\sqrt{2}}{2} + i \frac{\sqrt{2}}{2} \right)$

b) $i(\sin \theta + i \cos \theta)$

c) $-(\sin \theta + i \cos \theta)$

d) $(\sin \theta + i \cos \theta) \left(-\frac{\sqrt{2}}{2} + i \frac{\sqrt{2}}{2} \right)$

e) $(\sin \theta - i \cos \theta)$

f) $e^{i\theta}$

Two wave functions ψ_1 and ψ_2 are indistinguishable if $\psi_1^* \psi_1 = \psi_2^* \psi_2$. For the wave function in the problem, $(\sin \theta - i \cos \theta)(\sin \theta + i \cos \theta) = (\sin^2 \theta + \cos^2 \theta) = 1$.

a) $(\sin \theta - i \cos \theta) \left(\frac{\sqrt{2}}{2} - i \frac{\sqrt{2}}{2} \right) (\sin \theta + i \cos \theta) \left(\frac{\sqrt{2}}{2} + i \frac{\sqrt{2}}{2} \right) = (\sin^2 \theta + \cos^2 \theta) = 1$

indistinguishable.

b) $[-i(\sin \theta - i \cos \theta)][i(\sin \theta + i \cos \theta)] = (\sin^2 \theta + \cos^2 \theta) = 1$

indistinguishable

c) $[-(\sin \theta - i \cos \theta)][-(\sin \theta + i \cos \theta)] = (\sin^2 \theta + \cos^2 \theta) = 1$

indistinguishable

d) $(\sin \theta - i \cos \theta) \left(-\frac{\sqrt{2}}{2} - i \frac{\sqrt{2}}{2} \right) (\sin \theta + i \cos \theta) \left(-\frac{\sqrt{2}}{2} + i \frac{\sqrt{2}}{2} \right) = (\sin^2 \theta + \cos^2 \theta) = 1$

indistinguishable

e) $(\sin \theta + i \cos \theta)(\sin \theta - i \cos \theta) = (\sin^2 \theta + \cos^2 \theta) = 1$

indistinguishable

f) $e^{-i\theta} e^{i\theta} = 1$ indistinguishable

P15.25) Suppose that the wave function for a system can be written as

$$\psi(x) = \frac{1}{2}\phi_1(x) + \frac{1}{4}\phi_2(x) + \frac{3+\sqrt{2}i}{4}\phi_3(x) \text{ and that } \phi_1(x), \phi_2(x) \text{ and } \phi_3(x) \text{ are normalized}$$

eigenfunctions of the operator $\hat{E}_{kinetic}$ with eigenvalues E_1 , $3E_1$, and $7E_1$, respectively.

a) Verify that $\psi(x)$ is normalized.

b) What are the possible values that you could obtain in measuring the kinetic energy on identically prepared systems?

c) What is the probability of measuring each of these eigenvalues?

d) What is the average value of $E_{kinetic}$ that you would obtain from a large number of measurements?

a) We first determine if the wave function is normalized.

$$\begin{aligned} \int \psi^*(x)\psi(x)dx &= \frac{1}{4}\int \phi_1^*(x)\phi_1(x)dx + \frac{1}{16}\int \phi_2^*(x)\phi_2(x)dx + \left(\frac{3-\sqrt{2}i}{4}\right)\left(\frac{3+\sqrt{2}i}{4}\right)\int \phi_3^*(x)\phi_3(x)dx \\ &\quad + \frac{1}{4}\int \phi_1^*(x)\phi_2(x)dx + \frac{3+\sqrt{2}i}{16}\int \phi_1^*(x)\phi_3(x)dx + \frac{3-\sqrt{2}i}{16}\int \phi_3^*(x)\phi_1(x)dx - \frac{1}{2}\phi_1(x) \\ &\quad + \frac{3+\sqrt{2}i}{8}\int \phi_2^*(x)\phi_3(x)dx + \frac{3-\sqrt{2}i}{8}\int \phi_3^*(x)\phi_2(x)dx \end{aligned}$$

All but the first three integrals are zero because the functions $\phi_1(x)$, $\phi_2(x)$, and $\phi_3(x)$ are orthogonal. The first three integrals have the value one, because the functions are normalized. Therefore,

$$\int \psi^*(x)\psi(x)dx = \frac{1}{4} + \frac{1}{16} + \left(\frac{3-\sqrt{2}i}{4}\right)\left(\frac{3+\sqrt{2}i}{4}\right) = \frac{1}{4} + \frac{1}{16} + \frac{11}{16} = 1$$

b) The only possible values of the observable kinetic energy that you will measure are those corresponding to the finite number of terms in the superposition wave function. In this case, the only values that you will measure are E_1 , $3E_1$, and $7E_1$.

c) For a normalized superposition wave function, the probability of observing a particular eigenvalue is equal to the square of the magnitude of the coefficient of that kinetic energy eigenfunction in the superposition wave function. These coefficients have been calculated above. The probabilities of observing E_1 , $3E_1$, and $7E_1$ are $\frac{1}{4}$, $\frac{1}{16}$, and $\frac{11}{16}$, respectively.

d) The average value of the kinetic energy is given by

$$\langle E \rangle = \sum P_i E_i = \frac{1}{4}E_1 + \frac{1}{16}3E_1 + \frac{11}{16}7E_1 = 5.25E_1$$

Chapter 16: The Particle in the Box and the Real World

Questions on Concepts

Q16.1) Why must the amplitudes of the energy eigenfunctions in the finite depth box and in the adjoining barrier regions have the same value at the boundary?

If this were not the case, the probability density would have two different values at the barrier. This is not physically possible.

Q16.2) Why must the amplitudes of the first derivatives of the energy eigenfunctions in the finite depth box and in the adjoining barrier regions have the same value at the boundary?

In order to solve the Schrödinger equation, the second derivative $\frac{d^2\psi(x)}{dx^2}$ must exist. This requires that the first derivative $\frac{d\psi(x)}{dx}$ is a continuous function of the position.

Q16.3) The amplitude of the wave on the right side of the barrier in Figure 16.7 is much smaller than that of the wave incident on the barrier. What happened to the “rest of the wave”?

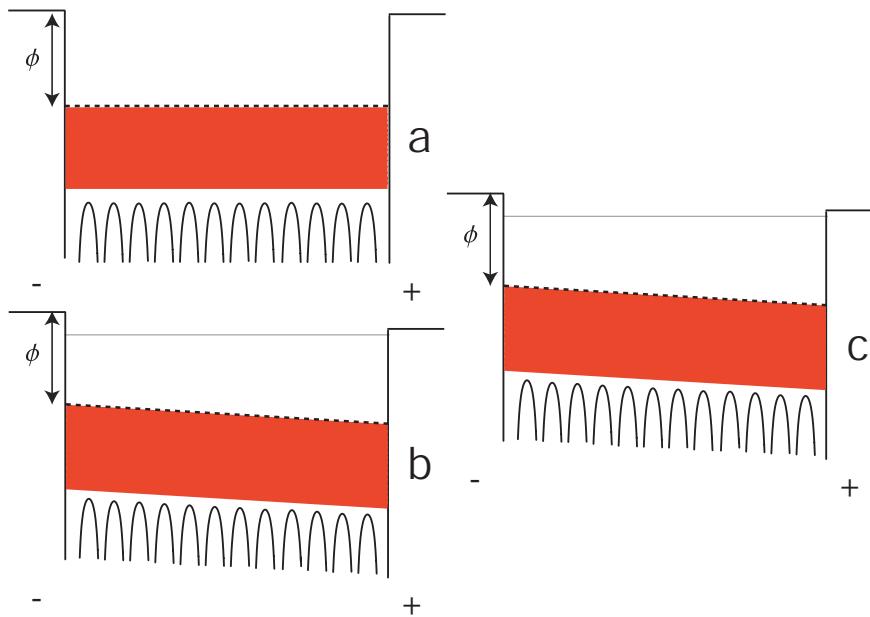
The “rest of the wave” was reflected from the barrier, and is traveling away from the barrier.

Q16.4) The overlap between wave functions can either be constructive or destructive, just as for waves. Can you distinguish between constructive and destructive overlap for the various energy levels in Figure 16.3?

Constructive interference occurs when the amplitudes add rather than subtract. It is observed for $n = 1$, $n = 3$, and $n = 5$. Destructive interference is observed for $n = 2$ and $n = 4$.

Q16.5) Redraw Figure 16.6 for an insulator.

For an insulator, the conduction band is completely filled. Consequently, when the field is applied, electrons can not migrate to the other end of the “box” because there are no allowed states in the band gap.



Q16.6) Explain, without using equations, why tunneling is more likely for the particle with $E = 3/4 V_0$ than for $E = 1/4 V_0$ in Figure 16.7.

Because the decay length, $1/\kappa$, is less for $E = 3/4 V_0$ than for $E = 1/4 V_0$, the exponentially decaying wave in the barrier has a higher amplitude at the end of the barrier if its energy is near the top of the barrier. This amplitude determines the amplitude of the traveling wave to the right of the barrier, and therefore the tunneling probability.

Q16.7) Why is it necessary to apply a bias voltage between the tip and surface in a scanning tunneling microscope (STM)?

The highest occupied energy levels in the tip and sample have the same energy without a bias voltage. Because tunneling occurs at constant energy, there are no empty levels for the electron to tunnel into. By applying a bias voltage of the appropriate polarity, the highest filled states in the tip and sample are offset, and tunneling can occur from the element that has the higher energy filled level.

Q16.8) An STM can also be operated in a mode in which electrons tunnel from the surface into the tip. Use Figure 16.8 to explain how you would change the experimental setup to reverse the tunneling current.

You would simply reverse the polarity of the battery. This would make the highest filled energy level in the surface higher than that in the tip. Therefore, the tunneling current would flow from the surface to the tip.

Q16.9) Explain how you can use size-quantized quantum dots to create a protein with a barcode that can be read using light.

Different fluorescent tags can be attached to the protein, for example one that emits red light, two that emit green light, and one that emits blue light. This combination of tags gives a different signal, or bar code, than a combination in which one tag emits red light, one tag emits green light, and two tags emit blue light.

Q16.10) Why is it necessary to functionalize CdSe quantum dots with groups such as organic acids to make them useful in bioanalytical applications?

The role of the functional groups is to make the CdSe quantum dots soluble in aqueous solutions.

Problems

P16.1) In this problem, you will solve for the total energy eigenfunctions and eigenvalues for an electron in a finite depth box. We first go through the calculation for the box parameters used in Figure 16.1. You will then carry out the calculation for a different set of parameters.

We describe the potential in this way:

$$V(x) = V_0 \quad \text{for } x \leq -\frac{a}{2} \quad \text{Region I}$$

$$V(x) = 0 \quad \text{for } -\frac{a}{2} < x < \frac{a}{2} \quad \text{Region II}$$

$$V(x) = V_0 \quad \text{for } x \geq \frac{a}{2} \quad \text{Region III}$$

The eigenfunctions must have the following form in these three regions:

$$\psi(x) = B \exp\left[+\sqrt{\frac{2m(V_0-E)}{\hbar^2}} x \right] + B' \exp\left[-\sqrt{\frac{2m(V_0-E)}{\hbar^2}} x \right] = Be^{+\kappa x} + B'e^{-\kappa x} \quad \text{Region I}$$

$$\psi(x) = C \sin \sqrt{\frac{2mE}{\hbar^2}} x + D \cos \sqrt{\frac{2mE}{\hbar^2}} x = C \sin kx + D \cos kx \quad \text{Region II}$$

$$\psi(x) = A \exp\left[-\sqrt{\frac{2m(V_0-E)}{\hbar^2}} x \right] + A' \exp\left[+\sqrt{\frac{2m(V_0-E)}{\hbar^2}} x \right] = A e^{-\kappa x} + A' e^{+\kappa x} \quad \text{Region III}$$

So that the wave functions remain finite at large positive and negative values of x , $A' = B' = 0$. An additional condition must also be satisfied. To arrive at physically meaningful solutions for the eigenfunctions, the wave functions in the separate regions must have the same amplitude and derivatives at the values of $x = a/2$ and $x = -a/2$ bounding the regions. This restricts the possible values for the coefficients A , B , C , and D . Show that applying these conditions gives the following equations:

$$B e^{-\kappa(a/2)} = -C \sin k \frac{a}{2} + D \cos k \frac{a}{2} \quad B \kappa e^{-\kappa(a/2)} = C k \cos k \frac{a}{2} + D k \sin k \frac{a}{2}$$

$$A e^{-\kappa(a/2)} = C \sin k \frac{a}{2} + D \cos k \frac{a}{2} \quad -A \kappa e^{-\kappa(a/2)} = C k \cos k \frac{a}{2} - D k \sin k \frac{a}{2}$$

These two pairs of equations differ on the right side only by the sign of one term. We can obtain a set of equations that contain fewer coefficients by adding and subtracting each pair of equations to give

$$(A+B)e^{-\kappa(a/2)} = 2D \cos\left(k \frac{a}{2}\right) \quad (A-B)e^{-\kappa(a/2)} = 2C \sin\left(k \frac{a}{2}\right)$$

$$(A+B)\kappa e^{-\kappa(a/2)} = 2Dk \sin\left(k \frac{a}{2}\right) \quad -(A-B)\kappa e^{-\kappa(a/2)} = 2Ck \cos\left(k \frac{a}{2}\right)$$

At this point we notice that by dividing the equations in each pair, the coefficients can be eliminated to give

$$\kappa = k \tan\left(k \frac{a}{2}\right) \text{ or } \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} = \sqrt{\frac{2mE}{\hbar^2}} \tan\left(\sqrt{\frac{2mE}{\hbar^2}} \frac{a}{2}\right) \text{ and}$$

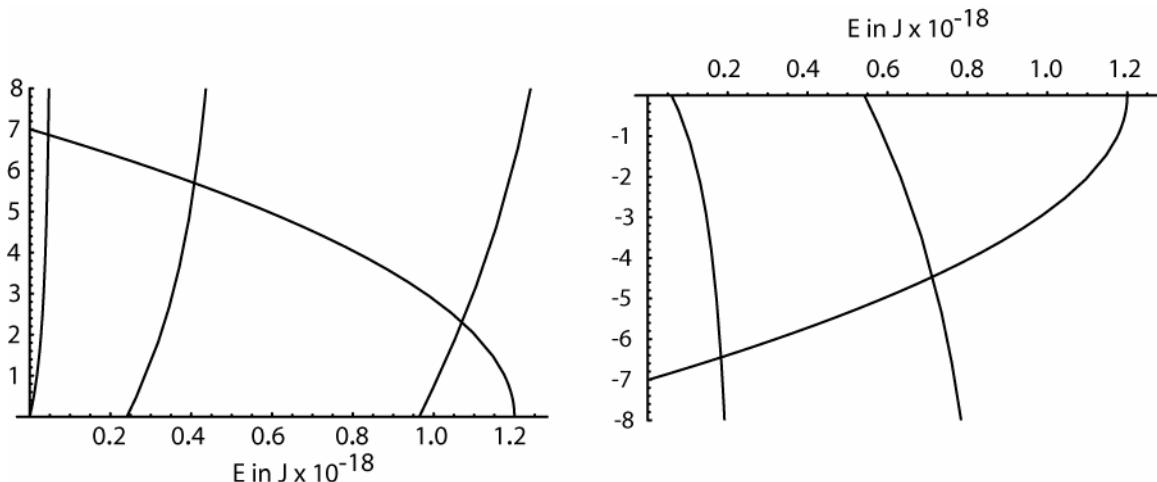
$$-\kappa = k \cotan\left(k \frac{a}{2}\right) \text{ or } -\sqrt{\frac{2m(V_0 - E)}{\hbar^2}} = \sqrt{\frac{2mE}{\hbar^2}} \cot\left(\sqrt{\frac{2mE}{\hbar^2}} \frac{a}{2}\right)$$

Multiplying these equations on both sides by $a/2$ gives dimensionless parameters and the final equations are

$$\sqrt{\frac{m(V_0 - E)a^2}{2\hbar^2}} = \sqrt{\frac{mEa^2}{2\hbar^2}} \tan \sqrt{\frac{mEa^2}{2\hbar^2}} \text{ and}$$

$$-\sqrt{\frac{m(V_0 - E)a^2}{2\hbar^2}} = \sqrt{\frac{mEa^2}{2\hbar^2}} \cot \sqrt{\frac{mEa^2}{2\hbar^2}}$$

The allowed energy values E must satisfy these equations. They can be obtained by graphing the two sides of each equation against E . The intersections of the two curves are the allowed energy eigenvalues. For the parameters in the caption of Figure 16.1, $V_0 = 1.20 \times 10^{-18}$ J and $a = 1.00 \times 10^{-9}$ m, the following two graphs are obtained.



The five allowed energy levels are at 4.61×10^{-20} , 4.09×10^{-19} , and 1.07×10^{-18} J (left figure), and 1.84×10^{-19} and 7.13×10^{-19} J (right figure).

- a) Given these values, calculate λ for each energy level. Is the relation $\lambda = 2a/n$ (for n an integer) that arose from the calculations on the infinitely deep box still valid? Compare the λ values with the corresponding energy level in the infinitely deep box. Explain why the differences arise.
- b) Repeat this calculation for $V_0 = 5.00 \times 10^{-19}$ J and $a = 0.900 \times 10^{-9}$ m. Do you think that there will be fewer or more bound states than for the problem just worked out? How many allowed energy levels are there for this well depth and what is the energy corresponding to each level?

a) Using the equation $\frac{\lambda}{a} = \frac{h}{a\sqrt{2mE}}$ we obtain the following values

E	λ/a	λ/a for infinite box
4.61×10^{-20} J	2.29	2.00
1.84×10^{-19} J	1.15	1.00
4.09×10^{-19} J	0.768	0.667
7.13×10^{-19} J	0.582	0.500
1.07×10^{-18} J	0.475	0.400

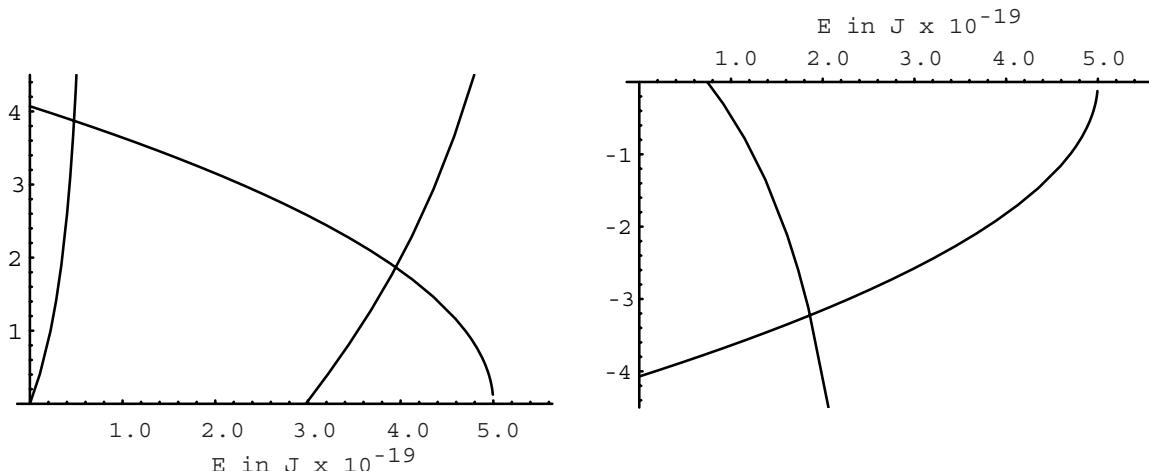
We see that λ/a is always greater for the finite depth box. This is necessary if the particle is to have a finite probability of being outside of the box. Note that if λ/a is less than that for the infinitely deep box, additional nodes are introduced inside the box.

- b) Because a finite depth box has fewer bound states than an infinitely deep box, one should expect that the number of bound states will decrease as the depth becomes less. Graphing the equations

$$\sqrt{\frac{m(V_0 - E)a^2}{2\hbar^2}} = \sqrt{\frac{mEa^2}{2\hbar^2}} \tan \sqrt{\frac{mEa^2}{2\hbar^2}} \quad \text{and}$$

$$-\sqrt{\frac{m(V_0 - E)a^2}{2\hbar^2}} = \sqrt{\frac{mEa^2}{2\hbar^2}} \cot \sqrt{\frac{mEa^2}{2\hbar^2}}$$

for $V_0 = 5.00 \times 10^{-19}$ J and $a = 0.900 \times 10^{-9}$ m gives



There are 3 bound states whose energies are $4.76 \times 10^{-20} \text{ J}$, $1.86 \times 10^{-19} \text{ J}$, and $3.95 \times 10^{-19} \text{ J}$.

P16.2) For the π -network of β -carotene modeled using the particle in the box, the position-dependent probability density of finding one of the 22 electrons is given by

$$P_n(x) = |\psi_n(x)|^2 = \frac{2}{a} \sin^2\left(\frac{n\pi x}{a}\right).$$

The quantum number n in this equation is determined

by the energy level of the electron under consideration. As we saw in Chapter 15, this function is strongly position dependent. The question addressed in this problem is as follows. Would you also expect the total probability density defined by

$P_{total}(x) = \sum_n |\psi_n(x)|^2$ to be strongly position dependent? The sum is over all the electrons in the π -network.

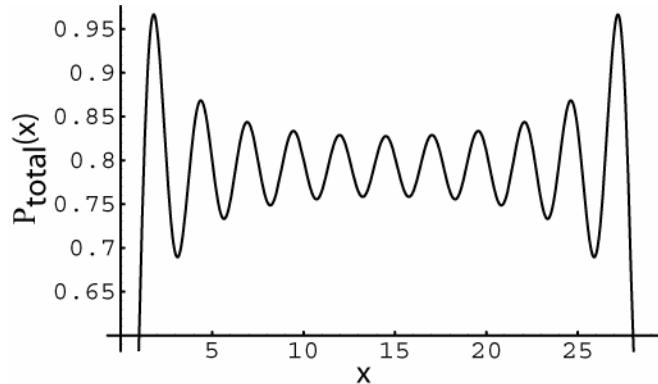
a) Calculate the total probability density $P_{total}(x) = \sum_n |\psi_n(x)|^2$ using the box length $a = 29.0 \text{ nm}$ and plot your results as a function of x . Does $P_{total}(x)$ have the same value near the ends and at the middle of the molecule?

b) Determine $\frac{\Delta P_{total}(x)}{\langle P_{total}(x) \rangle}$, where $\Delta P_{total}(x)$ is the peak-to-peak amplitude of $P_{total}(x)$ in the interval between 12.0 and 16.0 nm.

c) Compare the result of part (b) with what you would obtain for an electron in the highest occupied energy level.

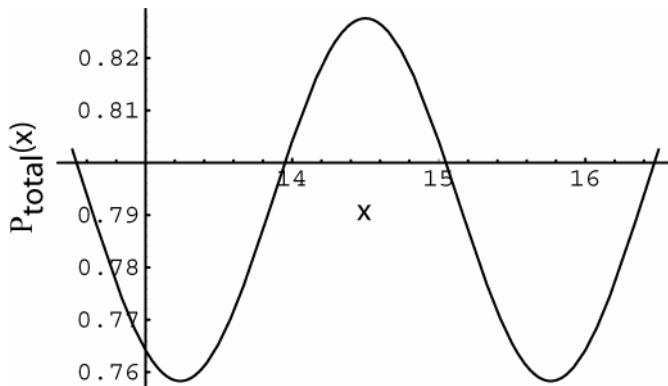
d) What value would you expect for $P_{total}(x)$ if the electrons were uniformly distributed over the molecule? How does this value compare with your result from part (a)?

a) Plotting the data for $P_{total}(x) = \sum_n |\psi_n(x)|^2$ gives the figure shown below.



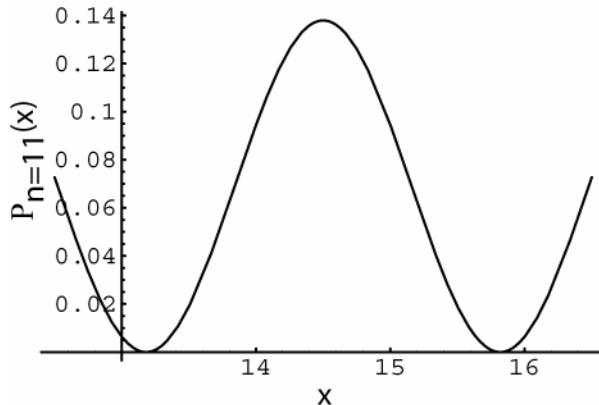
$P_{total}(x)$ varies more strongly near the ends of the chain than at the middle.

b) Plotting $P_{total}(x)$ over the interval 12 to 16 nm gives the figure shown below.



From this data, we see that $\frac{\Delta P_{total}(x)}{\langle P_{total}(x) \rangle} = \frac{0.07 \times 10^9 \text{ m}^{-1}}{0.79 \times 10^9 \text{ m}^{-1}} = 0.089$

c) Plotting $P_{n=11}(x)$ over the interval 12 to 16 nm gives the figure shown below.



From this data, we see that $\frac{\Delta P_{n=11}(x)}{\langle \Delta P_{total}(x) \rangle} = \frac{0.14 \times 10^9 \text{ m}^{-1}}{0.07 \times 10^9 \text{ m}^{-1}} = 2.0$

The variation of the probability density for the highest occupied state is approximately 20 times as large as that for the probability density for all electrons.

- d) There would be 22 electrons uniformly distributed over a length of 29 nm. Therefore the probability density would be $\frac{22}{29 \times 10^{-9} \text{ m}} = 0.76 \times 10^9 \text{ m}^{-1}$. This is very close to the average value obtained in part (a).

P16.3) Calculate the energy levels of the π -network in butadiene, C₄H₆, using the particle in the box model. To calculate the box length, assume that the molecule is linear and use the values 135 pm and 154 pm for C=C and C–C bonds. What is the wavelength of light required to induce a transition from the ground state to the first excited state? How does this compare with the experimentally observed value of 290 nm? What does the comparison made suggest to you about estimating the length of the π -network by adding bond lengths for this molecule?

The length of the box is $a = 2 \times 135 \text{ pm} + 154 \text{ pm} = 424 \text{ pm}$. The energy levels are given by

$$E_n = \frac{n^2 h^2}{8 m a^2} \text{ and the transition is between } n = 2 \text{ and } n = 3.$$

$$\lambda = \frac{c}{\nu} = \frac{c}{E/h} = \frac{8 m a^2 c}{h(n_2^2 - n_1^2)} = \frac{8 \times 9.11 \times 10^{-31} \text{ kg} \times (4.24 \times 10^{-10} \text{ m})^2 \times 2.998 \times 10^8 \text{ m s}^{-1}}{6.626 \times 10^{-34} \text{ J s} \times (3^2 - 2^2)} = 119 \text{ nm}$$

The calculated wavelength is lower than that observed. This suggests that the model is useful, but not quantitative. Within the model, one might conclude that the effective length of the π -network is longer than we used. This suggests that the π -network extends somewhat beyond the center of the terminal C atoms.

P16.4) Calculate the energy levels of the π -network in octatetraene, C₈H₁₀, using the particle in the box model. To calculate the box length, assume that the molecule is linear and use the values 135 and 154 pm for C=C and C–C bonds. What is the wavelength of light required to induce a transition from the ground state to the first excited state?

The length of the box is $a = 4 \times 135 \text{ pm} + 3 \times 154 \text{ pm} = 1002 \text{ pm}$. The energy levels are given by

$$E_n = \frac{n^2 h^2}{8 m a^2} \text{ and the transition is between } n = 4 \text{ and } n = 5.$$

$$\lambda = \frac{c}{\nu} = \frac{c}{E/h} = \frac{8 m a^2 c}{h(n_2^2 - n_1^2)} = \frac{8 \times 9.11 \times 10^{-31} \text{ kg} \times (10.02 \times 10^{-10} \text{ m})^2 \times 2.998 \times 10^8 \text{ ms}^{-1}}{6.626 \times 10^{-34} \text{ J s} \times (5^2 - 4^2)} \\ = 368 \text{ nm}$$

P16.5) Semiconductors can become conductive if their temperature is raised sufficiently to populate the (empty) conduction band from the highest filled levels in the valence band. The ratio of the populations in the highest level of the conduction band to that of

the lowest level in the conduction band is $\frac{n_{\text{conduction}}}{n_{\text{valence}}} = \frac{g_{\text{conduction}}}{g_{\text{valence}}} e^{-\Delta E/kT}$ where ΔE is the

band gap, which is 1.12 eV for Si and 5.5 eV for diamond. Assume for simplicity that the ratio of the degeneracies is one and that the semiconductor becomes sufficiently

conductive when $\frac{n_{\text{conduction}}}{n_{\text{valence}}} = 5.5 \times 10^{-7}$. At what temperatures will silicon and diamond

become sufficiently conductive? Given that the most stable form of carbon at normal pressures is graphite and that graphite sublimates near 3700 K, could you heat diamond enough to make it conductive and not sublimate it?

For silicon, we obtain

$$T_{Si} = \frac{-\Delta E}{k \ln \left[\left(\frac{g_{\text{valence}}}{g_{\text{conduction}}} \right) \left(\frac{n_{\text{conduction}}}{n_{\text{valence}}} \right) \right]} = \frac{-1.12 \text{ eV} \times 1.602 \times 10^{-19} \text{ J/eV}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times \ln(5.5 \times 10^{-7})} = 901 \text{ K}$$

For diamond, we obtain

$$T_C = \frac{-\Delta E}{k \ln \left[\left(\frac{g_{\text{valence}}}{g_{\text{conduction}}} \right) \left(\frac{n_{\text{conduction}}}{n_{\text{valence}}} \right) \right]} = \frac{-5.5 \text{ eV} \times 1.602 \times 10^{-19} \text{ J/eV}}{1.381 \times 10^{-23} \text{ J K}^{-1} \ln(5.5 \times 10^{-7})} = 4427 \text{ K}$$

We predict that diamond would not become conductive before it decomposes.

P16.6) In this problem, you will calculate the transmission probability through the barrier illustrated in Figure 16.7. We first go through the mathematics leading to the solution. You will then carry out further calculations.

The domain in which the calculation is carried out is divided into three regions for which the potentials are

$$V(x) = 0 \text{ for } x \leq 0 \quad \text{Region I}$$

$$V(x) = V_0 \text{ for } 0 < x < a \quad \text{Region II}$$

$$V(x) = 0 \text{ for } x \geq a \quad \text{Region III}$$

The wave functions must have the following form in the three regions if $E < V_0$:

$$\begin{aligned} \psi(x) &= A \exp\left[+i\sqrt{\frac{2mE}{\hbar^2}}x\right] + B \exp\left[-i\sqrt{\frac{2mE}{\hbar^2}}x\right] \\ &= A e^{+ikx} + B e^{-ikx} \end{aligned} \quad \text{Region I}$$

$$\begin{aligned} \psi(x) &= C \exp\left[-\sqrt{\frac{2m(V_0-E)}{\hbar^2}}x\right] + D \exp\left[+\sqrt{\frac{2m(V_0-E)}{\hbar^2}}x\right] \\ &= C e^{-\kappa x} + D e^{+\kappa x} \end{aligned} \quad \text{Region II}$$

$$\begin{aligned} \psi(x) &= F \exp\left[+i\sqrt{\frac{2mE}{\hbar^2}}x\right] + G \exp\left[-i\sqrt{\frac{2mE}{\hbar^2}}x\right] \\ &= F e^{+ikx} + G e^{-ikx} \end{aligned} \quad \text{Region III}$$

Assume that the wave approaches the barrier from the negative x direction. The

coefficient A cannot be set equal to zero because $A e^{+i\sqrt{\frac{2mE}{\hbar^2}}x}$ represents reflection from the barrier. However, G can be set equal to zero because there is no wave incident on the barrier from the positive x direction.

- a) The wave functions and their derivatives must be continuous at $x = 0$ and $x = a$. Show that the coefficients must satisfy the following conditions:

$$A + B = C + D \quad C e^{-\kappa a} + D e^{+\kappa a} = F e^{+ika}$$

$$A - B = -\frac{i\kappa}{k}(-C + D) \quad -C e^{-\kappa a} + D e^{+\kappa a} = \frac{ik}{\kappa} F e^{+ika}$$

- b) Because the transmission probability is given by $\left|\frac{F}{A}\right|^2$, it is useful to manipulate these

equations to get a relationship between F and A . By adding and subtracting the first pair of equations, A and B can be expressed in terms of C and D . The second pair of equations can be solved individually to give equations for D and C in terms of F .

Show that

$$D = \frac{ik e^{+ika} + \kappa e^{+ika}}{2\kappa e^{+ka}} F$$

$$C = \frac{-ik e^{+ika} + \kappa e^{+ika}}{2\kappa e^{-ka}} F, \text{ and}$$

$$A = \frac{(ik - \kappa)C + (ik + \kappa)D}{2ik}$$

c) Substitute these results for C and D in terms of F into $A = \frac{(ik - \kappa)C + (ik + \kappa)D}{2ik}$ to relate A and F . Show that

$$2ikA = \frac{e^{+ika}}{2\kappa} [(ik - \kappa)(-ik + \kappa)e^{+ka} + (ik + \kappa)(ik + \kappa)e^{-ka}] F$$

d) Using the hyperbolic trigonometric functions $\sinh x = \frac{e^x - e^{-x}}{2}$ and $\cosh x = \frac{e^x + e^{-x}}{2}$

and the relationship $\cosh^2 x + \sinh^2 x = 1$, show that

$$\left| \frac{F}{A} \right|^2 = \frac{16(\kappa k)^2}{16(\kappa k)^2 + (4(k^2 - \kappa^2)^2 + 16(\kappa k)^2) \sinh^2(\kappa a)} = \frac{1}{1 + \frac{(k^2 + \kappa^2)^2 \sinh^2(\kappa a)}{4(\kappa k)^2}}$$

e) Plot the transmission probability for an electron as a function of energy for $V_0 = 1.6 \times 10^{-19}$ J and $a = 9.0 \times 10^{-10}$ m up to an energy of 8×10^{-19} J. At what energy is the tunneling probability 0.1? At what energy is the tunneling probability 0.02?

f) Plot the transmission probability for an electron of energy 0.50×10^{-19} J as a function of the barrier width for $V_0 = 1.6 \times 10^{-19}$ J between 2×10^{-10} and 8×10^{-10} m. At what barrier width is the transmission probability 0.2?

a)

$$\psi(x) = A e^{+i\sqrt{\frac{2mE}{\hbar^2}}x} + B e^{-i\sqrt{\frac{2mE}{\hbar^2}}x} = A e^{+ikx} + B e^{-ikx} \quad \text{Region I}$$

$$\psi(x) = C e^{-\sqrt{\frac{2m(V_0-E)}{\hbar^2}}x} + D e^{+\sqrt{\frac{2m(V_0-E)}{\hbar^2}}x} = C e^{-\kappa x} + D e^{+\kappa x} \quad \text{Region II}$$

$$\psi(x) = F e^{+i\sqrt{\frac{2mE}{\hbar^2}}x} + G e^{-i\sqrt{\frac{2mE}{\hbar^2}}x} = F e^{+ikx} + G e^{-ikx} \quad \text{Region III}$$

At $x = 0$, the boundary between regions I and II, set the amplitudes of the wave functions equal.

$$A + B = C + D$$

Differentiate the wave functions and set $x = 0$.

$$ikA - ikB = -\kappa C + \kappa D$$

$$A - B = -\frac{i\kappa}{k}(-C + D)$$

At $x = a$, the boundary between regions II and III, set the amplitudes of the wave functions equal.

$$C e^{-\kappa a} + D e^{+\kappa a} = F e^{+ik a}$$

Differentiate the wave functions and set $x = a$.

$$-\kappa C e^{-\kappa a} + \kappa D e^{+\kappa a} = ikF e^{+ik a}$$

$$-C e^{-\kappa a} + D e^{+\kappa a} = \frac{ik}{\kappa} F e^{+ik a}$$

b) We begin by eliminating B from the set of equations.

Solving $ikA - ik(C + D - A) = -\kappa C + \kappa D$ for A gives

$$A = \frac{(ik - \kappa)C + (ik + \kappa)D}{2ik}$$

$$\text{Rewriting } C e^{-\kappa a} + D e^{+\kappa a} = F e^{+ik a} \text{ in the form } C = \frac{F e^{+ik a} - D e^{+\kappa a}}{e^{-\kappa a}}$$

and substituting this result into $-\kappa C e^{-\kappa a} + \kappa D e^{+\kappa a} = ikF e^{+ik a}$ gives

$$-\kappa \left(\frac{F e^{+ik a} - D e^{+\kappa a}}{e^{-\kappa a}} \right) e^{-\kappa a} + \kappa D e^{+\kappa a} = ikF e^{+ik a} \text{ or}$$

$$-\kappa F e^{+ik a} + 2\kappa D e^{+\kappa a} = ikF e^{+ik a}$$

resulting in an equation relating D and F

$$D = \frac{ik e^{+ik a} + \kappa e^{+ik a}}{2\kappa e^{+\kappa a}} F$$

To relate C and F we begin with the two equations

$$C e^{-\kappa a} + D e^{+\kappa a} = F e^{+ik a} \text{ and } -\kappa C e^{-\kappa a} + \kappa D e^{+\kappa a} = i k F e^{+ik a}$$

Solving the second equation for C and using our result for D , we obtain

$$\begin{aligned} C &= \frac{\kappa D e^{+\kappa a} - i k F e^{+ik a}}{\kappa e^{-\kappa a}} = \frac{\kappa \left(\frac{i k e^{ik a} + \kappa e^{ik a}}{2 \kappa e^{+\kappa a}} F \right) e^{+\kappa a} - i k F e^{+ik a}}{\kappa e^{-\kappa a}} \\ C &= \frac{-i k e^{+ik a} + \kappa e^{+ik a}}{2 \kappa e^{-\kappa a}} F \end{aligned}$$

c) We now use the expressions for C and D in terms of F to express A in terms of F .

We substitute these expressions for C and D into $A = \frac{(ik - \kappa)C + (ik + \kappa)D}{2ik}$ giving

$$A = \frac{(ik - \kappa) \frac{-i k e^{+ik a} + \kappa e^{+ik a}}{2 \kappa e^{-\kappa a}} F + (ik + \kappa) \frac{i k e^{+ik a} + \kappa e^{+ik a}}{2 \kappa e^{-\kappa a}} F}{2ik}$$

d) To obtain the ratio $\frac{F}{A}$, we proceed as follows.

$$2ik A = \frac{e^{+ik a}}{2\kappa} [(ik - \kappa)(-ik + \kappa)e^{+\kappa a} + (ik + \kappa)(ik + \kappa)e^{-\kappa a}] F$$

$$2ik A = \frac{e^{+ik a}}{2\kappa} [k^2 e^{-\kappa a} + 2ik\kappa e^{+\kappa a} - \kappa^2 e^{+\kappa a} + 2ik\kappa e^{-\kappa a} + \kappa^2 e^{-\kappa a}] F$$

Using the definitions $\sinh x = \frac{e^x - e^{-x}}{2}$ and $\cosh x = \frac{e^x + e^{-x}}{2}$

$$\frac{F}{A} = \frac{4ik\kappa e^{-ik a}}{(k^2 - \kappa^2)(e^{+\kappa a} - e^{-\kappa a}) + 2ik\kappa(e^{+\kappa a} - e^{-\kappa a})} = \frac{4ik\kappa e^{-ik a}}{2(k^2 - \kappa^2)\sinh \kappa a + 4ik\kappa \cosh \kappa a}$$

$$\left| \frac{F}{A} \right|^2 = \frac{4ik\kappa e^{-ik a}}{2(k^2 - \kappa^2)\sinh \kappa a + 4ik\kappa \cosh \kappa a} \frac{-4ik\kappa e^{+ik a}}{2(k^2 - \kappa^2)\sinh \kappa a - 4ik\kappa \cosh \kappa a}$$

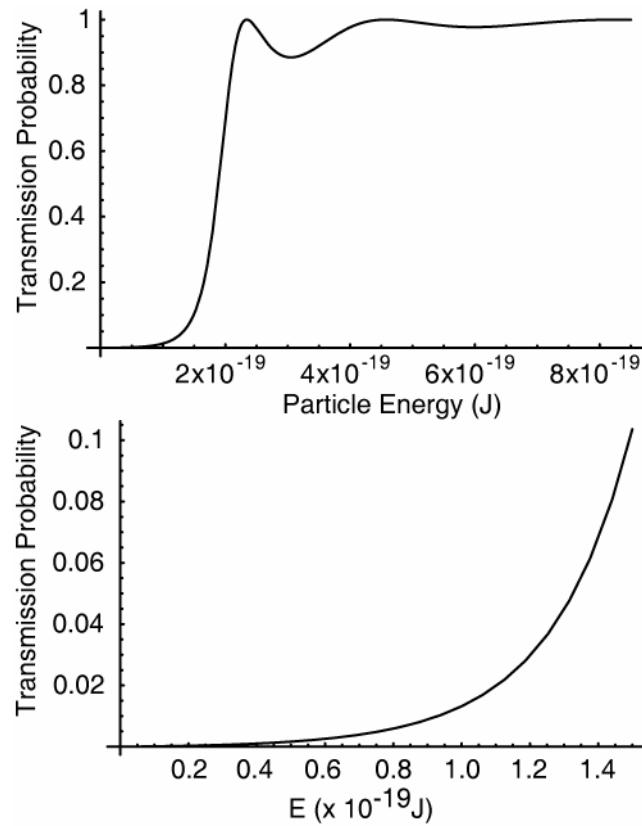
$$\left| \frac{F}{A} \right|^2 = \frac{16(k\kappa)^2}{4(k^2 - \kappa^2)\sinh^2 \kappa a + 16(k\kappa)^2 \cosh^2 \kappa a} = \frac{16(k\kappa)^2}{4(k^2 - \kappa^2)\sinh^2 \kappa a + 16(k\kappa)^2 (1 + \sinh^2 \kappa a)}$$

In the last step, we have used the relation $\sinh^2 x + \cosh^2 x = 1$

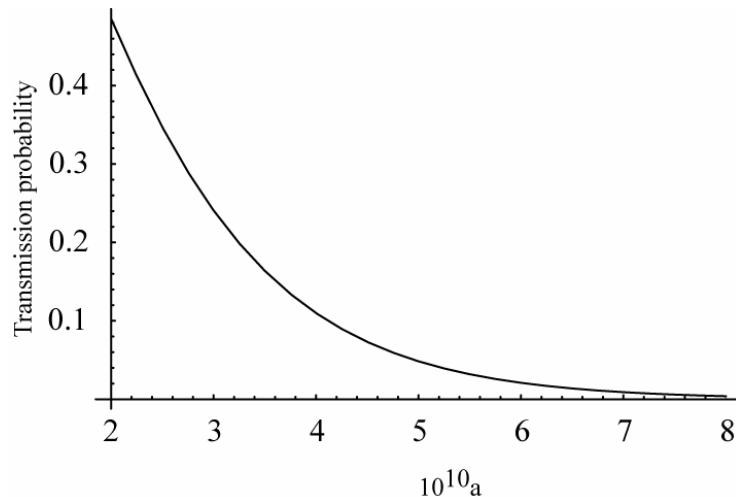
Our final result is a rather compact equation.

$$\left| \frac{F}{A} \right|^2 = \left| \frac{F}{A} \right|^2 = \frac{16(\kappa k)^2}{16(\kappa k)^2 + [4(k^2 - \kappa^2)^2 + 16(\kappa k)^2] \sinh^2(\kappa a)} = \frac{1}{1 + \frac{(k^2 + \kappa^2)^2 \sinh^2(\kappa a)}{4(\kappa k)^2}}$$

e) Plotting $\left| \frac{F}{A} \right|^2$ as a function of E , we obtain the following graph. By replotted the data over a smaller interval near $E = 1 \times 10^{-19}$ J, we find that $\left| \frac{F}{A} \right|^2 = 0.1$ for $E = 1.5 \times 10^{-19}$ J and 0.02 for $E = 1.1 \times 10^{-19}$ J.



f) The transmission probability as a function of the barrier width is shown below. The probability is 0.2 for a width of $a = 3.2 \times 10^{-10}$ m.



P16.7) The maximum safe current in a copper wire with a diameter of 3.0 mm is about 20 amperes. In an STM, a current of 1.0×10^{-9} A passes from the tip to the surface in a filament of diameter ~ 1.0 nm. Compare the current density in the copper wire with that in the STM.

The current density in the copper wire is given by

$$J_{Cu} = \frac{I}{A} = \frac{I}{\pi r^2} = \frac{20\text{A}}{\pi(1.5 \times 10^{-3}\text{m})^2} = 2.8 \times 10^6 \text{A/m}^2$$

The current density in the STM is given by

$$J_{STM} = \frac{I}{A} = \frac{I}{\pi r^2} = \frac{1.0 \times 10^{-9}\text{A}}{\pi(0.5 \times 10^{-9}\text{m})^2} = 1.3 \times 10^9 \text{A/m}^2$$

The current density is greater in the STM by nearly three orders of magnitude.

Chapter 17: Commuting and Noncommuting Operators and the Surprising Consequences of Entanglement

Problem numbers in italics indicate that the solution is included in the *Student's Solutions Manual*.

Questions on Concepts

Q17.1) Why does the Stern-Gerlach experiment show that the operator “measure the z component of the magnetic moment of an Ag atom” has only two eigenfunctions with eigenvalues that have the same magnitude and opposite sign?

Only two deflections are measured, showing that the operator has only two eigenvalues. Because the deflections are symmetric about zero, the magnitude of the eigenvalues must be equal, and their sign must be opposite.

Q17.2) Which result of the Stern-Gerlach experiment allows us to conclude that the operators for the z and x components of the magnetic moment do not commute?

The observation that two sets of deflections are observed after the third analyzer, which is oriented in the same way as the first, show that the operators for the z and x components of the magnetic moment do not commute.

Q17.3) Why is $\sqrt{\langle p^2 \rangle}$ rather than $\langle p \rangle$ used to calculate the relative uncertainty for the particle in the box?

Because the particle is equally likely to move to the right as the left, $\langle p \rangle$ is zero even though the magnitude of the momentum is not zero. Therefore, $\sqrt{\langle p^2 \rangle}$ is used to characterize the “average momentum.”

Q17.4) Why does the relative uncertainty in x for the particle in the box increase as $n \rightarrow \infty$?

This is the case because the quantum mechanical particle is more strongly localized than a classical particle for small energies, corresponding to small values of n .

Q17.5) Why is the statistical concept of variance a good measure of uncertainty in a quantum mechanical measurement?

The variance is used in error analysis if the result of an experiment has random errors associated with it. Because in quantum mechanics the outcome of a single

experiment is probabilistic rather than deterministic, the variance is a useful quantity in calculating the distribution of individual measurements.

Q17.6) How does our study of the eigenfunctions for the particle in the box let us conclude that the position uncertainty has its minimum value for $n = 1$?

The range of x over which the amplitude of the total energy eigenfunction is significantly different from zero is smaller for the ground state than for excited states. Therefore, the particle is more localized for the state $n = 1$.

Q17.7) How does the Heisenberg uncertainty principle allow us to conclude that it is not possible to make exact copies of quantum mechanical objects?

If we could make exact copies, we could measure the momentum in one system and the position in the other system. This would allow us to know both quantities exactly, which is a violation of the uncertainty principle.

Q17.8) Explain the following statement: If $\hbar = 0$, it would be possible to measure the position and momentum of a particle exactly and simultaneously.

In that case, the Heisenberg uncertainty principle would be $\Delta p \Delta x = 0$, and there are no uncertainties associated with the position and the momentum.

Q17.9) Why is it not possible to reconstruct the wave function of a quantum mechanical superposition state from experiments?

Consider Equation (17.2): $\psi = \frac{c_1}{\sqrt{2}}\alpha + \frac{c_2}{\sqrt{2}}\beta$ with $|c_1|^2 + |c_2|^2 = 1$. Only the

magnitudes $|c_1|_{\text{average}}^2 = |c_2|_{\text{average}}^2 = \frac{1}{2}$ can be determined in an experiment.

However, to reconstruct the wave function, we need c_1 and c_2 , and not just their magnitudes.

Q17.10) Have a closer look at Equation (17.6) and Figure 17.4. How would Figure 17.4 change if m increases? Generalize your conclusion to make a statement of how well the momentum is known if the position is known exactly.

The particle would be more localized because the uncertainty in momentum would increase. As shown by the Heisenberg uncertainty principle, the uncertainty in momentum becomes infinite if the uncertainty in position is zero.

Problems

P17.1) For linear operators \hat{A} , \hat{B} , and \hat{C} , show that $[\hat{A}, \hat{B}, \hat{C}] = [\hat{A}, \hat{B}] \hat{C} + \hat{B} [\hat{A}, \hat{C}]$.

$$\begin{aligned} [\hat{A}, \hat{B}] \hat{C} f(x) + \hat{B} [\hat{A}, \hat{C}] f(x) &= \hat{A} \hat{B} \hat{C} f(x) - \hat{B} \hat{A} \hat{C} f(x) + \hat{B} \hat{A} \hat{C} f(x) - \hat{B} \hat{C} \hat{A} f(x) \\ &= \hat{A} \hat{B} \hat{C} f(x) - \hat{B} \hat{C} \hat{A} f(x) = [\hat{A}, \hat{B} \hat{C}] f(x) \end{aligned}$$

P17.2) Evaluate the commutator $\left[\frac{d}{dx} - x, \frac{d}{dx} + x \right]$ by applying the operators to an arbitrary function $f(x)$.

$$\begin{aligned} \left[\frac{d}{dx} - x, \frac{d}{dx} + x \right] f(x) &= \left(\frac{d}{dx} - x \right) \left(\frac{d}{dx} + x \right) f(x) - \left(\frac{d}{dx} + x \right) \left(\frac{d}{dx} - x \right) f(x) \\ &= \left(\frac{d}{dx} - x \right) \left(\frac{df(x)}{dx} + xf(x) \right) - \left(\frac{d}{dx} + x \right) \left(\frac{df(x)}{dx} - xf(x) \right) \\ &= \frac{d^2 f(x)}{dx^2} + f(x) + x \frac{df(x)}{dx} - x \frac{df(x)}{dx} - x^2 f(x) - \frac{d^2 f(x)}{dx^2} + f(x) + x \frac{df(x)}{dx} - x \frac{df(x)}{dx} + x^2 f(x) \\ &= 2f(x) \text{ Therefore,} \\ \left[\frac{d}{dx} - x, \frac{d}{dx} + x \right] &= 2 \end{aligned}$$

P17.3) Evaluate the commutator $[\hat{x}, \hat{p}_x]$ by applying the operators to an arbitrary function $f(x)$. Without doing a calculation, what value would you expect the commutator $[\hat{p}_x, \hat{x}]$ to have?

$$\begin{aligned} [\hat{x}, \hat{p}_x] f(x) &= \hat{x} \hat{p}_x f(x) - \hat{p}_x \hat{x} f(x) \\ &= -i\hbar x \frac{df(x)}{dx} + i\hbar \frac{d}{dx} (x f(x)) \\ &= -i\hbar x \frac{df(x)}{dx} + i\hbar \frac{d}{dx} f(x) + i\hbar x \frac{df(x)}{dx} \\ [\hat{x}, \hat{p}_x] &= i\hbar \end{aligned}$$

Because the order of operation is interchanged, the commutator would have the same value, but a positive sign.

P17.4) Evaluate the commutator $\left[\frac{d}{dx}, x^2 \right]$ by applying the operators to an arbitrary function $f(x)$.

$$\begin{aligned} \left[\frac{d}{dx}, x^2 \right] f(x) &= \frac{d}{dx} (x^2 f(x)) - x^2 \frac{d}{dx} f(x) \\ &= 2x f(x) + x^2 \frac{d}{dx} f(x) - x^2 \frac{d}{dx} f(x) = 2x f(x) \\ \left[\frac{d}{dx}, x^2 \right] &= 2x \end{aligned}$$

P17.5) Evaluate the commutator $\left[\frac{d^2}{dx^2}, x \right]$ by applying the operators to an arbitrary function $f(x)$.

$$\begin{aligned} \left[\frac{d^2}{dx^2}, x \right] f(x) &= \frac{d^2}{dx^2} (x f(x)) - x \left(\frac{d^2}{dx^2} f(x) \right) \\ &= \left\{ 2 \frac{df(x)}{dx} + x \frac{d^2 f(x)}{dx^2} - x \frac{d^2 f(x)}{dx^2} \right\} = \left(2 \frac{d}{dx} \right) f(x) \\ \left[\frac{d^2}{dx^2}, x \right] &= 2 \frac{d}{dx} \end{aligned}$$

P17.6) Evaluate the commutator $[\hat{x}, \hat{p}_x^2]$ by applying the operators to an arbitrary function $f(x)$.

$$\begin{aligned} [\hat{x}, \hat{p}_x^2] f(x) &= \hat{x} \hat{p}_x [\hat{p}_x f(x)] - \hat{p}_x [\hat{p}_x \{\hat{x} f(x)\}] \\ &= \hbar^2 x \frac{d^2 f(x)}{dx^2} - \hbar^2 \frac{d}{dx} \left(\frac{d [x f(x)]}{dx} \right) \\ &= \hbar^2 x \frac{d^2 f(x)}{dx^2} - \hbar^2 \frac{d}{dx} \left(f(x) + x \frac{df(x)}{dx} \right) \\ &= \hbar^2 x \frac{d^2 f(x)}{dx^2} - \hbar^2 \left(\frac{d f(x)}{dx} + \frac{d f(x)}{dx} + x \frac{d^2 f(x)}{dx^2} \right) \\ &= -2\hbar^2 \frac{d f(x)}{dx} \\ [\hat{x}, \hat{p}_x^2] &= -2\hbar^2 \frac{d f(x)}{dx} = 2i\hbar \hat{p}_x \end{aligned}$$

P17.7) Evaluate the commutator $\left[\hat{x} \frac{\partial}{\partial y}, \hat{y} \right]$ by applying the operators to an arbitrary function $f(x,y)$.

$$\begin{aligned}\left[\hat{x} \frac{\partial}{\partial y}, \hat{y} \right] f(x,y) &= x \frac{\partial y f(x,y)}{\partial y} - yx \frac{\partial f(x,y)}{\partial y} \\ &= xf(x,y) + xy \frac{\partial f(x,y)}{\partial y} - yx \frac{\partial f(x,y)}{\partial y} = xf(x,y)\end{aligned}$$

Therefore $\left[\hat{x} \frac{\partial}{\partial y}, \hat{y} \right] = x$

P17.8) Evaluate the commutator $\left[\hat{p}_x, \hat{p}_x^2 \right]$ by applying the operators to an arbitrary function $f(x)$.

$$\begin{aligned}\left[\hat{p}_x, \hat{p}_x^2 \right] f(x) &= \left(-i\hbar \frac{d}{dx} \right) \left(-\hbar^2 \frac{d^2}{dx^2} \right) f(x) - \left(-\hbar^2 \frac{d^2}{dx^2} \right) \left(-i\hbar \frac{d}{dx} \right) f(x) \\ &= i\hbar^3 \left(\frac{d^3 f(x)}{dx^3} - \frac{d^3 f(x)}{dx^3} \right) = 0\end{aligned}$$

Therefore $\left[\hat{p}_x, \hat{p}_x^2 \right] = 0$

P17.9) Evaluate the commutator $\left[\frac{d}{dr}, \frac{1}{r} \right]$ by applying the operators to an arbitrary function $f(r)$.

$$\begin{aligned}\left[\frac{d}{dr}, \frac{1}{r} \right] f(r) &= \frac{d}{dr} \left(\frac{f(r)}{r} \right) - \frac{1}{r} \frac{df(r)}{dr} \\ &= -\frac{1}{r^2} f(r) + \frac{1}{r} \frac{df(r)}{dr} - \frac{1}{r} \frac{df(r)}{dr} = -\frac{1}{r^2} f(r)\\ \text{Therefore, } \left[\frac{d}{dr}, \frac{1}{r} \right] &= -\frac{1}{r^2}\end{aligned}$$

P17.10) If the wave function describing a system is not an eigenfunction of the operator \hat{B} , measurements on identically prepared systems will give different results. The variance of this set of results is defined in error analysis as $\sigma_B^2 = \langle (B - \langle B \rangle)^2 \rangle$, where B is

the value of the observable in a single measurement and $\langle B \rangle$ is the average of all measurements. Using the definition of average value from the quantum mechanical postulates, $\langle A \rangle = \int \psi^*(x) \hat{A} \psi(x) dx$, show that $\sigma_B^2 = \langle B^2 \rangle - \langle B \rangle^2$.

$$\begin{aligned}\langle (B - \langle B \rangle)^2 \rangle &= \int \psi^*(x) (\hat{B} - \langle \hat{B} \rangle)^2 \psi(x) dx \\ &= \int \psi^*(x) \hat{B}^2 \psi(x) dx + \int \psi^*(x) \langle \hat{B} \rangle^2 \psi(x) dx - 2 \int \psi^*(x) \langle \hat{B} \rangle \hat{B} \psi(x) dx\end{aligned}$$

Because $\langle \hat{B} \rangle^2$ and $\langle \hat{B} \rangle$ are numbers, they can be taken out of the integrals.

$$\begin{aligned}&= \int \psi^*(x) \hat{B}^2 \psi(x) dx + \langle B \rangle^2 \int \psi^*(x) \psi(x) dx - 2 \langle B \rangle \int \psi^*(x) \hat{B} \psi(x) dx \\ &= \langle B^2 \rangle + \langle B \rangle^2 - 2 \langle B \rangle \langle B \rangle = \langle B^2 \rangle - \langle B \rangle^2\end{aligned}$$

P17.11) Revisit the double-slit experiment of Example Problem 17.2. Using the same geometry and relative uncertainty in the momentum, what electron momentum would give a position uncertainty of 1.00×10^{-9} m? What is the ratio of the wavelength and the slit spacing for this momentum? Would you expect a pronounced diffraction effect for this wavelength?

$$\Delta p = \frac{1}{2} \frac{\hbar}{\Delta x} = \frac{1.055 \times 10^{-34} \text{ J s}}{2.00 \times 10^{-9} \text{ m}} = 5.275 \times 10^{-26} \text{ kg m s}^{-1}$$

$$p = \frac{\Delta p}{0.01} = 5.275 \times 10^{-24} \text{ kg m s}^{-1}$$

$$\lambda = \frac{h}{p} = \frac{6.626 \times 10^{-34} \text{ J s}}{5.275 \times 10^{-24} \text{ kg m s}^{-1}} = 1.26 \times 10^{-10} \text{ m}$$

Because $\frac{\lambda}{b} = \frac{1.26 \times 10^{-10} \text{ m}}{1.000 \times 10^{-9} \text{ m}} = 0.126$, the diffraction will hardly be noticeable.

P17.12) Revisit the TV picture tube of Example Problem 17.3. Keeping all other parameters the same, what electron energy would result in a position uncertainty of 1.00×10^{-8} m?

$$\Delta p = \frac{\hbar}{2\Delta x} = \frac{1.055 \times 10^{-34} \text{ J s}}{2.00 \times 10^{-8} \text{ m}} = 5.275 \times 10^{-27} \text{ kg m s}^{-1}$$

$$p = \frac{\Delta p}{0.01} = 5.275 \times 10^{-25} \text{ kg m s}^{-1}$$

$$E = \frac{p^2}{2m} = \frac{(5.275 \times 10^{-25} \text{ kg m s}^{-1})^2}{2 \times 9.11 \times 10^{-31} \text{ kg}} = 1.52 \times 10^{-19} \text{ J} = 0.95 \text{ eV}$$

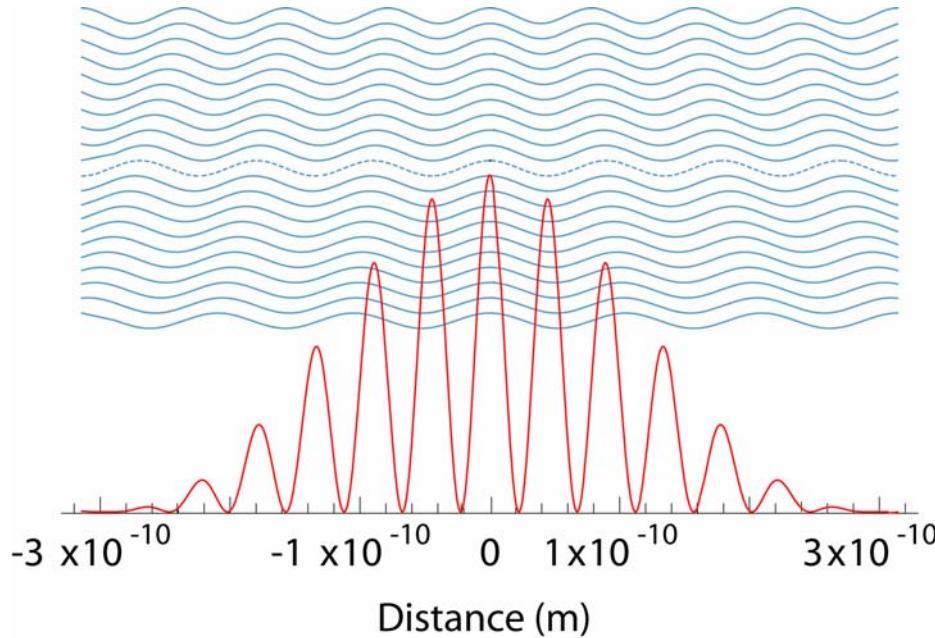
P17.13) The muzzle velocity of a rifle bullet is about 900 m s^{-1} . If the bullet weighs 30 g, and the uncertainty in its momentum is 0.10%, how accurately can the position of the bullet be measured?

$$p = mv = 30 \times 10^{-3} \text{ kg} \times 900 \text{ m s}^{-1} = 27 \text{ kg m s}^{-1}$$

$$\Delta p = 10^{-3} p = 2.7 \times 10^{-2} \text{ kg m s}^{-1}$$

$$\Delta x = \frac{\hbar}{2\Delta p} = \frac{1.055 \times 10^{-34} \text{ J s}}{2 \times 2.7 \times 10^{-2} \text{ kg m s}^{-1}} = 1.9 \times 10^{-33} \text{ m}$$

P17.14) Consider the results of Figure 17.4 more quantitatively. Describe the values of x and k by $x \pm \Delta x$ and $k_0 \pm \Delta k$. Evaluate Δx from the zero of distance to the point at which the envelope of $\psi^*(x)\psi(x)$ is reduced to one-half of its peak value. Evaluate Δk from $\Delta k = \left| \frac{1}{2}(k_0 - k_{\min}) \right|$ where k_0 is the average wavevector of the set of 21 waves (11th of 21) and k_{\min} corresponds to the 21st of the 21 waves. Is your estimated value of $\Delta p \Delta x = \hbar \Delta k \Delta x$ in reasonable agreement with the Heisenberg uncertainty principle?



From the graph, $\Delta x = 1.6 \times 10^{-10} \text{ m}$ and $\lambda_{\max} = 1.1 \times 10^{-10} \text{ m}$.

$$k_{\min} = \frac{2\pi}{\lambda_{\max}} = \frac{2\pi}{1.1 \times 10^{-10} \text{ m}} = 5.7 \times 10^{10} \text{ m}^{-1}$$

$$\Delta k = \left| \frac{1}{2} (k_0 - k_{\min}) \right| = \left| \frac{1}{2} (7.0 \times 10^{10} \text{ m}^{-1} - 5.7 \times 10^{10} \text{ m}^{-1}) \right| = 6.5 \times 10^9 \text{ m}^{-1}$$

$$\Delta p \Delta x = \hbar \Delta k \Delta x = \hbar \times 6.5 \times 10^9 \text{ m}^{-1} \times 1.6 \times 10^{-10} \text{ m} = 1.0 \hbar \geq 0.5 \hbar.$$

This is in reasonable agreement with the Heisenberg uncertainty principle.

P17.15) Apply the Heisenberg uncertainty principle to estimate the zero point energy for the particle in the box.

- a) First justify the assumption that $\Delta x \leq a$ and that, as a result, $\Delta p \geq \hbar/2a$. Justify the statement that, if $\Delta p \geq 0$, we cannot know that $E = p^2/2m$ is identically zero.
- b) Make this application more quantitative. Assume that $\Delta x = 0.50 a$ and $\Delta p = 0.50 p$ where p is the momentum in the lowest energy state. Calculate the total energy of this state based on these assumptions and compare your result with the ground-state energy for the particle in the box.
- c) Compare your estimates for Δp and Δx with the more rigorously derived uncertainties σ_p and σ_x of Equation (17.13).

a) Because the particle is in the box, $\Delta x \leq a$. From the uncertainty principle,

$$\Delta p_x \Delta x \geq \frac{\hbar}{2} \text{ so that } \Delta p_x \geq \frac{\hbar}{2a}.$$

b) Make this application more quantitative. Assume that $\Delta x = 0.50a$ and $\Delta p = 0.50p$ where p is the momentum in the lowest energy state. Calculate the total energy of this state based on these assumptions and compare your result with the ground state energy for the particle in the box.

$$\Delta p \Delta x \geq \frac{\hbar}{2}, \text{ therefore, } \frac{a}{2} \frac{p}{2} \geq \frac{\hbar}{2} \text{ or } p \geq \frac{2\hbar}{a} = \frac{\hbar}{\pi a}$$

$$E = \frac{p^2}{2m} \geq \frac{\hbar^2}{2\pi^2 m a^2}$$

This energy is smaller than the true ground state energy by the factor $\frac{2\pi^2}{8} = 2.48$.

c) Compare your estimates for Δp and Δx with the more rigorously derived uncertainties σ_p and σ_x of Equation (17.12).

$$\text{From Equation (17.12), } \frac{\sigma_p}{p} = \frac{\pi\hbar/a}{\sqrt{2mE}} = \frac{\pi\hbar/a}{\sqrt{2m \times \frac{\hbar^2}{8ma^2}}} = \frac{\hbar/2a}{\hbar/2a} = 1.$$

$\sigma_x = \sqrt{a^2 \left(\frac{1}{3} - \frac{1}{2\pi^2} \right) - \frac{a^2}{4}} = 0.181a$. Our estimate of the uncertainty in p was low and our estimate of the uncertainty in x was high.

P17.16) Another important uncertainty principle is encountered in time-dependent systems. It relates the lifetime of a state Δt with the measured spread in the photon energy ΔE associated with the decay of this state to a stationary state of the system. “Derive” the relation $\Delta E \Delta t \geq \hbar/2$ in the following steps.

a) Starting from $E = p_x^2/2m$ and $\Delta E = (dE/dp_x)\Delta p_x$ show that $\Delta E = v_x \Delta p_x$.

b) Using $v_x = \Delta x / \Delta t$, show that $\Delta E \Delta t = \Delta p_x \Delta x \geq \hbar/2$.

c) Estimate the width of a spectral line originating from the decay of a state of lifetime 1.0×10^{-9} s and 1.0×10^{-11} s in inverse seconds and inverse centimeters.

a) Starting from $E = \frac{p_x^2}{2m}$ and $\Delta E = \left(\frac{dE}{dp_x} \right) \Delta p_x$ show that $\Delta E = v_x \Delta p_x$.

$$\frac{dE}{dp_x} \Delta p_x = \frac{p_x}{m} \Delta p_x = v_x \Delta p_x$$

b) Using $v_x = \frac{\Delta x}{\Delta t}$ show that $\Delta E \Delta t = \Delta p_x \Delta x \geq \frac{\hbar}{2}$

$$\Delta E \Delta t = \frac{\Delta x}{\Delta t} \Delta p_x \Delta t = \Delta x \Delta p_x \geq \frac{\hbar}{2}$$

c) Estimate the width of a spectral line originating from the decay of a state of lifetime 1.0×10^{-9} s and 1.0×10^{-11} s in s^{-1} and cm^{-1} .

$$\Delta E \geq \frac{\hbar}{2\Delta t} = h\Delta\nu$$

$$\Delta\nu = \frac{1}{4\pi\Delta t} = \frac{1}{4\pi(1.0 \times 10^{-9} s)} = 8.0 \times 10^7 s^{-1}$$

$$\Delta\nu(cm^{-1}) = \frac{\Delta\nu(s^{-1})}{c} = \frac{8.0 \times 10^7 s^{-1}}{2.998 \times 10^{10} cm s^{-1}} = 0.00265 cm^{-1}$$

The corresponding answers for 1.0×10^{-11} s are $8.0 \times 10^9 s^{-1}$ and $0.265 cm^{-1}$, respectively.

P17.17) In this problem, we consider the calculations for σ_p and σ_x for the particle in the box shown in Figure 17.5 in more detail. In particular, we want to determine how the absolute uncertainty Δp_x and the relative uncertainty $\Delta p_x / p_x$ of a single peak corresponding to either the most probable positive or negative momentum depends on the quantum number n .

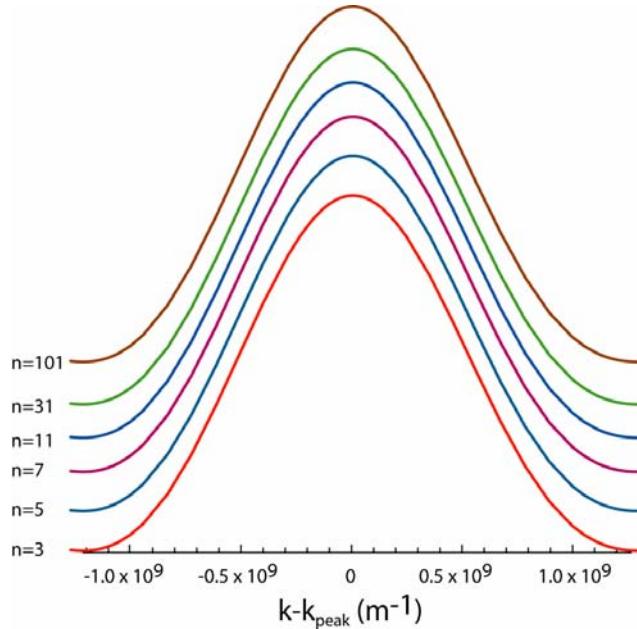
a) First we must relate k and p_x . From $E = p_x^2/2m$ and $E = n^2\hbar^2/8ma^2$, show that

$$p_x = nh/2a.$$

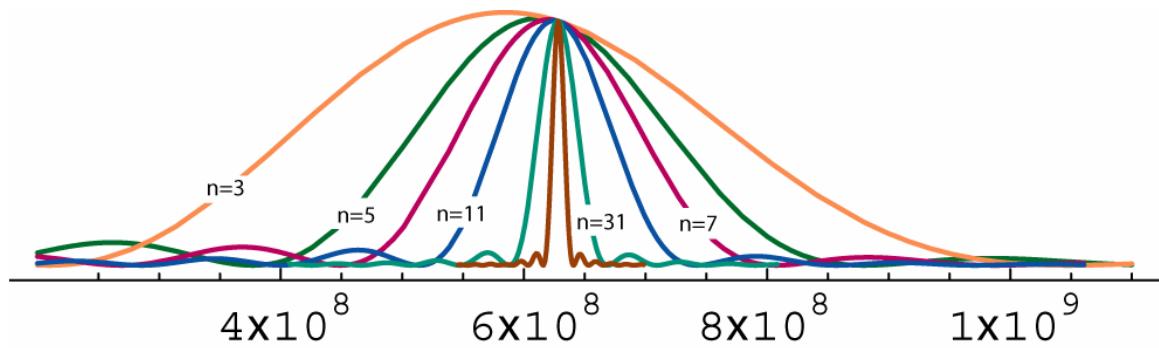
b) Use the result from part (a) together with the relation linking the length of the box and the allowed wavelengths to obtain $p_x = \hbar k$.

c) Relate Δp_x and $\Delta p_x / p_x$ with k and Δk .

d) The following graph shows $|A_k|^2$ versus $k - k_{peak}$. By plotting the results of Figure 17.4 in this way, all peaks appear at the same value of the abscissa. Successive curves have been shifted upward to avoid overlap. Use the width of the $|A_k|^2$ peak at half height as a measure of Δk . What can you conclude from this graph about the dependence of Δp_x on n ?



- e) The following graph shows $|A_k|^2$ versus k / n for $n = 3, n = 5, n = 7, n = 11, n = 31$, and $n = 101$. Use the width of the $|A_k|^2$ peak at half height as a measure of $\Delta k/n$. Using the graphs, determine the dependence of $\Delta p_x / p_x$ on n . One way to do this is to assume that the width depends on n like $(\Delta p_x / p_x) = n^\alpha$ where α is a constant to be determined. If this relationship holds, a plot of $\ln(\Delta p_x / p_x)$ versus $\ln n$ will be linear and the slope will give the constant α .



- a) First we must relate k and p_x . From $E = \frac{p_x^2}{2m}$ and $E = \frac{n^2 h^2}{8ma^2}$ show that $p_x = \frac{nh}{2a}$.

$$\frac{p_x^2}{2m} = \frac{n^2 h^2}{8ma^2} \text{ so } p_x^2 = \frac{n^2 h^2}{4a^2} \text{ and } |p_x| = \frac{nh}{2a}$$

b) Use the result from part (a) together with the relation linking the length of the box and the allowed wavelengths to obtain $p_x = \hbar k$.

$$|p_x| = \frac{nh}{2a} = \frac{nh}{2\left(\frac{n\lambda}{2}\right)} = \frac{h}{\lambda} = \frac{h}{\frac{2\pi}{k}} = \hbar k$$

c) Relate Δp_x and $\frac{\Delta p_x}{p_x}$ with k and Δk .

$$|p_x| = \hbar k \quad \Delta|p_x| = \hbar \Delta k$$

$$\frac{\Delta|p_x|}{p_x} = \frac{\hbar \Delta k}{\hbar k} = \frac{\Delta k}{k}$$

d) The graph below shows $|A_k|^2$ vs $k - k_{peak}$. By plotting the results of Figure 17.4 in this way, all peaks appear at the same value of the abscissa. Successive curves have been shifted upward to avoid overlap. Use the width of the $|A_k|^2$ peak at half height as a measure of Δk . What can you conclude from this graph about the dependence of Δp_x on n ?

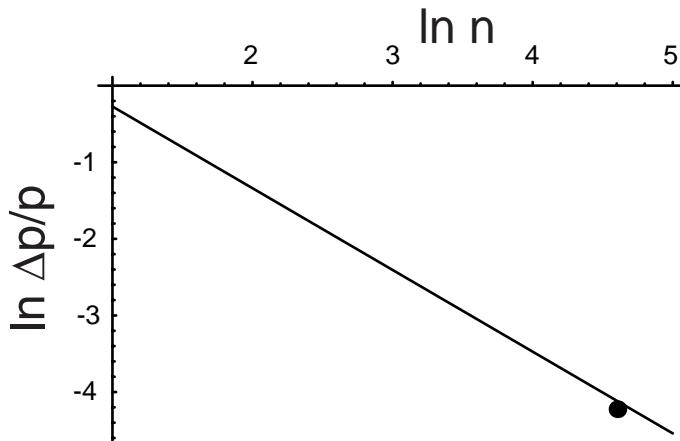
Because the half widths of the peaks for different n values are the same, we conclude that Δp_x is independent of n .

e) The graph below shows $|A_k|^2$ vs $\frac{k}{n}$ for $n = 3$ (broadest peak), $n = 5$, $n = 7$, $n = 11$, $n = 31$, and $n = 101$ (narrowest peak). Use the width of the $|A_k|^2$ peak at half height as a measure of $\Delta k/n$. Using the graphs, determine the dependence of $\frac{\Delta p_x}{p_x}$ on n . One way to do this is to assume that the width depends on n like $(\Delta p_x / p_x) = n^\alpha$ where α is a constant to be determined. If this relationship holds, a plot of $\ln\left(\frac{\Delta p_x}{p_x}\right)$ vs $\ln n$ will be linear and the slope will give the constant α .

From the graph, we determine the following data.

n	$\ln n$	$\Delta p/p$	$\ln \Delta p/p$
3	1.099	0.649	-0.433
5	1.609	0.381	-0.966
7	1.946	0.293	-1.229
11	2.397	0.190	-1.658
31	3.434	0.068	-2.684
101	4.615	0.015	-4.224

A plot of $\ln \Delta p/p$ vs $\ln n$ is shown below. A fit to the data gives a slope of -1.07 . Given the scatter in the data, we conclude that this is consistent with $\alpha = -1$. We conclude that $\Delta p/p$ depends inversely on n .



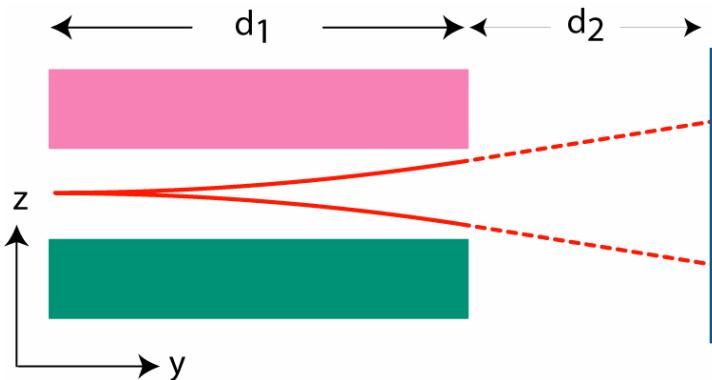
P17.18) What is wrong with the following argument? We know that the functions $\psi_n(x) = \sqrt{2/a} \sin(n\pi x/a)$ are eigenfunctions of the total energy operator for the particle in the infinitely deep box. We also know that in the box, $E = \frac{p_x^2}{2m} + V(x) = \frac{p_x^2}{2m}$. Therefore, the operator for E_{total} is proportional to the operator for p_x^2 . Because the operators for p_x^2 and p_x commute as you demonstrated in Problem P17.8, the functions $\psi_n(x) = \sqrt{2/a} \sin(n\pi x/a)$ are eigenfunctions of both the total energy and momentum operators.

As shown in Example Problem 17.1, the momentum and total energy operators only commute if $\frac{dV(x)}{dx} = 0$ over the whole range of x for the system of interest. However, $\frac{dV(x)}{dx} \neq 0$ at both ends of the box. Therefore, the total energy and momentum operators do not commute for this potential. Therefore the total energy eigenfunctions are not also eigenfunctions of the momentum operator.

P17.19) In this problem, you will carry out the calculations that describe the Stern-Gerlach experiment shown in Figure 17.2. Classically, a magnetic dipole μ has the potential energy $E = -\mu \cdot \mathbf{B}$. If the field has a gradient in the z direction, the magnetic moment will experience a force, leading it to be deflected in the z direction. Because

classically μ can take on any value in the range $-|\mu| \leq \mu_z \leq |\mu|$, a continuous range of positive and negative z deflections of a beam along the y direction will be observed. From a quantum mechanical perspective, the forces are the same as in the classical picture, but μ_z can only take on a discrete set of values. Therefore, the incident beam will be split into a discrete set of beams that have different deflections in the z direction.

a) The geometry of the experiment is shown here. In the region of the magnet indicated by d_1 , the Ag atom experiences a constant force. It continues its motion in the force-free region indicated by d_2 .



If the force inside the magnet is F_z , show that $|z| = \frac{1}{2} \frac{F_z}{m_{Ag}} t_1^2 + t_2 v_z(t_1)$. The times t_1 and t_2

correspond to the regions d_1 and d_2 .

Integrating $m_{Ag} \frac{d^2 z}{dt^2} = F_z$ with the initial conditions $z(0) = 0$ and $\left(\frac{dz}{dt}\right)_{t=0} = 0$ gives

$v_z = \frac{F_z}{m_{Ag}} t$ and $z(t) = \frac{F_z}{2m_{Ag}} t^2$. Therefore $z(t_1) = \frac{F_z}{2m_{Ag}} t_1^2$. In the region outside the

magnet, no forces act on the atom and the velocity of the particle remains constant at the value of $v_z(t_1)$. Therefore, the z distance traversed in time t_2 is $t_2 v_z(t_1)$. Therefore,

$$|z| = \frac{1}{2} \frac{F_z}{m_{Ag}} t_1^2 + t_2 v_z(t_1)$$

b) Show that assuming a small deflection,

$$|z| = F_z \left(\frac{d_1 d_2 + \frac{1}{2} d_1^2}{m_{Ag} v_y^2} \right)$$

For a small deflection, $d_1 = v_y t_1$ and $d_2 = v_y t_2$. Expressing these equations in terms of t_1

and t_2 and substituting in $|z| = \frac{1}{2} \frac{F_z}{m_{Ag}} t_1^2 + t_2 v_z(t_1)$ gives

$$\begin{aligned} |z| &= \frac{1}{2} \frac{F_z}{m_{Ag}} \left(\frac{d_1}{v_y} \right)^2 + \frac{d_2}{v_y} v_z(t_1) = \frac{1}{2} \frac{F_z}{m_{Ag}} \left(\frac{d_1}{v_y} \right)^2 + \frac{d_2}{v_y} \frac{F_z}{m_{Ag}} t_1 \frac{d_1}{v_y t_1} \\ &= F_z \left(\frac{d_1 d_2 + \frac{1}{2} d_1^2}{m_{Ag} v_y^2} \right) \end{aligned}$$

c) The magnetic moment of the electron is given by $|\mu| = \frac{g_s \mu_B}{2}$. In this equation, μ_B is the Bohr magneton and has the value 9.274×10^{-24} J/Tesla. The gyromagnetic ratio of the electron g_s has the value 2.00231. If $\partial B_z / \partial z = 1000$ Tesla m $^{-1}$, and d_1 and d_2 are 0.200 and 0.250 m, respectively, and $v_y = 500$ m s $^{-1}$, what values of z will be observed?

$$F_z = \frac{\partial B_z}{\partial z} \times \frac{g_s \mu_B}{2} = 1000 \text{ Tesla cm}^{-1} \times \frac{2.00231 \times 9.274 \times 10^{-24} \text{ J Tesla}^{-1}}{2} = 9.29 \times 10^{-21} \text{ N}$$

$$|z| = F_z \left(\frac{d_1 d_2 + \frac{1}{2} d_1^2}{m_{Ag} v_y^2} \right)$$

$$|z| = 9.29 \times 10^{-21} \text{ N} \times \left(\frac{0.200 \text{ m} \times 0.250 \text{ m} + \frac{1}{2} (0.200 \text{ m})^2}{107.9 \text{ amu} \times 1.661 \times 10^{-27} \text{ kg amu}^{-1} \times (500 \text{ m s}^{-1})^2} \right) = 1.45 \times 10^{-2} \text{ m}$$

$$z = \pm 1.45 \times 10^{-2} \text{ m}$$

P17.20) Consider the entangled wave function for two photons,

$$\psi_{12} = \frac{1}{\sqrt{2}} (\psi_1(H)\psi_2(V) + \psi_1(V)\psi_2(H)).$$

Assume that the polarization operator \hat{P}_i has the properties

$$\hat{P}_i \psi_i(H) = -\psi_i(H) \text{ and } \hat{P}_i \psi_i(V) = +\psi_i(V) \text{ where } i = 1 \text{ or } i = 2.$$

- a) Show that ψ_{12} is not an eigenfunction of \hat{P}_1 or \hat{P}_2 .
- b) Show that each of the two terms in ψ_{12} is an eigenfunction of the polarization operator \hat{P}_1 .
- c) What is the average value of the polarization P_1 that you will measure on identically prepared systems? It is not necessary to do a calculation to answer this question.

- a) Show that ψ_{12} is not an eigenfunction of \hat{P}_1 or \hat{P}_2 .

$$P_1 \psi_{12} = \frac{1}{\sqrt{2}}(-\psi_1(H)\psi_2(V) - \psi_1(V)\psi_2(H)) \neq c \frac{1}{\sqrt{2}}(\psi_1(H)\psi_2(V) - \psi_1(V)\psi_2(H))$$

$$P_2 \psi_{12} = \frac{1}{\sqrt{2}}(\psi_1(H)\psi_2(V) + \psi_1(V)\psi_2(H)) \neq c \frac{1}{\sqrt{2}}(\psi_1(H)\psi_2(V) - \psi_1(V)\psi_2(H))$$

Therefore, the wave function is not an eigenfunction of the polarization operator.

- b) Show that each of the two terms in ψ_{12} is an eigenfunction of the polarization operator \hat{P}_1 .

$$P_1 \left[\frac{1}{\sqrt{2}}(\psi_1(H)\psi_2(V)) \right] = -\frac{1}{\sqrt{2}}(\psi_1(H)\psi_2(V))$$

$$P_1 \left[-\frac{1}{\sqrt{2}}(\psi_1(V)\psi_2(H)) \right] = -\frac{1}{\sqrt{2}}(\psi_1(V)\psi_2(H))$$

- c) What is the average value of the polarization P_1 that you will measure on identically prepared systems? It is not necessary to do a calculation to answer this question.

A measurement will project the system into the wave function

$\psi_1(H)\psi_2(V)$ or $-\psi_1(V)\psi_2(H)$ with equal probability. Therefore it is equally likely to measure the eigenvalue +1 as -1 and the average of the measured values will be zero.

Chapter 18: A Quantum Mechanical Model for the Vibration and Rotation of Molecules

Problem numbers in italics indicate that the solution is included in the *Student's Solutions Manual*.

Questions on Concepts

Q18.1) What is the functional dependence of the total energy of the quantum harmonic oscillator on the position variable x ?

It is independent of x . Both the kinetic and potential energy depend on x , but the total energy is independent of x .

Q18.2) The two linearly independent total energy eigenfunctions for rotation in two dimensions are $\Phi_+(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l\phi}$ and $\Phi_-(\phi) = \frac{1}{\sqrt{2\pi}} e^{-im_l\phi}$. What is the difference in motion for these two solutions? Explain your answer.

From Section 18.4, the angular momentum operator for rotation in two dimensions is $\hat{l} = -i\hbar \frac{\partial}{\partial \phi}$ if we apply this operator to the two eigenfunctions

$$\Phi_+(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l\phi} \text{ and } \Phi_-(\phi) = \frac{1}{\sqrt{2\pi}} e^{-im_l\phi},$$

$$\hat{l}\Phi_+(\phi) = -i\hbar \frac{\partial}{\partial \phi} \Phi_+(\phi) = \frac{m_l\hbar}{\sqrt{2\pi}} e^{im_l\phi} = m_l\hbar\Phi_+(\phi) \text{ and}$$

$$\hat{l}\Phi_-(\phi) = -i\hbar \frac{\partial}{\partial \phi} \Phi_-(\phi) = \frac{-m_l\hbar}{\sqrt{2\pi}} e^{-im_l\phi} = -m_l\hbar\Phi_-(\phi)$$

Therefore, the direction of rotation is opposite for these two eigenfunctions.

Q18.3) Spatial quantization was discussed in Supplemental Section 18.8. Suppose that we have a gas consisting of atoms, each of which has a nonzero angular momentum. Are all of their angular momentum vectors aligned?

No. Only the application of an external field that makes the energy depend on the component of the angular momentum will lead to spatial quantization. Even in this case, not all molecules will have the same component of angular momentum along the field direction. The number of molecules with a particular value for the component of angular momentum along the field direction will be determined by the Boltzmann distribution.

Q18.4) Why can the angular momentum vector lie on the z axis for two-dimensional rotation in the x - y plane but not for rotation in three-dimensional space?

For rotation in two dimensions, the angular momentum vector has only one component, and the vector is perpendicular to the plane of rotation. For rotation in three dimensions, the angular momentum vector has three components. Because the corresponding angular momentum operators do not commute, all three components of the angular momentum can't be known simultaneously. Therefore, the angular momentum vector can't lie on the z axis, because this requires that the x and y components are known to be zero, and the z component is known through the value of L^2 .

Q18.5) The zero point energy of the particle in the box goes to zero as the length of the box approaches infinity. What is the appropriate analogue for the quantum harmonic oscillator?

The force constant k goes to zero. This corresponds in a diatomic molecule to a very weak bond, such as for Ar_2 .

Q18.6) Explain in words why the amplitude of the total energy eigenfunctions for the quantum mechanical harmonic oscillator increases with $|x|$ as shown in Figure 18.4.

The velocity of the particle goes through zero at the classical turning point. Therefore, it spends more time near the turning point than in the same interval near $x = 0$. Therefore, the probability density must be highest at the classical turning point.

Q18.7) Why does the energy of a rotating molecule depend on l , but not on m_l ?

The energy depends only on the frequency of rotation, and not on the orientation of the rotation axis. The quantum number l determines the speed, and m_l determines the orientation of the rotational axis.

Q18.8) Are the real functions listed in Equations (18.34) and (18.35) eigenfunctions of l_z ? Justify your answer.

No. They are formed by the combination of $Y_l^{m_l}$ and $Y_l^{-m_l}$. Therefore, the functions are eigenfunctions of \hat{H} and \hat{l}^2 , but not of \hat{l}_z .

Q18.9) Why is only one quantum number needed to characterize the eigenfunctions for rotation in two dimensions, whereas two quantum numbers are needed to characterize the eigenfunctions for rotation in three dimensions?

For rotation in two dimensions, the angular momentum vector is perpendicular to the plane of rotation, and therefore has only one component. Only one quantum

number is needed to describe this vector. By contrast, the angular momentum vector for 3-D rotation has three components. However, the commutation relations say that we can only know the magnitude of the vector and one of its components simultaneously. Two quantum numbers are needed to describe this vector.

Q18.10) What makes the z direction special such that \hat{l}^2 , \hat{H} , and \hat{l}_z commute, whereas \hat{l}^2 , \hat{H} , and \hat{l}_x do not commute?

There is nothing special about the z direction. We choose the z direction because the angular momentum operator for this component has a simple form. We can rotate our coordinate system to make any direction that we choose to lie along the z axis.

Problems

P18.1) The force constant for a H^{19}F molecule is 966 N m^{-1} .

- Calculate the zero point vibrational energy for this molecule for a harmonic potential.
- Calculate the light frequency needed to excite this molecule from the ground state to the first excited state.

a)

$$E_1 = h \sqrt{\frac{k}{\mu}} \left(1 + \frac{1}{2}\right) = \frac{3}{2} \times 1.055 \times 10^{-34} \text{ J s} \times \sqrt{\frac{966 \text{ N m}^{-1}}{\frac{1.0078 \times 18.9984}{1.0078 + 18.9984} \times 1.66 \times 10^{-27} \text{ kg amu}^{-1}}}$$

$$E_1 = 1.23 \times 10^{-19} \text{ J}$$

$$E_0 = \hbar \sqrt{\frac{k}{\mu}} \left(\frac{1}{2}\right) = \frac{1}{3} E_1 = 4.10 \times 10^{-20} \text{ J}$$

$$\text{b)} \nu = \frac{E_1 - E_0}{h} = \frac{1.23 \times 10^{-19} \text{ J} - 4.10 \times 10^{-20} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 1.24 \times 10^{14} \text{ s}^{-1}$$

P18.2) By substituting in the Schrödinger equation for the harmonic oscillator, show that the ground-state vibrational wave function is an eigenfunction of the total energy operator. Determine the energy eigenvalue.

$$\begin{aligned}
 & -\frac{\hbar^2}{2\mu} \frac{d^2\psi_n(x)}{dx^2} + \frac{kx^2}{2}\psi_n(x) = E_n\psi_n(x) \\
 & -\frac{\hbar^2}{2\mu} \frac{d^2\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2}}{dx^2} + \frac{kx^2}{2}\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2} = \frac{\hbar^2}{2\mu} \frac{d\left\{\alpha x\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2}\right\}}{dx} + \frac{kx^2}{2}\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2} \\
 & = \frac{\hbar^2}{2\mu} \left\{ \alpha\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2} - \alpha^2 x^2 \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2} \right\} + \frac{kx^2}{2}\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2} \\
 & = \frac{\hbar^2}{2\mu} \left\{ \alpha\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2} - \alpha^2 x^2 \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2} \right\} + \frac{\hbar^2 \alpha^2 x^2}{2\mu} \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2} = \frac{\hbar^2}{2\mu} \alpha \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2} \\
 & = \frac{\hbar^2}{2\mu} \sqrt{\frac{k\mu}{\hbar^2}} \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2} = \frac{\hbar}{2} \sqrt{\frac{k}{\mu}} \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2} = E_1\psi_1(x) \text{ with } E_1 = \frac{\hbar}{2} \sqrt{\frac{k}{\mu}}
 \end{aligned}$$

P18.3) Show by carrying out the appropriate integration that the total energy

eigenfunctions for the harmonic oscillator $\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2}$ and

$\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2}$ are orthogonal over the interval $-\infty < x < \infty$ and that

$\psi_2(x)$ is normalized over the same interval. In evaluating integrals of this type,

$\int_{-\infty}^{\infty} f(x) dx = 0$ if $f(x)$ is an odd function of x and $\int_{-\infty}^{\infty} f(x) dx = 2 \int_0^{\infty} f(x) dx$ if $f(x)$ is an even function of x .

We use the standard integrals $\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$ and

$$\begin{aligned}
 \int_0^{\infty} e^{-ax^2} dx &= \left(\frac{\pi}{4a}\right)^{1/2} \\
 \int_{-\infty}^{\infty} \psi_2^*(x) \psi_0(x) dx &= \int_{-\infty}^{\infty} \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha x^2} dx \\
 &= \left(\frac{\alpha^2}{4\pi^2}\right)^{1/4} \int_{-\infty}^{\infty} (2\alpha x^2 - 1) e^{-\alpha x^2} dx = 2 \left(\frac{\alpha^2}{4\pi^2}\right)^{1/4} \int_0^{\infty} (2\alpha x^2 - 1) e^{-\alpha x^2} dx \\
 &= \left(\frac{\alpha^2}{4\pi^2}\right)^{1/4} \left(2\alpha \frac{1}{4\alpha} \sqrt{\frac{\pi}{\alpha}} - \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} \right) = 0
 \end{aligned}$$

$$\begin{aligned}
 \int_{-\infty}^{\infty} \psi_2^*(x) \psi_2(x) dx &= \int_{-\infty}^{\infty} \left(\frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} \left(\frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} dx \\
 &= 2 \left(\frac{\alpha}{4\pi} \right)^{1/2} \int_0^{\infty} (4\alpha^2 x^4 - 4\alpha x^2 + 1) e^{-\alpha x^2} dx \\
 &= 2 \left(\frac{\alpha}{4\pi} \right)^{1/2} \left(4\alpha^2 \frac{3}{2^3 \alpha^2} \sqrt{\frac{\pi}{\alpha}} - 4\alpha \frac{1}{2^2 \alpha} \sqrt{\frac{\pi}{\alpha}} + \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} \right) = 2 \left(\frac{\alpha}{4\pi} \right)^{1/2} \sqrt{\frac{\pi}{\alpha}} \left(\frac{3}{2} - 1 + \frac{1}{2} \right) = 1
 \end{aligned}$$

P18.4) Evaluate the average kinetic and potential energies, $\langle E_{kinetic} \rangle$ and $\langle E_{potential} \rangle$, for the ground state ($n = 0$) of the harmonic oscillator by carrying out the appropriate integrations.

We use the standard integrals $\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$ and

$$\begin{aligned}
 \int_0^{\infty} e^{-ax^2} dx &= \left(\frac{\pi}{4a} \right)^{1/2} \\
 \langle E_{potential} \rangle &= \int \psi_0^*(x) \left(\frac{1}{2} k x^2 \right) \psi_0(x) dx \\
 &= \frac{1}{2} k \left(\frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = k \left(\frac{\alpha}{\pi} \right)^{1/2} \int_0^{\infty} x^2 e^{-\alpha x^2} dx \\
 &= k \left(\frac{\alpha}{\pi} \right)^{1/2} \frac{1}{4\alpha} \sqrt{\frac{\pi}{\alpha}} = k \frac{1}{4\alpha} = \frac{\hbar}{4} \sqrt{\frac{k}{\mu}}
 \end{aligned}$$

$$\begin{aligned}
 \langle E_{kinetic} \rangle &= \int \psi_0^*(x) \left(-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} \right) \psi_0(x) dx \\
 &= \int_{-\infty}^{\infty} \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{1}{2}\alpha x^2} \left(-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} \right) \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{1}{2}\alpha x^2} dx \\
 &= -\frac{\hbar^2}{\mu} \left(\frac{\alpha}{\pi} \right)^{1/2} \int_0^{\infty} e^{-\alpha x^2} (\alpha x^2 - \alpha) dx \\
 &= -\frac{\hbar^2}{\mu} \left(\frac{\alpha}{\pi} \right)^{1/2} \left(\frac{\alpha}{4} \sqrt{\frac{\pi}{\alpha}} - \frac{\alpha}{2} \sqrt{\frac{\pi}{\alpha}} \right) = \frac{\hbar^2 \alpha}{\mu} \frac{\alpha}{4} \\
 &= \frac{\hbar^2}{4\mu} \sqrt{\frac{k\mu}{\hbar^2}} = \frac{\hbar}{4} \sqrt{\frac{k}{\mu}}
 \end{aligned}$$

P18.5) Evaluate the average kinetic and potential energies, $\langle E_{kinetic} \rangle$ and $\langle E_{potential} \rangle$, for the second excited state ($n = 2$) of the harmonic oscillator by carrying out the appropriate integrations.

We use the standard integrals $\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$ and

$$\begin{aligned}
 \int_0^\infty e^{-ax^2} dx &= \left(\frac{\pi}{4a} \right)^{1/2} \\
 \langle E_{potential} \rangle &= \int \psi_2^*(x) V(x) \psi_2(x) dx \\
 &= \int_{-\infty}^{\infty} \left(\frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} \frac{1}{2} k x^2 \left(\frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} dx \\
 &= \frac{1}{2} k \left(\frac{\alpha}{4\pi} \right)^{1/2} \int_{-\infty}^{\infty} x^2 (2\alpha x^2 - 1)^2 e^{-\alpha x^2} dx \\
 &= k \left(\frac{\alpha}{4\pi} \right)^{1/2} \int_0^{\infty} (4\alpha^2 x^6 - 4\alpha x^4 + x^2) e^{-\alpha x^2} dx \\
 &= k \left(\frac{\alpha}{4\pi} \right)^{1/2} \left(4\alpha^2 \frac{15}{2^4 \alpha^3} \sqrt{\frac{\pi}{\alpha}} - 4\alpha \frac{3}{2^3 \alpha^2} \sqrt{\frac{\pi}{\alpha}} + \frac{1}{2^2 \alpha} \sqrt{\frac{\pi}{\alpha}} \right) \\
 &= \frac{5k}{4\alpha} = \frac{5\hbar}{4} \sqrt{\frac{k}{\mu}} \\
 \langle E_{kinetic} \rangle &= \int \psi_2^*(x) \left(-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} \right) \psi_2(x) dx \\
 &= \int_{-\infty}^{\infty} \left(\frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} \left(-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} \right) \left(\frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} dx \\
 &= \int_{-\infty}^{\infty} \left(\frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} \left(-\frac{\hbar^2}{2\mu} \right) \left(\frac{\alpha}{4\pi} \right)^{1/4} \alpha (2\alpha^2 x^4 - 11\alpha x^2 + 5) e^{-\frac{1}{2}\alpha x^2} dx \\
 &= \alpha \left(-\frac{\hbar^2}{\mu} \right) \left(\frac{\alpha}{4\pi} \right)^{1/2} \int_0^{\infty} (2\alpha x^2 - 1)(2\alpha^2 x^4 - 11\alpha x^2 + 5) e^{-\alpha x^2} dx \\
 &= \alpha \left(-\frac{\hbar^2}{\mu} \right) \left(\frac{\alpha}{4\pi} \right)^{1/2} \int_0^{\infty} (4\alpha^3 x^6 - 24\alpha^2 x^4 + 21\alpha x^2 - 5) e^{-\alpha x^2} dx \\
 &= \alpha \left(-\frac{\hbar^2}{\mu} \right) \left(\frac{\alpha}{4\pi} \right)^{1/2} \left(4\alpha^3 \frac{15}{2^4 \alpha^3} \sqrt{\frac{\pi}{\alpha}} - 24\alpha^2 \frac{3}{2^3 \alpha^2} \sqrt{\frac{\pi}{\alpha}} + \alpha \frac{21}{2^2 \alpha} \sqrt{\frac{\pi}{\alpha}} - 5 \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} \right) \\
 &= \frac{5 \hbar^2 \alpha}{4 \mu} = \frac{5}{4} \hbar \sqrt{\frac{k}{\mu}}
 \end{aligned}$$

P18.6) Evaluate the average vibrational amplitude of the quantum harmonic oscillator about its equilibrium value, $\langle x \rangle$, for the ground state ($n = 0$) and first two excited states ($n = 1$ and $n = 2$). Use the hint about evaluating integrals in Problem P18.3.

$\langle x \rangle = \int_{-\infty}^{\infty} \psi_n^*(x) x \psi_n d x = \int_{-\infty}^{\infty} x (\psi_n)^2 d x$. Because $(\psi_n)^2$ is an even function of x for all n , the product $x(\psi_n)^2$ is an odd function of x . Therefore, $\langle x \rangle = 0$ for all n .

P18.7) Evaluate the average linear momentum of the quantum harmonic oscillator, $\langle p_x \rangle$, for the ground state ($n = 0$) and first two excited states ($n = 1$ and $n = 2$). Use the hint about evaluating integrals in Problem P18.3.

We use the standard integrals $\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$ and

$$\int_0^{\infty} e^{-ax^2} dx = \left(\frac{\pi}{4a} \right)^{1/2}$$

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \psi_n^*(x) \left(-i\hbar \frac{d}{dx} \right) \psi_n d x$$

$$\text{for } n = 0, \langle p_x \rangle = \int_{-\infty}^{\infty} \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{1}{2}\alpha x^2} \left(-i\hbar \frac{d}{dx} \right) \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{1}{2}\alpha x^2} d x$$

$$\langle p_x \rangle = \left(\frac{\alpha}{\pi} \right)^{1/2} (-i\hbar) \int_{-\infty}^{\infty} -\alpha x e^{-\alpha x^2} d x$$

Because the integrand is an odd function of x , $\langle p_x \rangle = 0$ for $n = 0$.

$$\text{for } n = 1, \langle p_x \rangle = \int_{-\infty}^{\infty} \left(\frac{4\alpha^3}{\pi} \right)^{1/4} x e^{-\frac{1}{2}\alpha x^2} \left(-i\hbar \frac{d}{dx} \right) \left(\frac{4\alpha^3}{\pi} \right)^{1/4} x e^{-\frac{1}{2}\alpha x^2} d x$$

$$\langle p_x \rangle = \left(\frac{4\alpha^3}{\pi} \right)^{1/2} (-i\hbar) \int_{-\infty}^{\infty} x(1 - \alpha x^2) e^{-\alpha x^2} d x$$

Because the integrand is an odd function of x , $\langle p_x \rangle = 0$ for $n = 1$.

$$\text{for } n = 2, \langle p_x \rangle = \int_{-\infty}^{\infty} \left(\frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} \left(-i\hbar \frac{d}{dx} \right) \left(\frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} d x$$

$$\langle p_x \rangle = \left(\frac{\alpha}{4\pi} \right)^{1/2} (-i\hbar) \int_{-\infty}^{\infty} (2\alpha x^2 - 1) e^{-\alpha x^2} (-2\alpha^2 x^3 + 4\alpha x + \alpha) d x$$

$$\langle p_x \rangle = \left(\frac{\alpha}{4\pi} \right)^{1/2} (-i\hbar) \int_{-\infty}^{\infty} e^{-\alpha x^2} (-4\alpha^3 x^5 + 12\alpha^2 x^3 - 5\alpha x) d x$$

Because the integrand is an odd function of x , $\langle p_x \rangle = 0$ for $n = 3$.

The result is general. $\langle p_x \rangle = 0$ for all values of n .

P18.8) Evaluate the average of the square of the vibrational amplitude of the quantum harmonic oscillator about its equilibrium value, $\langle x^2 \rangle$, for the ground state ($n = 0$) and first two excited states ($n = 1$ and $n = 2$). Use the hint about evaluating integrals in Problem P18.3.

We use the standard integrals $\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$ and

$$\int_0^\infty e^{-ax^2} dx = \left(\frac{\pi}{4a} \right)^{1/2}$$

$$\langle x^2 \rangle = \int_{-\infty}^\infty \psi_n^*(x) (x^2) \psi_n(x) dx$$

$$\text{for } n = 0, \langle x^2 \rangle = \int_{-\infty}^\infty \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{1}{2}\alpha x^2} (x^2) \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{1}{2}\alpha x^2} dx$$

$$\langle x^2 \rangle = \left(\frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^\infty x^2 e^{-\alpha x^2} dx = 2 \left(\frac{\alpha}{\pi} \right)^{1/2} \int_0^\infty x^2 e^{-\alpha x^2} dx$$

$$\langle x^2 \rangle = 2 \left(\frac{\alpha}{\pi} \right)^{1/2} \frac{1}{2^2 \alpha} \sqrt{\frac{\pi}{\alpha}} = \frac{1}{2\alpha} = \frac{\hbar}{2\sqrt{k\mu}}$$

$$\text{for } n = 1, \langle x^2 \rangle = \int_{-\infty}^\infty \left(\frac{4\alpha^3}{\pi} \right)^{1/4} x e^{-\frac{1}{2}\alpha x^2} (x^2) \left(\frac{4\alpha^3}{\pi} \right)^{1/4} x e^{-\frac{1}{2}\alpha x^2} dx$$

$$\langle x^2 \rangle = \left(\frac{4\alpha^3}{\pi} \right)^{1/2} \int_{-\infty}^\infty x^4 e^{-\alpha x^2} dx = 2 \left(\frac{4\alpha^3}{\pi} \right)^{1/2} \int_0^\infty x^4 e^{-\alpha x^2} dx$$

$$\langle x^2 \rangle = 2 \left(\frac{4\alpha^3}{\pi} \right)^{1/2} \frac{3}{2^3 \alpha^2} \sqrt{\frac{\pi}{\alpha}} = \frac{3}{2\alpha} = \frac{3\hbar}{2\sqrt{k\mu}}$$

$$\text{for } n = 2, \langle x^2 \rangle = \int_{-\infty}^\infty \left(\frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} (x^2) \left(\frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} dx$$

$$\langle x^2 \rangle = \left(\frac{\alpha}{4\pi} \right)^{1/2} \int_{-\infty}^\infty (4\alpha^2 x^6 - 4\alpha x^4 + x^2) e^{-\alpha x^2} dx = 2 \left(\frac{\alpha}{4\pi} \right)^{1/2} \int_0^\infty (4\alpha^2 x^6 - 4\alpha x^4 + x^2) e^{-\alpha x^2} dx$$

$$\langle x^2 \rangle = 2 \left(\frac{\alpha}{4\pi} \right)^{1/2} \left(4\alpha^2 \frac{15}{2^4 \alpha^3} \sqrt{\frac{\pi}{\alpha}} - 4\alpha \frac{3}{2^3 \alpha^2} \sqrt{\frac{\pi}{\alpha}} + \frac{1}{2^2} \sqrt{\frac{\pi}{\alpha}} \right) = \frac{5}{2\alpha} = \frac{5\hbar}{2\sqrt{k\mu}}$$

P18.9) Evaluate the average of the square of the linear momentum of the quantum harmonic oscillator $\langle p_x^2 \rangle$, for the ground state ($n = 0$) and first two excited states ($n = 1$ and $n = 2$). Use the hint about evaluating integrals in Problem P18.3.

We use the standard integrals $\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$ and

$$\int_0^\infty e^{-ax^2} dx = \left(\frac{\pi}{4a} \right)^{1/2}$$

$$\langle p_x^2 \rangle = \int \psi_0^*(x) \left(-\hbar^2 \frac{d^2}{dx^2} \right) \psi_0(x) dx$$

For $n = 0$

$$\begin{aligned} &= \int_{-\infty}^{\infty} \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{1}{2}\alpha x^2} \left(-\hbar^2 \frac{d^2}{dx^2} \right) \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{1}{2}\alpha x^2} dx \\ &= -\hbar^2 \left(\frac{\alpha}{\pi} \right)^{1/2} \int_0^\infty e^{-\alpha x^2} (\alpha x^2 - \alpha) dx \end{aligned}$$

$$= -\hbar^2 \left(\frac{\alpha}{\pi} \right)^{1/2} \left(\frac{\alpha}{4} \sqrt{\frac{\pi}{\alpha}} - \frac{\alpha}{2} \sqrt{\frac{\pi}{\alpha}} \right) = \hbar^2 \frac{\alpha}{2} = \frac{1}{2} \hbar \sqrt{k\mu}$$

For $n = 1$

$$\begin{aligned} \langle p_x^2 \rangle &= \int \psi_1^*(x) \left(-\hbar^2 \frac{\partial^2}{\partial x^2} \right) \psi_1(x) dx \\ &= \int_{-\infty}^{\infty} \left(\frac{4\alpha^3}{\pi} \right)^{1/4} x e^{-\frac{1}{2}\alpha x^2} \left(-\hbar^2 \frac{\partial^2}{\partial x^2} \right) \left(\frac{4\alpha^3}{\pi} \right)^{1/4} x e^{-\frac{1}{2}\alpha x^2} dx \\ &= -\hbar^2 \left(\frac{4\alpha^3}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} (\alpha^2 x^4 - 3\alpha x^2) e^{-\alpha x^2} dx \\ &= -\hbar^2 \left(\frac{4\alpha^3}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} (\alpha^2 x^4 - 3\alpha x^2) e^{-\alpha x^2} dx \\ &= -\hbar^2 \left(\frac{4\alpha^3}{\pi} \right)^{1/2} \left(\alpha^2 \left[\sqrt{\frac{\pi}{\alpha}} \frac{3}{4\alpha^2} \right] - 3\alpha \left[\sqrt{\frac{\pi}{\alpha}} \frac{1}{2\alpha} \right] \right) \\ &= \frac{3}{2} \hbar^2 \alpha = \frac{3}{2} \hbar \sqrt{k\mu} \end{aligned}$$

For $n = 2$,

$$\begin{aligned}
 \langle p_x^2 \rangle &= \int_{-\infty}^{\infty} \left(\frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} \left(-\hbar^2 \frac{\partial^2}{\partial x^2} \right) \left(\frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} dx \\
 &= -\hbar^2 \left(\frac{\alpha}{4\pi} \right)^{1/2} \int_{-\infty}^{\infty} (2\alpha x^2 - 1) e^{-\alpha x^2} \alpha (2\alpha^2 x^4 - 11\alpha x^2 + 5) dx \\
 &= -2\hbar^2 \left(\frac{\alpha}{4\pi} \right)^{1/2} \int_0^{\infty} (2\alpha x^2 - 1) e^{-\alpha x^2} \alpha (2\alpha^2 x^4 - 11\alpha x^2 + 5) dx \\
 &= -2\hbar^2 \left(\frac{\alpha}{4\pi} \right)^{1/2} \int_0^{\infty} e^{-\alpha x^2} (4\alpha^4 x^6 - 24\alpha^3 x^4 + 21\alpha^2 x^2 - 5\alpha) dx \\
 &= -2\hbar^2 \left(\frac{\alpha}{4\pi} \right)^{1/2} \left(4\alpha^3 \frac{15}{2^4 \alpha^3} \sqrt{\frac{\pi}{\alpha}} - 24\alpha^2 \frac{3}{2^3 \alpha^2} \sqrt{\frac{\pi}{\alpha}} + \alpha \frac{21}{2^2 \alpha} \sqrt{\frac{\pi}{\alpha}} - 5 \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} \right) \\
 &= \frac{5}{2} \hbar^2 \alpha = \frac{5}{2} \hbar \sqrt{k \mu}
 \end{aligned}$$

P18.10) Using your results for Problems P18.6 through P18.9, calculate the uncertainties in the position and momentum $\sigma_p^2 = \langle p^2 \rangle - \langle p \rangle^2$ and $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$ for the ground state

($n = 0$) and first two excited states ($n = 1$ and $n = 2$) of the quantum harmonic oscillator. Compare your results with the predictions of the Heisenberg uncertainty principle.

$$\sigma_p^2 = \langle p^2 \rangle - \langle p \rangle^2 \text{ and } \sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$$

$$\text{For } n = 0, \sigma_p^2 = \frac{1}{2} \hbar \sqrt{k \mu} - 0 = \frac{1}{2} \hbar \sqrt{k \mu}$$

$$\sigma_x^2 = \frac{\hbar}{2\sqrt{k \mu}} - 0 = \frac{\hbar}{2\sqrt{k \mu}}$$

$$\Delta p \Delta x = \sqrt{\sigma_p^2 \sigma_x^2} = \frac{1}{2} \hbar \geq \frac{1}{2} \hbar$$

$$\text{For } n = 1, \sigma_p^2 = \frac{3}{2} \hbar \sqrt{k \mu} - 0 = \frac{3}{2} \hbar \sqrt{k \mu}$$

$$\sigma_x^2 = \frac{3\hbar}{2\sqrt{k \mu}} - 0 = \frac{3\hbar}{2\sqrt{k \mu}}$$

$$\Delta p \Delta x = \sqrt{\sigma_p^2 \sigma_x^2} = \frac{3}{2} \hbar \geq \frac{1}{2} \hbar$$

$$\text{For } n = 2, \sigma_p^2 = \frac{5}{2} \hbar \sqrt{k \mu} - 0 = \frac{5}{2} \hbar \sqrt{k \mu}$$

$$\sigma_x^2 = \frac{5\hbar}{2\sqrt{k\mu}} - 0 = \frac{5\hbar}{2\sqrt{k\mu}}$$

$$\Delta p \Delta x = \sqrt{\sigma_p^2 \sigma_x^2} = \frac{5}{2} \hbar \geq \frac{1}{2} \hbar$$

P18.11) The vibrational frequency of ${}^1\text{H}{}^{35}\text{Cl}$ is $8.963 \times 10^{13} \text{ s}^{-1}$. Calculate the force constant of the molecule. How large a mass would be required to stretch a classical spring with this force constant by 1.00 cm? Use the gravitational acceleration on Earth at sea level for this problem.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}; k = 4\pi^2 \mu \nu^2$$

$$k = 4 \times \pi^2 \times \frac{1.008 \times 34.969}{1.008 + 34.969} \text{ amu} \times \frac{1.661 \times 10^{-27} \text{ kg}}{\text{amu}} \times (8.963 \times 10^{13} \text{ s}^{-1})^2$$

$$k = 516 \text{ kg s}^{-2}$$

$$F = kx = mg$$

$$m = \frac{kx}{g} = \frac{516 \text{ kg s}^{-2} \times 10^{-2} \text{ m}}{9.81 \text{ m s}^{-2}} = 0.525 \text{ kg}$$

P18.12) Two 1.00-g masses are attached by a spring with a force constant $k = 500 \text{ kg s}^{-2}$. Calculate the zero point energy of the system and compare it with the thermal energy kT . If the zero point energy were converted to translational energy, what would be the speed of the masses?

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{m}{2} = 0.500 \times 10^{-3} \text{ kg}$$

$$E_0 = \frac{\hbar}{2} \sqrt{\frac{k}{\mu}} = \frac{1.055 \times 10^{-34} \text{ J s}}{2} \sqrt{\frac{500 \text{ kg s}^{-2}}{0.500 \times 10^{-3} \text{ kg}}} = 5.28 \times 10^{-32} \text{ J}$$

$$\frac{E_0}{kT} = \frac{5.28 \times 10^{-32} \text{ J}}{300 \text{ K} \times 1.381 \times 10^{-23} \text{ J K}^{-1}} = 1.27 \times 10^{-11}$$

$$\frac{1}{2}mv^2 = 5.28 \times 10^{-32} \text{ J}$$

$$v = \sqrt{\frac{2 \times 5.28 \times 10^{-32} \text{ J}}{2.00 \times 10^{-3} \text{ kg}}} = 7.27 \times 10^{-15} \text{ m s}^{-1}$$

P18.13) Use $\sqrt{\langle x^2 \rangle}$ as calculated in Problem P18.8 as a measure of the vibrational amplitude for a molecule. What fraction is $\sqrt{\langle x^2 \rangle}$ of the 127-pm bond length of the HCl

Chapter 18/A Quantum Mechanical Model for the Vibration and Rotation of Molecules

molecule for $n = 0, 1$, and 2 ? The force constant for the ${}^1\text{H}{}^{35}\text{Cl}$ molecule is 516 N m^{-1} . Use your results from Problem P18.8 in this problem.

For $n = 0$,

$$\sqrt{\langle x^2 \rangle} = \left(\frac{\hbar}{2\sqrt{k\mu}} \right)^{\frac{1}{2}} = \left(\frac{1.055 \times 10^{-34} \text{ J s}}{2 \times \sqrt{516 \text{ N m}^{-1} \times \frac{1.0078 \times 34.9688}{1.0078 + 34.9688} \times 1.66 \times 10^{-27} \text{ kg amu}^{-1}}} \right)^{\frac{1}{2}} = 7.59 \times 10^{-12} \text{ m}$$

$$\frac{\sqrt{\langle x^2 \rangle}}{\text{bond length}} = \frac{7.59 \times 10^{-12} \text{ m}}{127 \times 10^{-12} \text{ m}} = 5.97 \times 10^{-2}$$

For $n = 1$

$$\sqrt{\langle x^2 \rangle} = \left(\frac{3\hbar}{2\sqrt{k\mu}} \right)^{\frac{1}{2}} = \left(\frac{3 \times 1.055 \times 10^{-34} \text{ J s}}{2 \times \sqrt{516 \text{ N m}^{-1} \times \frac{1.0078 \times 34.9688}{1.0078 + 34.9688} \times 1.66 \times 10^{-27} \text{ kg amu}^{-1}}} \right)^{\frac{1}{2}} = 1.31 \times 10^{-11} \text{ m}$$

$$\frac{\sqrt{\langle x^2 \rangle}}{\text{bond length}} = \frac{1.31 \times 10^{-11} \text{ m}}{127 \times 10^{-12} \text{ m}} = 0.103$$

For $n = 2$

$$\sqrt{\langle x^2 \rangle} = \left(\frac{5\hbar}{2\sqrt{k\mu}} \right)^{\frac{1}{2}} = \left(\frac{5 \times 1.055 \times 10^{-34} \text{ J s}}{2 \times \sqrt{516 \text{ N m}^{-1} \times \frac{1.0078 \times 34.9688}{1.0078 + 34.9688} \times 1.66 \times 10^{-27} \text{ kg amu}^{-1}}} \right)^{\frac{1}{2}} = 1.70 \times 10^{-11} \text{ m}$$

$$\frac{\sqrt{\langle x^2 \rangle}}{\text{bond length}} = \frac{1.70 \times 10^{-11} \text{ m}}{127 \times 10^{-12} \text{ m}} = 0.134$$

P18.14) ${}^1\text{H}{}^{35}\text{Cl}$ has a force constant $k = \text{N m}^{-1}$ and a moment of inertia of $2.644 \times 10^{-47} \text{ kg m}^2$. Calculate the frequency of the light corresponding to the lowest energy pure vibrational and pure rotational transitions. In what regions of the electromagnetic spectrum do the transitions lie?

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi} \sqrt{\frac{516 \text{ kg s}^{-2}}{\frac{1.008 \times 34.969 \text{ amu}}{1.008 + 34.969} \times \frac{1.661 \times 10^{-27} \text{ kg}}{\text{amu}}}} = 8.963 \times 10^{13} \text{ s}^{-1}$$

This frequency lies in the infrared region of the electromagnetic spectrum.

The lowest energy transition is $J = 0 \rightarrow J = 1$.

$$\Delta E_{rot} = 2(J+1) \frac{\hbar^2}{2\mu r_0^2} = \frac{\hbar^2}{\mu r_0^2} = \frac{(1.055 \times 10^{-34} \text{ J s})^2}{2.644 \times 10^{-47} \text{ kg m}^2} = 4.20 \times 10^{-22} \text{ J}$$

$$\nu = \frac{\Delta E_{rot}}{\hbar} = 6.35 \times 10^{11} \text{ s}^{-1}$$

This frequency lies in the microwave region of the electromagnetic spectrum.

P18.15) The vibrational frequency for N₂ expressed in wave numbers is 2358 cm⁻¹. What is the force constant associated with the N ≡ N triple bond? How much would a classical spring with this force constant be elongated if a mass of 1.00 kg were attached to it? Use the gravitational acceleration on Earth at sea level for this problem.

$$\nu = c\tilde{v} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\text{so } k = (2\pi c\tilde{v})^2 \mu$$

$$k = (2\pi \times 2.998 \times 10^{10} \text{ cm s}^{-1} \times 2358 \text{ cm}^{-1})^2 \times \frac{14.01 \text{ amu} \times 14.01 \text{ amu}}{2 \times 14.01 \text{ amu}} \times \frac{1.661 \times 10^{-27} \text{ kg}}{\text{amu}}$$

$$k = 2299 \text{ N m}^{-1}$$

$$x = \frac{F}{k} = \frac{mg}{k} = \frac{1.00 \text{ kg} \times 9.81 \text{ m s}^{-2}}{2299 \text{ N m}^{-1}} = 4.28 \times 10^{-3} \text{ m}$$

P18.16) The force constant for the ¹H³⁵Cl molecule is 516 N m⁻¹. Calculate the vibrational zero point energy of this molecule. If this amount of energy were converted to translational energy, how fast would the molecule be moving? Compare this speed to the

root mean square speed from the kinetic gas theory, $|\mathbf{v}|_{rms} = \sqrt{\frac{3kT}{m}}$ for $T = 300 \text{ K}$.

$$E = \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} = \frac{1}{2} \times 1.055 \times 10^{-34} \text{ J s} \times \sqrt{\frac{516 \text{ N m}^{-1}}{\frac{1.0078 \times 34.9688}{1.0078 + 34.9688} \times 1.66 \times 10^{-27} \text{ kg amu}^{-1}}} = 2.97 \times 10^{-20} \text{ J}$$

The speed if converted to translational energy would be

$$|\mathbf{v}| = \sqrt{\frac{2E}{m}} = \sqrt{\frac{2 \times 2.97 \times 10^{-20} \text{ J}}{(1.0078 + 34.9688) \times 1.66 \times 10^{-27} \text{ kg amu}^{-1}}} = 997 \text{ m s}^{-1}$$

The average speed from the kinetic gas theory is

$$|v_{\text{rms}}| = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3 \times 1.381 \times 10^{-23} \text{ J K}^{-1} \times 300 \text{ K}}{(1.0078 + 34.9688) \times 1.66 \times 10^{-27} \text{ kg amu}^{-1}}} = 456 \text{ m s}^{-1}$$

$$\frac{|v|}{|v_{\text{rms}}|} = \frac{997 \text{ m s}^{-1}}{456 \text{ m s}^{-1}} = 2.19$$

P18.17) A gas-phase $^1\text{H}^{19}\text{F}$ molecule, with a bond length of 91.7 pm, rotates in a three-dimensional space.

- a) Calculate the zero point energy associated with this rotation.
- b) What is the smallest quantum of energy that can be absorbed by this molecule in a rotational excitation?

a) There is no zero point energy because the rotation is not constrained.

b) The smallest energy that can be absorbed is

$$E = \frac{\hbar^2}{2I} J(J+1) = \frac{\hbar^2}{2I} 1(1+1) = \frac{2 \times (1.055 \times 10^{-34} \text{ J s})^2}{2 \times \frac{1.0078 \times 18.9984}{1.0078 + 18.9984} \times 1.66 \times 10^{-27} \text{ kg amu}^{-1} \times (91.7 \times 10^{-12} \text{ m})^2}$$

$$E = 8.33 \times 10^{-22} \text{ J}$$

P18.18) A $^1\text{H}^{19}\text{F}$ molecule, with a bond length 91.7 pm, absorbed on a surface rotates in two dimensions.

- a) Calculate the zero point energy associated with this rotation.
- b) What is the smallest quantum of energy that can be absorbed by this molecule in a rotational excitation?

a) There is no zero point energy because the rotation is not constrained.

b) The smallest energy that can be absorbed is

$$E = \frac{\hbar^2 m_l^2}{2I} = \frac{\hbar^2}{2I} = \frac{(1.055 \times 10^{-34} \text{ J s})^2}{2 \times \frac{1.0078 \times 18.9984}{1.0078 + 18.9984} \times 1.66 \times 10^{-27} \text{ kg amu}^{-1} \times (91.7 \times 10^{-12} \text{ m})^2}$$

$$E = 4.17 \times 10^{-22} \text{ J}$$

P18.19) The moment of inertia of $^1\text{H}^{35}\text{Cl}$ is $2.644 \times 10^{-47} \text{ kg m}^2$. Calculate $\frac{E_{\text{rot}}}{kT}$ for

$J = 0, 5, 10,$ and 20 at 298 K . For which of these values of J is $\frac{E_{\text{rot}}}{kT} \approx 1$?

$$E = \frac{\hbar^2}{2I} J(J+1) = \frac{\hbar^2}{2I} 1(1+1) = \frac{(1.055 \times 10^{-34} \text{ J s})^2}{2 \times 2.664 \times 10^{-47} \text{ kg m}^2} J(J+1) = 2.089 \times 10^{-22} J(J+1)$$

$$E_{J=0} = 0$$

$$E_{J=5} = 30 \times 2.089 \times 10^{-22} \text{ J} = 6.267 \times 10^{-21} \text{ J}$$

$$\frac{E_{J=5}}{kT} = \frac{6.267 \times 10^{-21} \text{ J}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K}} = 1.51$$

$$E_{J=10} = 110 \times 2.089 \times 10^{-22} \text{ J} = 2.297 \times 10^{-20} \text{ J}$$

$$\frac{E_{J=10}}{kT} = \frac{2.528 \times 10^{-20} \text{ J}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K}} = 5.55$$

$$E_{J=20} = 20 \times 21 \times 2.089 \times 10^{-22} \text{ J} = 8.774 \times 10^{-20} \text{ J}$$

$$\frac{E_{J=20}}{kT} = \frac{8.774 \times 10^{-20} \text{ J}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K}} = 21.2$$

$$\frac{E_{rot}}{kT} \approx 1 \text{ for } J = 5.$$

P18.20) Using the Boltzmann distribution, calculate $\frac{n_J}{n_0}$ for ${}^1\text{H}{}^{35}\text{Cl}$ for the J values of

Problem P18.19 at $T = 298 \text{ K}$. Does $\frac{n_J}{n_0}$ go through a maximum as J increases? If so, what can you say about the value of J corresponding to the maximum?

$$\frac{n_J}{n_0} = (2J+1)e^{-(E_J - E_0)/kT} = (2J+1)\exp[-E_J/kT]$$

$$\frac{n_0}{n_0} = 1$$

$$\frac{n_5}{n_0} = (2 \times 5 + 1)\exp[-(6.267 \times 10^{-21} \text{ J})/(1.381 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K})] = 2.42$$

$$\frac{n_{10}}{n_0} = (2 \times 10 + 1)\exp[-(2.297 \times 10^{-20} \text{ J})/(1.381 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K})] = 0.082$$

$$\frac{n_{20}}{n_0} = (2 \times 20 + 1)\exp[-(8.774 \times 10^{-20} \text{ J})/(1.381 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K})] = 2.60 \times 10^{-8}$$

$\frac{n_J}{n_0}$ goes through a maximum because it has a value greater than one for $J = 5$. You can only conclude that $J_{max} < 10$.

P18.21) By substituting in the Schrödinger equation for rotation in three dimensions, show that the rotational wave function $\left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2 \theta - 1)$ is an eigenfunction of the total energy operator. Determine the energy eigenvalue.

$$\begin{aligned}
 & -\frac{\hbar^2}{2\mu r_0^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} \right] = EY(\theta, \phi) \\
 & -\frac{\hbar^2}{2\mu r_0^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \left\{ \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2 \theta - 1) \right\}}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \left\{ \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2 \theta - 1) \right\}}{\partial \phi^2} \right] \\
 & = -\frac{\hbar^2}{2\mu r_0^2} \left(\frac{5}{16\pi} \right)^{1/2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} ((-6\cos \theta \sin^2 \theta)) \right] = -\frac{\hbar^2}{2\mu r_0^2} \left(\frac{5}{16\pi} \right)^{1/2} \left[\frac{1}{\sin \theta} (6\sin^3 \theta - 12\cos^2 \theta \sin \theta) \right] \\
 & = -\frac{\hbar^2}{2\mu r_0^2} \left(\frac{5}{16\pi} \right)^{1/2} [(6\{1-\cos^2\} - 12\cos^2 \theta)] = -\frac{\hbar^2}{2\mu r_0^2} \left(\frac{5}{16\pi} \right)^{1/2} [(6 - 18\cos^2 \theta)] = \frac{6\hbar^2}{2\mu r_0^2} \left(\frac{5}{16\pi} \right)^{1/2} (3\cos^2 \theta - 1) \\
 & \text{The energy eigenvalue is } \frac{3\hbar^2}{\mu r_0^2}, \text{ corresponding to } E_l = \frac{\hbar^2}{2I} l(l+1) \text{ with } l = 2.
 \end{aligned}$$

P18.22) Show by carrying out the necessary integration that the eigenfunctions of the Schrödinger equation for rotation in two dimensions, $\frac{1}{\sqrt{2\pi}} e^{im_l \phi}$ and $\frac{1}{\sqrt{2\pi}} e^{in_l \phi}$, $m_l \neq n_l$ are orthogonal.

$$\begin{aligned}
 & \left(\frac{1}{\sqrt{2\pi}} \right)^2 \int_0^{2\pi} e^{im_l \phi} e^{-in_l \phi} d\phi = \frac{1}{2\pi} \int_0^{2\pi} (\cos(m_l - n_l)\phi + i \sin(m_l - n_l)\phi) d\phi \\
 & = \frac{1}{2\pi} (\cos 2\pi(m_l - n_l) - 1 + i \sin 2\pi(m_l - n_l)) = 0
 \end{aligned}$$

because $(m_l - n_l)$ is an integer

P18.23) In this problem you will derive the commutator $[\hat{l}_x, \hat{l}_y] = i\hbar \hat{l}_z$.

a) The angular momentum vector in three dimensions has the form $\mathbf{l} = \mathbf{i}l_x + \mathbf{j}l_y + \mathbf{k}l_z$ where the unit vectors in the x , y , and z directions are denoted by \mathbf{i} , \mathbf{j} , and \mathbf{k} .

Determine l_x , l_y , and l_z by expanding the 3×3 cross product $\mathbf{l} = \mathbf{r} \times \mathbf{p}$. The vectors \mathbf{r} and \mathbf{p} are given by $\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z$ and $\mathbf{p} = \mathbf{i}p_x + \mathbf{j}p_y + \mathbf{k}p_z$.

b) Substitute the operators for position and momentum in your expressions for l_x and l_y . Always write the position operator to the left of the momentum operator in a simple product of the two.

c) Show that $[\hat{l}_x, \hat{l}_y] = i\hbar \hat{l}_z$.

a)

$$\begin{aligned}
 \mathbf{l} &= \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = \mathbf{i} \begin{vmatrix} y & z \\ p_y & p_z \end{vmatrix} - \mathbf{j} \begin{vmatrix} x & z \\ p_x & p_z \end{vmatrix} + \mathbf{k} \begin{vmatrix} x & y \\ p_x & p_y \end{vmatrix} \\
 &= \mathbf{i}(y p_z - z p_y) - \mathbf{j}(x p_z - z p_x) + \mathbf{k}(x p_y - y p_x) \\
 &= \mathbf{i}(y p_z - z p_y) + \mathbf{j}(z p_x - x p_z) + \mathbf{k}(x p_y - y p_x)
 \end{aligned}$$

b)

$$\begin{aligned}
 \hat{l} &= \mathbf{i} \left(-i\hbar y \frac{\partial}{\partial z} + i\hbar z \frac{\partial}{\partial y} \right) + \mathbf{j} \left(-i\hbar z \frac{\partial}{\partial x} + i\hbar x \frac{\partial}{\partial z} \right) + \mathbf{k} \left(-i\hbar x \frac{\partial}{\partial y} + i\hbar y \frac{\partial}{\partial x} \right) \\
 \hat{l}_x &= -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \quad \hat{l}_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \quad \hat{l}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)
 \end{aligned}$$

c)

$$\begin{aligned}
 [\hat{l}_x, \hat{l}_y] &= \hat{l}_x \hat{l}_y - \hat{l}_y \hat{l}_x = \\
 &= -\hbar^2 \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \left(x \frac{\partial f}{\partial z} - z \frac{\partial f}{\partial x} \right) + \hbar^2 \left(x \frac{\partial}{\partial z} - z \frac{\partial}{\partial x} \right) \left(y \frac{\partial f}{\partial z} - z \frac{\partial f}{\partial y} \right) \\
 &= -\hbar^2 y \frac{\partial}{\partial z} \left(x \frac{\partial f}{\partial z} - z \frac{\partial f}{\partial x} \right) + \hbar^2 z \frac{\partial}{\partial y} \left(x \frac{\partial f}{\partial z} - z \frac{\partial f}{\partial x} \right) + \hbar^2 x \frac{\partial}{\partial z} \left(y \frac{\partial f}{\partial z} - z \frac{\partial f}{\partial y} \right) - \hbar^2 z \frac{\partial}{\partial x} \left(y \frac{\partial f}{\partial z} - z \frac{\partial f}{\partial y} \right) \\
 &= -\hbar^2 y x \frac{\partial^2 f}{\partial z^2} + \hbar^2 y \frac{\partial f}{\partial x} + \hbar^2 y z \frac{\partial^2 f}{\partial z \partial x} + \hbar^2 z x \frac{\partial^2 f}{\partial y \partial z} - \hbar^2 z^2 \frac{\partial^2 f}{\partial y \partial x} \\
 &\quad + \hbar^2 x y \frac{\partial^2 f}{\partial z^2} - \hbar^2 x z \frac{\partial^2 f}{\partial y \partial z} - \hbar^2 x \frac{\partial f}{\partial y} - \hbar^2 y z \frac{\partial^2 f}{\partial z \partial x} + \hbar^2 z^2 \frac{\partial^2 f}{\partial y \partial x} = \\
 &= \hbar^2 y \frac{\partial f}{\partial x} - \hbar^2 x \frac{\partial f}{\partial y} \\
 [\hat{l}_x, \hat{l}_y] &= -\hbar^2 \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = i\hbar \times i\hbar \left(y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right) = i\hbar \hat{l}_z
 \end{aligned}$$

P18.24) For molecular rotation, the symbol J rather than l is used as the quantum number for angular momentum. A ${}^1\text{H}{}^{35}\text{Cl}$ molecule whose bond length and force constant are 127 pm and 516 N m^{-1} , respectively, has the rotational quantum number $l = 10$ and vibrational quantum number $n = 0$.

a) Calculate the rotational and vibrational energy of the molecule. Compare each of these energies with kT at 300 K.

Chapter 18/A Quantum Mechanical Model for the Vibration and Rotation of Molecules

b) Calculate the period for vibration and rotation. How many times does the molecule rotate during one vibrational period?

a)

$$E_{rot} = \frac{J(J+1)\hbar^2}{2\mu r^2} = \frac{10 \times 11 \times (1.055 \times 10^{-34} \text{ J s})^2}{2 \times \frac{1.0078 \text{ amu} \times 34.9688 \text{ amu}}{1.0078 \text{ amu} + 34.9688 \text{ amu}} \times \frac{1.661 \times 10^{-27} \text{ kg}}{\text{amu}} \times (1.275 \times 10^{-10} \text{ m})^2}$$

$$E_{rot} = 2.55 \times 10^{-20} \text{ J}$$

$$\frac{E_{rot}}{kT} = \frac{2.55 \times 10^{-20} \text{ J}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 300 \text{ K}} = 6.15$$

$$E_{vib} = \left(n + \frac{1}{2} \right) \hbar \sqrt{\frac{k}{\mu}} = \frac{1}{2} \times 1.055 \times 10^{-34} \text{ J s} \times \sqrt{\frac{516 \text{ N m}^{-1}}{\frac{1.0078 \text{ amu} \times 34.9688 \text{ amu}}{1.0078 \text{ amu} + 34.9688 \text{ amu}} \times \frac{1.661 \times 10^{-27} \text{ kg}}{\text{amu}}}}$$

$$E_{vib} = 2.97 \times 10^{-20} \text{ J}$$

$$\frac{E_{vib}}{kT} = \frac{2.97 \times 10^{-20} \text{ J}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 300 \text{ K}} = 7.17$$

b) Calculate the period for vibration and rotation. How many times does the molecule vibrate during one rotational period?

$$E_{rot} = \frac{1}{2} I \omega^2; \quad \omega = 2\pi\nu = \frac{2\pi}{T_{rot}}$$

$$T_{rot} = \frac{2\pi}{\omega} = \frac{2\pi}{\sqrt{\frac{2E_{rot}}{I}}}$$

$$= \frac{2\pi}{\sqrt{\frac{2 \times 2.55 \times 10^{-20} \text{ J}}{\frac{1.0078 \text{ amu} \times 34.9688 \text{ amu}}{1.0078 \text{ amu} + 34.9688 \text{ amu}} \times \frac{1.661 \times 10^{-27} \text{ kg}}{\text{amu}} \times (1.275 \times 10^{-10} \text{ m})^2}}} = 1.43 \times 10^{-13} \text{ s}$$

$$T_{vib} = \frac{1}{\nu} = 2\pi \sqrt{\frac{\mu}{k}} = 2\pi \sqrt{\frac{\frac{1.0078 \text{ amu} \times 34.9688 \text{ amu}}{1.0078 \text{ amu} + 34.9688 \text{ amu}} \times \frac{1.661 \times 10^{-27} \text{ kg}}{\text{amu}}}{516 \text{ N m}^{-1}}} = 1.12 \times 10^{-14} \text{ s}$$

It vibrates $\frac{T_{rot}}{T_{vib}} = \frac{1.43 \times 10^{-13} \text{ s}}{1.12 \times 10^{-14} \text{ s}} = 12.8$ times in one rotational period.

P18.25) At what values of θ does $Y_2^0(\theta, \phi) = \left(\frac{5}{16\pi} \right)^{1/2} (3\cos^2 \theta - 1)$ have nodes? Are the nodes points, lines, planes, or other surfaces?

$Y_2^0(\theta, \phi)$ has nodes when $(3\cos^2 \theta - 1)$ has nodes. This occurs for $\theta = 0.955$ and $\pi - 0.955$ radians or 54.7 and 125.3 degrees. These surfaces are cones.

P18.26) The wave functions p_x and d_{xz} are linear combinations of the spherical harmonic functions, which are eigenfunctions of the operators \hat{H} , \hat{l}^2 , and \hat{l}_z for rotation in three dimensions. The combinations have been chosen to yield real functions. Are these functions still eigenfunctions of \hat{l}_z ? Answer this question by applying the operator to the functions.

$$\hat{L}_z p_x = -i\hbar \frac{\partial}{\partial \theta} \sqrt{\frac{3}{4\pi}} \sin \theta \cos \phi = i\hbar \sqrt{\frac{3}{4\pi}} \sin \theta \sin \phi. \text{ This shows that } p_x \text{ is not an eigenfunction of } \hat{L}_z.$$

$$\hat{L}_z d_{xz} = -i\hbar \frac{\partial}{\partial \theta} \sqrt{\frac{15}{4\pi}} \sin \theta \cos \theta \cos \phi = i\hbar \sqrt{\frac{15}{4\pi}} \sin \theta \cos \theta \sin \phi. \text{ This shows that } d_{xz} \text{ is not an eigenfunction of } \hat{L}_z.$$

P18.27) Show that the function $Y_2^0(\theta, \phi) = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2 \theta - 1)$ is normalized over the interval $0 \leq \theta \leq \pi$ and $0 \leq \phi \leq 2\pi$.

$$\begin{aligned} \iint (Y_2^0(\theta, \phi))^2 d\tau &= \left(\frac{5}{16\pi}\right)^{1/2} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta (3\cos^2 \theta - 1)^2 d\theta \\ &= 2\pi \left(\frac{5}{16\pi}\right)^{1/2} \int_0^\pi \sin \theta (9\cos^4 \theta - 6\cos^2 \theta + 1) d\theta \\ \iint (Y_2^0(\theta, \phi))^2 d\tau &= \left(\frac{5}{16\pi}\right)^{1/2} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta (3\cos^2 \theta - 1)^2 d\theta \\ &= 2\pi \left(\frac{5}{16\pi}\right)^{1/2} \int_0^\pi \sin \theta (9\cos^4 \theta - 6\cos^2 \theta + 1) d\theta \\ &= \frac{5}{8} \left(-\frac{9}{5} \cos^5 \theta + 2\cos^3 \theta - \cos \theta \right)_0^\pi = \frac{5}{8} \left(\frac{18}{5} - 4 + 2 \right) = 1 \end{aligned}$$

P18.28) Is it possible to know simultaneously the angular orientation of a molecule rotating in a two dimensional space and its angular momentum? Answer this question by evaluating the commutator $\left[\phi, -i\hbar \frac{\partial}{\partial \phi} \right]$.

$$\left[\phi, -i\hbar \frac{\partial}{\partial \phi} \right] f(\phi) = -i\hbar \phi \frac{df(\phi)}{d\phi} + i\hbar \frac{d[\phi f(\phi)]}{d\phi} \phi = i\hbar f(\phi)$$

$$\left[\phi, -i\hbar \frac{\partial}{\partial \phi} \right] = i\hbar$$

Because the commutator is not equal to zero, it is not possible to simultaneously know the angular orientation of a molecule rotating in a two-dimensional space and its angular momentum.

P18.29) At 300 K, most molecules are in their ground vibrational state. Is this also true for their rotational degree of freedom? Calculate $\frac{n_{J=1}}{n_{J=0}}$ and $\frac{n_{J=5}}{n_{J=0}}$ for the H³⁵Cl molecule whose bond length is 1.27×10^{-10} m. Make sure that you take the degeneracy of the levels into account.

$$\frac{n_{J=1}}{n_{J=0}} = \frac{2J+1}{1} e^{\frac{\hbar^2 J(J+1)}{2I_k T}}$$

$$= 3 \exp \left[-\frac{(1.055 \times 10^{-34} \text{ J s})^2 1(1+1)}{2 \times \frac{1.0078 \times 34.9688}{1.0078 + 34.9688} \text{ amu} \times 1.66 \times 10^{-27} \text{ kg amu}^{-1} \times (1.27 \times 10^{-10} \text{ m})^2 \times 1.381 \times 10^{-23} \text{ J K}^{-1} \times 300 \text{ K}} \right]$$

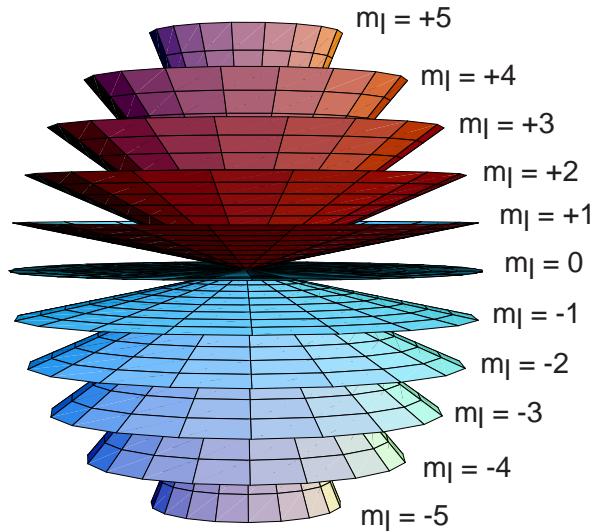
$$\frac{n_{J=1}}{n_{J=0}} = 2.708$$

$$\frac{n_{J=5}}{n_{J=0}} = \frac{2J+1}{1} e^{\frac{\hbar^2 J(J+1)}{2I_k T}}$$

$$= 11 \exp \left[-\frac{(1.055 \times 10^{-34} \text{ J s})^2 5(5+1)}{2 \times \frac{1.0078 \times 34.9688}{1.0078 + 34.9688} \text{ amu} \times 1.66 \times 10^{-27} \text{ kg amu}^{-1} \times (1.27 \times 10^{-10} \text{ m})^2 \times 1.381 \times 10^{-23} \text{ J K}^{-1} \times 300 \text{ K}} \right]$$

$$\frac{n_{J=5}}{n_{J=0}} = 2.369$$

P18.30) Draw a picture (to scale) showing all angular momentum cones consistent with $l = 5$. Calculate the half angles for each of the cones.



The half angles of the cones measured from the positive and negative z axis are

$$\theta_{m_l=5} = \cos^{-1}\left(\frac{5}{\sqrt{5(5+1)}}\right) = 0.420 \text{ radians}$$

$$\theta_{m_l=4} = \cos^{-1}\left(\frac{4}{\sqrt{5(5+1)}}\right) = 0.752 \text{ radians}$$

$$\theta_{m_l=3} = \cos^{-1}\left(\frac{3}{\sqrt{5(5+1)}}\right) = 0.991 \text{ radians}$$

$$\theta_{m_l=2} = \cos^{-1}\left(\frac{2}{\sqrt{5(5+1)}}\right) = 1.20 \text{ radians}$$

$$\theta_{m_l=1} = \cos^{-1}\left(\frac{1}{\sqrt{5(5+1)}}\right) = 1.39 \text{ radians}$$

$$\theta_{m_l=0} = \cos^{-1}\left(\frac{0}{\sqrt{5(5+1)}}\right) = 1.57 \text{ radians}$$

as well as π minus these values for the negative values of m_l .

Chapter 19: The Vibrational and Rotational Spectroscopy of Diatomic Molecules

Problem numbers in italics indicate that the solution is included in the *Student's Solutions Manual*.

Questions on Concepts

Q19.1) A molecule in an excited state can decay to the ground state either by stimulated emission or spontaneous emission. Use the Einstein coefficients to predict how the relative probability of these processes changes as the frequency of the transition doubles.

The ratio $\frac{A_{21}}{B_{21}} = \frac{16\pi^2\hbar v^3}{c^3}$ increases as the cube of the frequency. Therefore, the probability of spontaneous emission increases by a factor 8 relative to that for stimulated emission as the frequency doubles.

Q19.2) What feature of the Morse potential makes it suitable for modeling dissociation of a diatomic molecule?

In contrast to the harmonic potential, the Morse potential levels off as the bond length becomes large. This is necessary to model dissociation.

Q19.3) What is the difference between a permanent and a dynamic dipole moment?

The permanent dipole moment arises from a difference in electronegativity between the bonded atoms. The dynamic dipole moment is the variation in the dipole moment as the molecule vibrates.

Q19.4) If the rotational levels of a diatomic molecule were equally spaced and the selection rule remained unchanged, how would the appearance of the rotational-vibrational spectrum in Figure 19.16 change?

Only the two peaks corresponding to the 0-1 and 1-0 transitions would be observed.

Q19.5) The number of molecules in a given energy level is proportional to $e^{-\frac{\Delta E}{kT}}$ where ΔE is the difference in energy between the level in question and the ground state. How is it possible that a higher lying rotational energy level can have a higher population than the ground state?

Although the number of molecules in a given energy level is proportional to $e^{-\frac{\Delta E}{kT}}$, it is also proportional to the degeneracy of the level, $2J+1$. For small

values of $\frac{\Delta E}{kT}$, the degeneracy of a level can increase faster with J than falls.

Under this condition, a higher lying rotational energy level can have a higher population than the ground state.

Q19.6) Solids generally expand as the temperature increases. Such an expansion results from an increase in the bond length between adjacent atoms as the vibrational amplitude increases. Will a harmonic potential lead to thermal expansion? Will a Morse potential lead to thermal expansion?

Because a harmonic potential is symmetric about the equilibrium distance, the average bond length is independent of the energy level, and therefore independent of distance. A harmonic potential will not give rise to thermal expansion. A Morse potential falls off more slowly for distances greater than the equilibrium value than for distances smaller than the equilibrium value. Therefore, the bond length increases with the quantum number, and a Morse potential will give rise to thermal expansion.

Q19.7) What is the explanation for the absence of a peak in the rotational-vibrational spectrum near 3000 cm^{-1} in Figure 19.14?

This energy would correspond to the $J = 0 \rightarrow J = 0$ transition, which is forbidden by the selection rule for rotational transitions in diatomic molecules.

Q19.8) In Figure 19.13, $\frac{n_J}{n_0}$ increases initially with J for all three temperatures for CO,

but only for the two highest temperatures for HD. Explain this difference.

The way that $\frac{n_J}{n_0}$ changes with J is determined by two opposing trends. The

degeneracy ratio $\frac{g_J}{g_0}$ increases with J , and the exponential term $e^{-\frac{\Delta E}{kT}}$ decreases

with temperature. If $\frac{\Delta E}{kT}$ is not very large at a particular value of T , the

degeneracy ratio term will dominate at low values of J , and $\frac{n_J}{n_0}$ will increase with

J . This is the case for CO. If $\frac{\Delta E}{kT}$ is large, the exponential term will dominate,

and $\frac{n_J}{n_0}$ decreases as J increases from the value zero. This is the case for HD at the two lowest temperatures.

Q19.9) Does the initial excitation in Raman spectroscopy take place to a stationary state of the system? Explain your answer.

No. The initial excitation is to a virtual state, for which the energy is not constant with time. This state is not a stationary state of the system.

Q19.10) If a spectral peak is broadened, can you always conclude that the excited state has a short lifetime?

No, because the broadening could be due to a heterogeneous environment, in which case the observed broadening gives no information about the lifetime.

Problems

P19.1) A strong absorption band in the infrared region of the electromagnetic spectrum is observed at $\tilde{\nu} = 2170 \text{ cm}^{-1}$ for $^{12}\text{C}^{16}\text{O}$. Assuming that the harmonic potential applies, calculate the fundamental frequency ν in units of inverse seconds, the vibrational period in seconds, and the zero point energy for the molecule in joules and electron-volts.

$$\nu = \tilde{\nu} c = 2170 \text{ cm}^{-1} \times 3.00 \times 10^{10} \text{ cm s}^{-1} = 6.51 \times 10^{13} \text{ s}^{-1}$$

$$T = \frac{1}{\nu} = \frac{1}{6.51 \times 10^{13} \text{ s}^{-1}} = 1.54 \times 10^{-14} \text{ s}$$

$$E = \frac{1}{2} h \nu = \frac{1}{2} \times 6.626 \times 10^{-34} \text{ Js} \times 6.51 \times 10^{13} \text{ s}^{-1} = 2.16 \times 10^{-20} \text{ J} \times \frac{6.241 \times 10^{18} \text{ eV}}{\text{J}} = 0.134 \text{ eV}$$

P19.2) Isotopic substitution is used to identify characteristic groups in an unknown compound using vibrational spectroscopy. Consider the C=C bond in ethene (C_2H_4). By what factor would the frequency change if deuterium were substituted for all the hydrogen atoms? Treat the H and D atoms as being rigidly attached to the carbon.

$$\frac{\nu_{\text{D}}}{\nu_{\text{H}}} = \sqrt{\frac{\mu_{\text{CH}_2-\text{CH}_2}}{\mu_{\text{CD}_2-\text{CD}_2}}} = \sqrt{\frac{\frac{(14.01)^2}{28.02} \text{ amu}}{\frac{(16.02)^2}{32.04} \text{ amu}}} = 0.935$$

P19.3) The force constants for H_2 and Br_2 are 575 and 246 N m⁻¹, respectively.

Calculate the ratio of the vibrational state populations $\frac{n_1}{n_0}$ and $\frac{n_2}{n_0}$ at $T = 300 \text{ K}$ and $T = 1000 \text{ K}$.

The vibrational energy is given by $E_n = \left(n + \frac{1}{2}\right)h\nu = \left(n + \frac{1}{2}\right)h\sqrt{\frac{k}{\mu}}$

For H₂

$$E_0 = \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} = \frac{1}{2} \times 1.055 \times 10^{-34} \text{ J s} \times \sqrt{\frac{575 \text{ N m}^{-1}}{\frac{1.0078 \times 1.0078}{1.0078 + 1.0078} \text{ amu} \times 1.661 \times 10^{-27} \text{ kg amu}^{-1}}} = 4.37 \times 10^{-20} \text{ J}$$

$$E_1 = \frac{3}{2} \hbar \sqrt{\frac{k}{\mu}} = \frac{3}{2} \times 1.055 \times 10^{-34} \text{ J s} \times \sqrt{\frac{575 \text{ N m}^{-1}}{\frac{1.0078 \times 1.0078}{1.0078 + 1.0078} \text{ amu} \times 1.661 \times 10^{-27} \text{ kg amu}^{-1}}} = 1.31 \times 10^{-19} \text{ J}$$

$$E_2 = \frac{5}{2} \hbar \sqrt{\frac{k}{\mu}} = \frac{5}{2} \times 1.055 \times 10^{-34} \text{ J s} \times \sqrt{\frac{575 \text{ N m}^{-1}}{\frac{1.0078 \times 1.0078}{1.0078 + 1.0078} \text{ amu} \times 1.661 \times 10^{-27} \text{ kg amu}^{-1}}} = 2.19 \times 10^{-19} \text{ J}$$

For Br₂

$$E_0 = \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} = \frac{1}{2} \times 1.055 \times 10^{-34} \text{ J s} \times \sqrt{\frac{246 \text{ N m}^{-1}}{\frac{78.9183 \times 78.9183}{78.9183 + 78.9183} \text{ amu} \times 1.661 \times 10^{-27} \text{ kg amu}^{-1}}} = 3.23 \times 10^{-21} \text{ J}$$

$$E_1 = \frac{3}{2} \hbar \sqrt{\frac{k}{\mu}} = \frac{3}{2} \times 1.055 \times 10^{-34} \text{ J s} \times \sqrt{\frac{246 \text{ N m}^{-1}}{\frac{78.9183 \times 78.9183}{78.9183 + 78.9183} \text{ amu} \times 1.661 \times 10^{-27} \text{ kg amu}^{-1}}} = 9.70 \times 10^{-21} \text{ J}$$

$$E_2 = \frac{5}{2} \hbar \sqrt{\frac{k}{\mu}} = \frac{5}{2} \times 1.055 \times 10^{-34} \text{ J s} \times \sqrt{\frac{246 \text{ N m}^{-1}}{\frac{78.9183 \times 78.9183}{78.9183 + 78.9183} \text{ amu} \times 1.661 \times 10^{-27} \text{ kg amu}^{-1}}} = 1.62 \times 10^{-20} \text{ J}$$

$$\text{For H}_2 \text{ at } 300 \text{ K, } \frac{n_1}{n_0} = e^{\frac{-E_1 - E_0}{kT}} = e^{\frac{-(1.31 - 0.437) \times 10^{-19} \text{ J}}{1.381 \times 10^{-23} \times 300 \text{ K}}} = 6.81 \times 10^{-10}$$

$$\text{For H}_2 \text{ at } 1000 \text{ K, } \frac{n_1}{n_0} = e^{\frac{-E_1 - E_0}{kT}} = e^{\frac{-(1.31 - 0.437) \times 10^{-19} \text{ J}}{1.381 \times 10^{-23} \times 1000 \text{ K}}} = 1.78 \times 10^{-3}$$

$$\text{For H}_2 \text{ at } 300 \text{ K, } \frac{n_2}{n_0} = e^{\frac{-E_2 - E_0}{kT}} = e^{\frac{-(2.19 - 0.437) \times 10^{-19} \text{ J}}{1.381 \times 10^{-23} \times 300 \text{ K}}} = 4.65 \times 10^{-19}$$

$$\text{For H}_2 \text{ at } 1000 \text{ K, } \frac{n_2}{n_0} = e^{\frac{-E_2 - E_0}{kT}} = e^{\frac{-(2.19 - 0.437) \times 10^{-19} \text{ J}}{1.381 \times 10^{-23} \times 1000 \text{ K}}} = 3.07 \times 10^{-6}$$

$$\text{For Br}_2 \text{ at } 300 \text{ K, } \frac{n_1}{n_0} = e^{-\frac{E_1 - E_0}{kT}} = e^{\frac{(9.70 - 3.23) \times 10^{-21} \text{ J}}{1.381 \times 10^{-23} \times 300 \text{ K}}} = 0.212$$

$$\text{For Br}_2 \text{ at } 1000 \text{ K, } \frac{n_1}{n_0} = e^{-\frac{E_1 - E_0}{kT}} = e^{\frac{(9.70 - 3.23) \times 10^{-21} \text{ J}}{1.381 \times 10^{-23} \times 1000 \text{ K}}} = 0.628$$

$$\text{For Br}_2 \text{ at } 300 \text{ K, } \frac{n_2}{n_0} = e^{-\frac{E_2 - E_0}{kT}} = e^{\frac{(1.62 - 0.323) \times 10^{-20} \text{ J}}{1.381 \times 10^{-23} \times 300 \text{ K}}} = 4.50 \times 10^{-2}$$

$$\text{For Br}_2 \text{ at } 1000 \text{ K, } \frac{n_2}{n_0} = e^{-\frac{E_2 - E_0}{kT}} = e^{\frac{(1.62 - 0.323) \times 10^{-20} \text{ J}}{1.381 \times 10^{-23} \times 1000 \text{ K}}} = 0.394$$

P19.4) The ${}^1\text{H}{}^{35}\text{Cl}$ molecule can be described by a Morse potential with $D_e = 7.41 \times 10^{-19} \text{ J}$. The force constant k for this molecule is 516.3 N m^{-1} and $\nu = 8.97 \times 10^{13} \text{ s}^{-1}$.

a. Calculate the lowest four energy levels for a Morse potential using the formula

$$E_n = h\nu \left(n + \frac{1}{2} \right) - \frac{(h\nu)^2}{4D_e} \left(n + \frac{1}{2} \right)^2.$$

b. Calculate the fundamental frequency ν_0 corresponding to the transition $n = 0 \rightarrow n = 1$ and the frequencies of the first three overtone vibrations. How large would the relative error be if you assume that the first three overtone frequencies are $2\nu_0$, $3\nu_0$, and $4\nu_0$?

$$E_n = h\nu \left(n + \frac{1}{2} \right) - \frac{(h\nu)^2}{4D_e} \left(n + \frac{1}{2} \right)^2 = 6.626 \times 10^{-34} \text{ J s} \times 8.97 \times 10^{13} \text{ s}^{-1} \times \left(n + \frac{1}{2} \right) - \frac{(6.626 \times 10^{-34} \text{ J s} \times 8.97 \times 10^{13} \text{ s}^{-1})^2}{4 \times 7.41 \times 10^{-19} \text{ J}}$$

$$E_n = 5.944 \times 10^{-20} \times \left(n + \frac{1}{2} \right) \text{ J} - 1.192 \times 10^{-21} \times \left(n + \frac{1}{2} \right)^2 \text{ J}$$

$$E_0 = 2.942 \times 10^{-20} \text{ J}$$

$$E_1 = 8.647 \times 10^{-20} \text{ J}$$

$$E_2 = 1.411 \times 10^{-19} \text{ J}$$

$$E_3 = 1.934 \times 10^{-19} \text{ J}$$

$$\nu_{0 \rightarrow 1} = \frac{E_1 - E_0}{h} = \frac{8.647 \times 10^{-20} \text{ J} - 2.942 \times 10^{-20} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 8.61 \times 10^{13} \text{ s}^{-1}$$

$$\nu_{0 \rightarrow 2} = \frac{E_2 - E_0}{h} = \frac{14.11 \times 10^{-20} \text{ J} - 2.942 \times 10^{-20} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 1.69 \times 10^{14} \text{ s}^{-1}$$

$$\nu_{0 \rightarrow 3} = \frac{E_3 - E_0}{h} = \frac{19.34 \times 10^{-20} \text{ J} - 2.942 \times 10^{-20} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 2.47 \times 10^{14} \text{ s}^{-1}$$

$$\text{Error}(\nu_{0 \rightarrow 2}) = \frac{\nu_{0 \rightarrow 2} - 2\nu_{0 \rightarrow 1}}{\nu_{0 \rightarrow 2}} = -1.89\%$$

$$\text{Error}(\nu_{0 \rightarrow 3}) = \frac{\nu_{0 \rightarrow 2} - 3\nu_{0 \rightarrow 1}}{\nu_{0 \rightarrow 2}} = -4.57\%$$

P19.5) Using the formula for the energy levels for the Morse potential,

$E_n = h\nu \left(n + \frac{1}{2} \right) - \frac{(h\nu)^2}{4D_e} \left(n + \frac{1}{2} \right)^2$, show that the energy spacing between adjacent levels

is given by $E_{n+1} - E_n = h\nu - \frac{(h\nu)^2}{2D_e}(1+n)$. For ${}^1\text{H}{}^{35}\text{Cl}$, $D_e = 7.41 \times 10^{-19} \text{ J}$ and $\nu = 8.97 \times 10^{13} \text{ s}^{-1}$. Calculate the smallest value of n for which $E_{n+1} - E_n < 0.5(E_1 - E_0)$.

$$E_{n+1} - E_n = h\nu \left(n + \frac{3}{2} \right) - \frac{(h\nu)^2}{4D_e} \left(n + \frac{3}{2} \right)^2 - h\nu \left(n + \frac{1}{2} \right) + \frac{(h\nu)^2}{4D_e} \left(n + \frac{1}{2} \right)^2$$

$$E_{n+1} - E_n = h\nu \left[\left(n + \frac{3}{2} \right) - \left(n + \frac{1}{2} \right) \right] - \frac{(h\nu)^2}{4D_e} \left[\left(n + \frac{3}{2} \right)^2 - \left(n + \frac{1}{2} \right)^2 \right]$$

$$E_{n+1} - E_n = h\nu - \frac{(h\nu)^2}{4D_e} \left[n^2 + 3n + \frac{9}{4} - n^2 - n - \frac{1}{4} \right] = h\nu - \frac{(h\nu)^2}{2D_e}(n+1)$$

$$E_{n+1} - E_n = 5.944 \times 10^{-20} \text{ J} - 2.384 \times 10^{-21}(n+1) \text{ J}$$

$$E_1 - E_0 = h\nu - \frac{(h\nu)^2}{2D_e} = 6.626 \times 10^{-34} \text{ J s} \times 8.97 \times 10^{13} \text{ s}^{-1} - \frac{(6.626 \times 10^{-34} \text{ J s} \times 8.97 \times 10^{13} \text{ s}^{-1})^2}{2 \times 7.41 \times 10^{-19} \text{ J}}$$

$$E_1 - E_0 = 5.705 \times 10^{-20} \text{ J}$$

$$0.5 \times 5.705 \times 10^{-20} \text{ J} = 5.944 \times 10^{-20} \text{ J} - 2.386 \times 10^{-21}(n+1) \text{ J}$$

$$n = 11.97$$

The lowest integral value for which the equation is satisfied is $n = 12$.

P19.6) Show that the Morse potential approaches the harmonic potential for small values of the vibrational amplitude. (*Hint:* Expand the Morse potential in a Taylor-Maclaurin series.)

$$V(R) = D_e \left[1 - e^{-\alpha(R-R_e)} \right]^2$$

Expanding in a Taylor-Maclaurin series and keeping only the first term,

$$\begin{aligned} V(R) &= D_e \left[1 - \left[e^{-\alpha(R-R_e)} \right]_{R=R_e} - \left[\frac{\partial e^{-\alpha(R-R_e)}}{\partial(R-R_e)} \right]_{R=R_e} (R-R_e) \right]^2 \\ &= D_e \left[1 - 1 - \alpha(R-R_e) \right]^2 = D_e \alpha^2 (R-R_e)^2 \end{aligned}$$

P19.7) A measurement of the vibrational energy levels of $^{12}\text{C}^{16}\text{O}$ gives the relationship

$$\tilde{v}(n) = 2170.21 \left(n + \frac{1}{2} \right) \text{ cm}^{-1} - 13.461 \left(n + \frac{1}{2} \right)^2 \text{ cm}^{-1} \quad \text{where } n \text{ is the vibrational quantum number.}$$

The fundamental vibrational frequency is $\tilde{v}_0 = 2170.21 \text{ cm}^{-1}$. From these data, calculate the depth D_e of the Morse potential for $^{12}\text{C}^{16}\text{O}$. Calculate the bond energy of the molecule.

We convert the expression to one in terms of energy

$$E(n) = 2170.21 \times hc \left(n + \frac{1}{2} \right) - 13.461 \times hc \left(n + \frac{1}{2} \right)^2$$

and compare it with Equation (19.5) for the Morse potential.

$$E_n = h\nu \left(n + \frac{1}{2} \right) - \frac{(h\nu)^2}{4D_e} \left(n + \frac{1}{2} \right)^2$$

from which we see that

$$13.461 \times hc = \frac{(h\nu)^2}{4D_e}$$

$$\begin{aligned} D_e &= \frac{h\nu^2}{4 \times 13.461 \times c} = \frac{hc\tilde{v}^2}{4 \times 13.461} \\ &= \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^{10} \text{ cm s}^{-1} \times (2170 \text{ cm}^{-1})^2}{4 \times 13.461} = 1.738 \times 10^{-18} \text{ J} \end{aligned}$$

$$\begin{aligned} D_0 &= D_e - \frac{1}{2} hc\tilde{v}_0 = 1.738 \times 10^{-18} \text{ J} - \frac{1}{2} \times 6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^{10} \text{ cm s}^{-1} \times 2170 \text{ cm}^{-1} \\ &= 1.717 \times 10^{-18} \text{ J} \end{aligned}$$

The bond energy per mole is $D_0 N_A = 1.034 \times 10^3 \text{ kJ mol}^{-1}$.

P19.8) The fundamental vibrational frequencies for $^1\text{H}^{19}\text{F}$ and $^2\text{D}^{19}\text{F}$ are 4138.52 and 2998.25 cm^{-1} , respectively, and D_e for both molecules is 5.86 eV. What is the difference in the bond energy of the two molecules?

$$\begin{aligned} & \left(D_e - \frac{1}{2} h c \tilde{\nu}_{\text{HF}} \right)_{\text{HF}} - \left(D_e - \frac{1}{2} h c \tilde{\nu}_{\text{DF}} \right)_{\text{DF}} = \frac{1}{2} h c (\tilde{\nu}_{\text{HF}} - \tilde{\nu}_{\text{DF}}) \\ & = \frac{1}{2} \times 6.626 \times 10^{-34} \text{ J s} \times 3.00 \times 10^{10} \text{ cm s}^{-1} \times (4138.52 \text{ cm}^{-1} - 2998.25 \text{ cm}^{-1}) = 1.133 \times 10^{-20} \text{ J} \end{aligned}$$

P19.9) In this problem, you will derive the equations used to explain the Michelson interferometer for incident light of a single frequency.

- a) Show that the expression $A(t) = \frac{A_0}{\sqrt{2}} (1 + e^{i\delta(t)}) \exp i(k y_D - \omega t)$ represents the sum of two waves of the form $\frac{A_0}{\sqrt{2}} \exp i(kx - \omega t)$, one of which is phase shifted by the amount $\delta(t)$ evaluated at the position y_D .

$$\begin{aligned} & \frac{A_0}{\sqrt{2}} \exp i(kx - \omega t) + \frac{A_0}{\sqrt{2}} \exp i(kx - \omega t + \delta(t)) = \frac{A_0}{\sqrt{2}} (\exp i(kx - \omega t) + \exp i\delta(t) \exp i(kx - \omega t)) \\ & = \frac{A_0}{\sqrt{2}} (1 + e^{i\delta(t)}) \exp i(kx - \omega t) = \frac{A_0}{\sqrt{2}} (1 + e^{i\delta(t)}) \exp i(k y_D - \omega t) \end{aligned}$$

when evaluated at $x = y_D$.

- b) Show using the definition $I(t) = A(t)A^*(t)$, that $I(t) = \frac{I_0}{2} (1 + \cos \delta(t))$.

$$\begin{aligned} A(t)A^*(t) &= \frac{A_0}{\sqrt{2}} (1 + e^{i\delta(t)}) \exp i(k y_D - \omega t) \frac{A_0}{\sqrt{2}} (1 + e^{-i\delta(t)}) \exp i(-k y_D + \omega t) \\ A(t)A^*(t) &= \frac{A_0^2}{2} (1 + e^{i\delta(t)}) (1 + e^{-i\delta(t)}) = \frac{A_0^2}{2} (1 + \cos \delta(t) + i \sin \delta(t)) A_0^2 (1 + \cos \delta(t)) \end{aligned}$$

- c) Expressing $\delta(t)$ in terms of $\Delta d(t)$, show that $I(t) = \frac{I_0}{2} \left(1 + \cos \frac{2\pi \Delta d(t)}{\lambda} \right)$.

$$A(t)A^*(t) = A_0^2 (1 + \cos \delta(t)) \text{ and with } \delta(t) = 2\pi \frac{\Delta d(t)}{\lambda},$$

$$A(t)A^*(t) = A_0^2 \left(1 + \cos \left[2\pi \frac{\Delta d(t)}{\lambda} \right] \right)$$

d) Expressing $\Delta d(t)$ in terms of the mirror velocity v , show that

$$I(t) = \frac{I_0}{2} \left(1 + \cos \frac{2v}{c} \omega t \right).$$

$$\Delta d(t) = 2vt \text{ and } \frac{1}{\lambda} = \frac{v}{c} = \frac{\omega}{2\pi c}. \text{ Therefore}$$

$$A(t) A^*(t) = A_0^2 \left(1 + \cos \frac{2v}{c} \omega t \right)$$

P19.10) Greenhouse gases generated from human activity absorb infrared radiation from the Earth and keep it from being dispersed outside our atmosphere. This is a major cause of global warming. Compare the path length required to absorb 99% of the Earth's radiation near a wavelength of $7 \mu\text{m}$ for CH_3CCl_3 [$\epsilon(\lambda) = 1.8 \text{ (cm atm)}^{-1}$] and the chlorofluorocarbon CFC-14 [$\epsilon(\lambda) = 4.1 \times 10^3 \text{ (cm atm)}^{-1}$] assuming that each of these gases has a partial pressure of 2.0×10^{-6} bar.

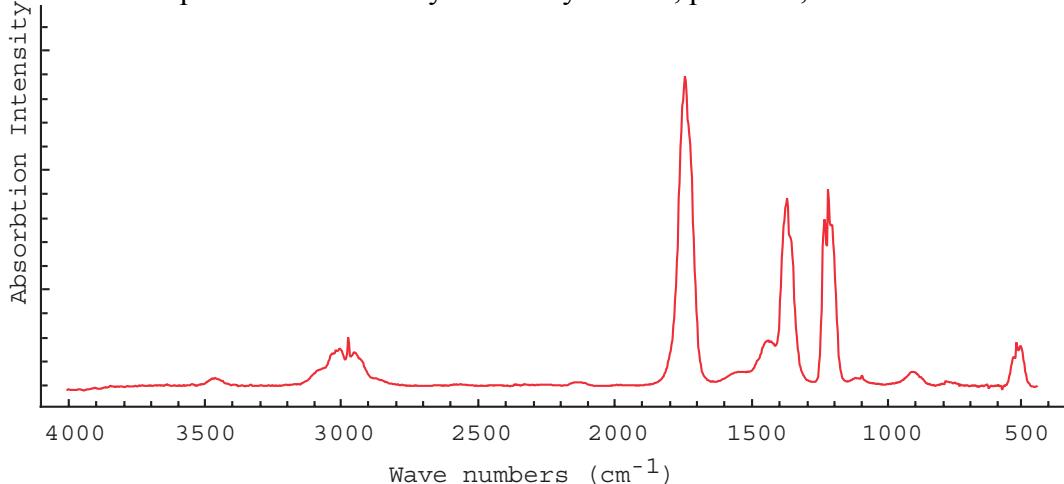
Rearranging the Beer-Lambert equation, we have for CH_3CCl_3

$$l = -\frac{1}{M\epsilon(\lambda)} \ln \left(\frac{I(\lambda)}{I_0(\lambda)} \right) = -\frac{1}{1.8 \text{ (cm atm)}^{-1} \times 2.0 \times 10^{-6} \text{ atm}} \times \ln 0.01 = 1.28 \times 10^6 \text{ cm}$$

For CFC-14 we have

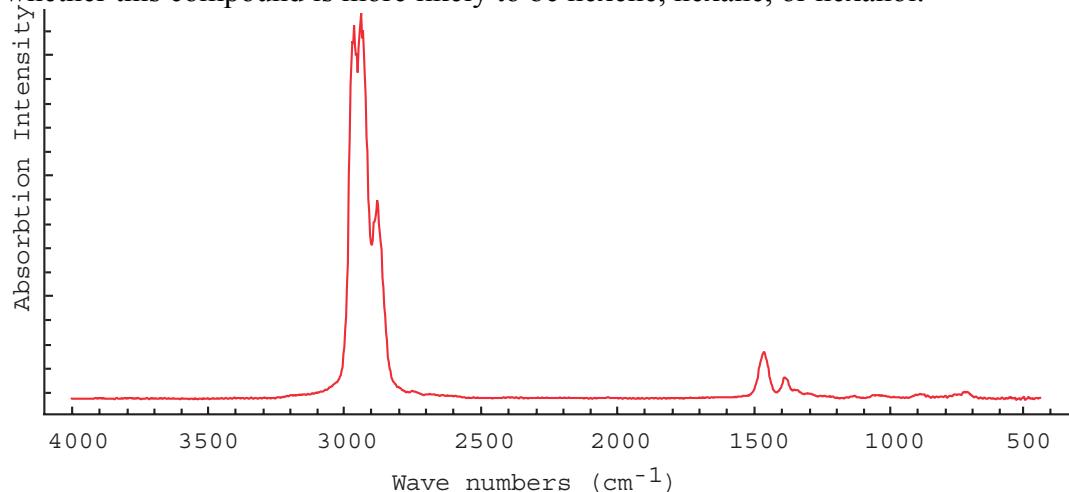
$$l = -\frac{1}{M\epsilon(\lambda)} \ln \left(\frac{I(\lambda)}{I_0(\lambda)} \right) = -\frac{1}{4.1 \times 10^3 \text{ (cm atm)}^{-1} \times 2.0 \times 10^{-6} \text{ atm}} \times \ln 0.01 = 5.61 \times 10^2 \text{ cm}$$

P19.11) An infrared absorption spectrum of an organic compound is shown in the following figure. Using the characteristic group frequencies listed in Section 19.6, decide whether this compound is more likely to be ethyl amine, pentanol, or acetone.



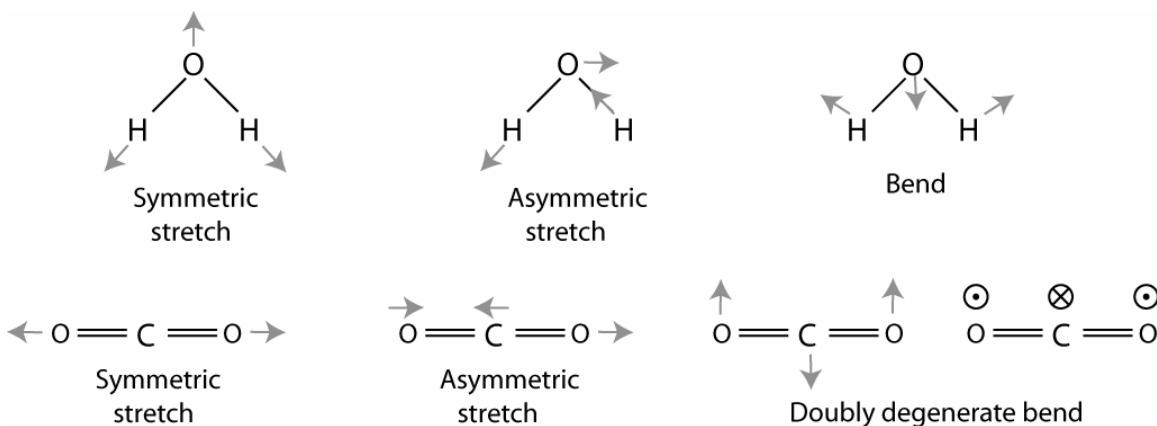
The major peak near 1700 cm^{-1} is the C=O stretch and the peak near 1200 cm^{-1} is a C–C–C stretch. These peaks are consistent with the compound being acetone. Ethyl amine should show a strong peak near 3350 cm^{-1} and pentanol should show a strong peak near 3400 cm^{-1} . Because these peaks are absent, these compounds can be ruled out.

P19.12) An infrared absorption spectrum of an organic compound is shown in the following figure. Use the characteristic group frequencies listed in Section 19.6 to decide whether this compound is more likely to be hexene, hexane, or hexanol.



The group of peaks near 2900 cm^{-1} are due to CH_3 and CH_2 stretching vibrations and the small peak near 1400 cm^{-1} is due to a CH_3 umbrella bending mode. These peaks are consistent with the compound being hexane. Hexene should show a strong peak near 1650 cm^{-1} and hexanol should show a strong peak near 3400 cm^{-1} . Because these peaks are absent, these compounds can be ruled out.

P19.13) Calculating the motion of individual atoms in the vibrational modes of molecules (called normal modes) is an advanced topic. Given the normal modes shown in the following figure, decide which of the following modes of CO_2 and H_2O have a nonzero dynamical dipole moment and are therefore infrared active. The motion of the atoms in the second of the two doubly degenerate bend modes for CO_2 is identical to the first, but is perpendicular to the plane of the page.



All three vibrational modes of water will lead to a change in the dipole moment and are therefore infrared active. The symmetric stretch of carbon dioxide will not lead to a change in the dipole moment and is infrared inactive. The other two modes will lead to a change in the dipole moment and are infrared active.

P19.14) The rotational constant for $^{127}\text{I}^{79}\text{Br}$ determined from microwave spectroscopy is $0.1141619 \text{ cm}^{-1}$. The atomic masses of ^{127}I and ^{79}Br are 126.904473 amu and 78.918336 amu , respectively. Calculate the bond length in $^{127}\text{I}^{79}\text{Br}$ to the maximum number of significant figures consistent with this information.

$$B = \frac{h}{8\pi^2 \mu r_0^2}; \quad r_0 = \sqrt{\frac{h}{8\pi^2 \mu B}}$$

$$r_0 = \sqrt{\frac{6.6260755 \times 10^{-34} \text{ J s}}{8\pi^2 \times \frac{126.904473 \times 78.918336 \text{ amu}}{(126.904473 + 78.918336)} \times 1.6605402 \times 10^{-27} \text{ kg amu}^{-1} \times 0.1141619 \text{ cm}^{-1} \times 2.99792458 \times 10^{10} \text{ cm s}^{-1}}}$$

$$r_0 = 1.742035 \times 10^{-10} \text{ m}$$

P19.15) The rotational constant for $^2\text{D}^{19}\text{F}$ determined from microwave spectroscopy is 11.007 cm^{-1} . The atomic masses of ^{19}F and ^2D are 18.9984032 and 2.0141018 amu , respectively. Calculate the bond length in $^2\text{D}^{19}\text{F}$ to the maximum number of significant figures consistent with this information.

$$B = \frac{h}{8\pi^2 \mu r_0^2}; \quad r_0 = \sqrt{\frac{h}{8\pi^2 \mu B}}$$

$$r_0 = \sqrt{\frac{6.6260755 \times 10^{-34} \text{ J s}}{8\pi^2 \times \frac{2.0141018 \times 18.9984032 \text{ amu}}{(2.0141018 + 18.9984032)} \times 1.6605402 \times 10^{-27} \text{ kg amu}^{-1} \times 11.007 \text{ cm}^{-1} \times 2.99792458 \times 10^{10} \text{ cm s}^{-1}}}$$

$$r_0 = 9.1707 \times 10^{-11} \text{ m}$$

P19.16) Calculate the moment of inertia, the magnitude of the rotational angular momentum, and the energy in the $J=1$ rotational state for $^1\text{H}_2$ in which the bond length of $^1\text{H}_2$ is 74.6 pm . The atomic mass of ^1H is 1.007825 amu .

$$\begin{aligned}
 I &= \mu r_0^2 = \frac{1.007825^2 \text{ amu}}{2 \times 1.007825} \times 1.6605402 \times 10^{-27} \text{ kg amu}^{-1} \times (74.6 \times 10^{-12} \text{ m})^2 \\
 &= 4.657 \times 10^{-48} \text{ kg m}^2 \\
 |J| &= \sqrt{J(J+1)}\hbar = \sqrt{2} \times 1.0554 \times 10^{-34} \text{ J s} = 1.4914 \times 10^{-34} \text{ J s} \\
 &= 1.49 \times 10^{-34} \text{ kg m s}^{-2} \\
 E_J &= \frac{J(J+1)\hbar^2}{2I} = \frac{2 \times (1.0554 \times 10^{-34} \text{ J s})^2}{2 \times 4.657 \times 10^{-48} \text{ kg m}^2} = 2.39 \times 10^{-21} \text{ J}
 \end{aligned}$$

P19.17) Calculate the moment of inertia, the magnitude of the angular momentum, and the energy in the $J=1$ rotational state for $^{16}\text{O}_2$ in which the bond length is 120.8 pm. The atomic mass of ^{16}O is 15.99491 amu.

$$\begin{aligned}
 I &= \mu r_0^2 = \frac{15.99491^2 \text{ amu}}{2 \times 15.99491} \times 1.6605402 \times 10^{-27} \text{ kg amu}^{-1} \times (120.8 \times 10^{-12} \text{ m})^2 \\
 &= 1.938 \times 10^{-46} \text{ kg m}^2 \\
 |J| &= \sqrt{J(J+1)}\hbar = \sqrt{2} \times 1.0554 \times 10^{-34} \text{ J s} = 1.4914 \times 10^{-34} \text{ J s} \\
 &= 1.491 \times 10^{-34} \text{ kg m s}^{-2} \\
 E_J &= \frac{J(J+1)\hbar^2}{2I} = \frac{2 \times (1.0554 \times 10^{-34} \text{ J s})^2}{2 \times 1.938 \times 10^{-46} \text{ kg m}^2} = 5.743 \times 10^{-23} \text{ J}
 \end{aligned}$$

P19.18) The rigid rotor model can be improved by recognizing that in a realistic anharmonic potential, the bond length increases with the vibrational quantum number n . Therefore the rotational constant will depend on n , and it can be shown that

$$B_n = B - \left(n + \frac{1}{2} \right) \alpha, \text{ where } B \text{ is the rigid rotor value. The constant } \alpha \text{ can be obtained}$$

from experimental spectra. For $^1\text{H}^{79}\text{Br}$, $B = 8.473 \text{ cm}^{-1}$ and $\alpha = 0.226 \text{ cm}^{-1}$. Using this more accurate formula for B_n , calculate the bond length for HBr in the ground state and for $n = 3$.

For $n = 0$

$$\begin{aligned}
 B &= \frac{h}{8\pi^2 \mu r_0^2}; \quad r_0 = \sqrt{\frac{h}{8\pi^2 \mu B_n}} \\
 r_0 &= \sqrt{\frac{6.6260755 \times 10^{-34} \text{ J s}}{8\pi^2 \times \frac{1.0078250 \times 78.918336 \text{ amu}}{1.0078250 + 78.918336} \times 1.6605402 \times 10^{-27} \text{ kg amu}^{-1} \times \left(8.473 - \frac{0.226}{2} \right) \text{ cm}^{-1} \times 2.99792458 \times 10^{10} \text{ cm s}^{-1}}} \\
 r_0 &= 1.424 \times 10^{-10} \text{ m}
 \end{aligned}$$

For $n = 3$

$$B = \frac{h}{8\pi^2 \mu r_0^2}; \quad r_0 = \sqrt{\frac{h}{8\pi^2 \mu B}}$$

$$r_0 = \sqrt{\frac{6.6260755 \times 10^{-34} \text{ J s}}{8\pi^2 \times \frac{1.0078250 \times 78.918336 \text{ amu}}{1.0078250 + 78.918336} \times 1.6605402 \times 10^{-27} \text{ kg amu}^{-1} \times \left(8.472 - \frac{3 \times 0.226}{2}\right) \text{ cm}^{-1} \times 2.99792458 \times 10^{10} \text{ cm s}^{-1}}}$$

$$r_0 = 1.443 \times 10^{-10} \text{ m}$$

P19.19) Because the intensity of a transition to first order is proportional to the population of the originating state, the J value for which the maximum intensity is observed in a rotational-vibrational spectrum is not generally $J = 0$. Treat J in the equation $\frac{n_J}{n_0} = \frac{g_J}{g_0} e^{-(\varepsilon_J - \varepsilon_0)/kT} = (2J+1)e^{-\hbar^2 J(J+1)/2IkT}$ as a continuous variable.

a. Show that

$$\frac{d\left(\frac{n_J}{n_0}\right)}{dJ} = 2e^{-\hbar^2 J(J+1)/2IkT} - \frac{(2J+1)^2 \hbar^2}{2IkT} e^{-\hbar^2 J(J+1)/2IkT}$$

$$\frac{d\left(\frac{n_J}{n_0}\right)}{dJ} = 2e^{-\hbar^2 J(J+1)/2IkT} + (2J+1)e^{-\hbar^2 J(J+1)/2IkT} \frac{d(-\hbar^2 J(J+1)/2IkT)}{dJ}$$

$$= 2e^{-\hbar^2 J(J+1)/2IkT} + (2J+1)e^{-\hbar^2 J(J+1)/2IkT} \left(-\frac{\hbar^2 (2J+1)}{2IkT}\right)$$

$$= 2e^{-\hbar^2 J(J+1)/2IkT} - \frac{(2J+1)^2 \hbar^2}{2IkT} e^{-\hbar^2 J(J+1)/2IkT}$$

b) Show that setting $\frac{d\left(\frac{n_J}{n_0}\right)}{dJ} = 0$ gives the equation $2 - \frac{(2J_{\max}+1)^2 \hbar^2}{2IkT} = 0$

$$\frac{d\left(\frac{n_J}{n_0}\right)}{dJ} = 2e^{-\hbar^2 J(J+1)/2IkT} - \frac{(2J+1)^2 \hbar^2}{2IkT} e^{-\hbar^2 J(J+1)/2IkT} = 0$$

cancelling $e^{-\hbar^2 J(J+1)/2IkT}$ on both sides of the equation, $2 - \frac{(2J+1)^2 \hbar^2}{2IkT} = 0$

$$\text{c) Show that the solution of this quadratic equation is } J_{\max} = \frac{1}{2} \left[\sqrt{\frac{4IkT}{\hbar^2}} - 1 \right]$$

In Problems P19.20 and P19.21 we assume that the intensity of the individual peaks is solely determined by the population in the originating state and that it does not depend on the initial and final J values.

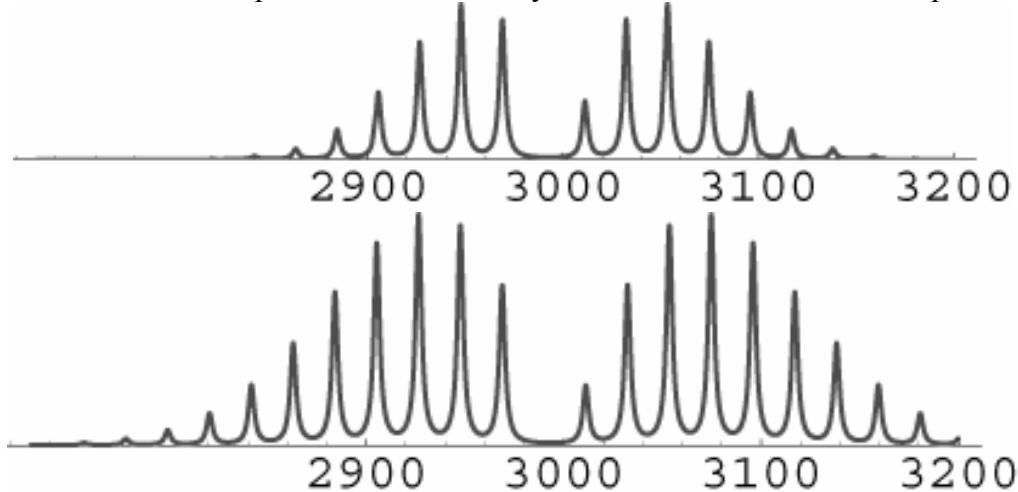
$$2 - \frac{(2J+1)^2 \hbar^2}{2IkT} = 0; \quad -\frac{2\hbar^2}{IkT} J^2 - \frac{2\hbar^2}{IkT} J - \frac{2\hbar^2}{IkT} + 2 = 0$$

$$\text{Solving this quadratic equation, } J_{\max} = -\frac{1}{2} \pm \frac{\sqrt{2}}{2} \sqrt{\frac{2IkT}{\hbar^2}}$$

Only the + solution gives $J > 0$

$$J_{\max} = \frac{1}{2} \left[\sqrt{\frac{4IkT}{\hbar^2}} - 1 \right]$$

P19.20) In Problem P19.19 you obtained the result $J_{\max} = \frac{1}{2} \left[\sqrt{\frac{4IkT}{\hbar^2}} - 1 \right]$. Using this result, estimate T for the simulated ${}^1\text{H}{}^{35}\text{Cl}$ rotational spectra in the following figure. Give realistic estimates of the precision with which you can determine T from the spectra.



$$J_{\max} = \frac{1}{2} \left[\sqrt{\frac{4IkT}{\hbar^2}} - 1 \right]; \quad T = \frac{(2J_{\max} + 1)^2 \hbar^2}{4Ik}$$

$$T = \frac{(2J_{\max} + 1)^2 \hbar^2}{4Ik}$$

For the upper spectrum, $J_{\max} = 2$ in both the P and R branches.

$$T = \frac{5^2 \times (1.054 \times 10^{-34} \text{ J s})^2}{4 \times \frac{1.0078 \times 34.9689}{1.0078 + 34.9689} \text{ amu} \times 1.1661 \times 10^{-27} \text{ kg amu}^{-1} \times (1.2746 \times 10^{-10} \text{ m})^2 \times 1.3807 \times 10^{-23} \text{ J K}^{-1}}$$

$$T = 190 \text{ K}$$

Setting $J_{max} = 1$ and 3 gives temperatures of 68 K and 372 K. Given an uncertainty of ± 0.5 in J_{max} , a reasonable estimate of the temperature in the upper spectrum is $190 \text{ K} \pm 70 \text{ K}$.

For the lower spectrum, $J_{max} = 3$ in both the P and R branches, giving $T = 372 \text{ K}$. Setting $J_{max} = 2$ and 4 gives temperatures of 190 K and 616 K. Given an uncertainty of ± 0.5 in J_{max} , a reasonable estimate of the temperature in the lower spectrum is $372 \text{ K} \pm 120 \text{ K}$.

Evaluating the intensities for all values of J and not just J_{max} would reduce the uncertainty considerably. The spectra were calculated using values of 150 K and 320 K.

P19.21) Overtone transitions in vibrational absorption spectra for which

$\Delta n = +2, +3, \dots$ are forbidden for the harmonic potential $V = \frac{1}{2}kx^2$ because

$\mu_x^{mn} = 0$ for $|m - n| \neq 1$ as shown in Section 19.4. However, overtone transitions are allowed for the more realistic anharmonic potential. In this problem, you will explore how the selection rule is modified by including anharmonic terms in the potential. We do so in an indirect manner by including additional terms in the expansion of the dipole

moment $\mu_x(x) = \mu_{0x} + x \left(\frac{d\mu_x}{dx} \right)_{r_e} + \dots$, but assuming that the harmonic oscillator total

energy eigenfunctions are still valid. This approximation is valid if the anharmonic correction to the harmonic potential is small. You will show that including the next term in the expansion of the dipole moment, which is proportional to x^2 , makes the transitions $\Delta n = \pm 2$ allowed.

a) Show that Equation (19.8) becomes

$$\begin{aligned} \mu_x^{m0} &= A_m A_0 \mu_{0x} \int_{-\infty}^{\infty} H_m(\alpha^{1/2}x) H_0(\alpha^{1/2}x) e^{-\alpha x^2} dx \\ &\quad + A_m A_0 \left(\frac{d\mu_x}{dx} \right)_{x=0} \int_{-\infty}^{\infty} H_m(\alpha^{1/2}x) x H_0(\alpha^{1/2}x) e^{-\alpha x^2} dx \\ &\quad + \frac{A_m A_0}{2!} \left(\frac{d^2\mu_x}{dx^2} \right)_{x=0} \int_{-\infty}^{\infty} H_m(\alpha^{1/2}x) x^2 H_0(\alpha^{1/2}x) e^{-\alpha x^2} dx \end{aligned}$$

$$\begin{aligned}
 \mu_x^{mn} &= \int \psi_m^*(x) \mu_x(x) \psi_n(x) d\tau = A_m A_n \int H_m(\alpha^{1/2}x) \left(\mu_{0x} + x \left(\frac{d\mu_x}{dx} \right)_{r_e} + \frac{1}{2!} x^2 \left(\frac{d^2\mu_x}{dx^2} \right)_{r_e} \right) H_n(\alpha^{1/2}x) d\tau \\
 &= A_m A_n \mu_{0x} \int_{-\infty}^{\infty} H_m(\alpha^{1/2}x) H_n(\alpha^{1/2}x) e^{-\alpha x^2} dx \\
 &\quad + A_m A_n \left(\frac{d\mu_x}{dx} \right)_{r_e} \int_{-\infty}^{\infty} H_m(\alpha^{1/2}x) x H_n(\alpha^{1/2}x) e^{-\alpha x^2} dx \\
 &\quad + \frac{A_m A_n}{2!} \left(\frac{d^2\mu_x}{dx^2} \right)_{r_e} \int_{-\infty}^{\infty} H_m(\alpha^{1/2}x) x^2 H_n(\alpha^{1/2}x) e^{-\alpha x^2} dx
 \end{aligned}$$

b) Evaluate the effect of adding the additional term to μ_x^{mn} . You will need the recursion

$$\alpha^{1/2}x H_n(\alpha^{1/2}x) = n H_{n-1}(\alpha^{1/2}x) + \frac{1}{2} H_{n+1}(\alpha^{1/2}x).$$

Show that both the transitions $n = 0 \rightarrow n = 1$ and $n = 0 \rightarrow n = 2$ are allowed in this case.

$$\begin{aligned}
 x^2 H_n(\alpha^{1/2}x) &= x(x H_n(\alpha^{1/2}x)) = n \alpha^{-1/2} x H_{n-1}(\alpha^{1/2}x) + \frac{1}{2} \alpha^{-1/2} x H_{n+1}(\alpha^{1/2}x) \\
 &= n \alpha^{-1/2} \left\{ (n-1) \alpha^{-1/2} H_{n-2}(\alpha^{1/2}x) + \frac{1}{2} \alpha^{-1/2} H_n(\alpha^{1/2}x) \right\} \\
 &\quad + \frac{1}{2} \alpha^{-1/2} \left\{ (n+1) \alpha^{-1/2} H_n(\alpha^{1/2}x) + \frac{1}{2} \alpha^{-1/2} H_{n+2}(\alpha^{1/2}x) \right\} \\
 &= \frac{n(n-1)}{\alpha} H_{n-2}(\alpha^{1/2}x) + \frac{2n+1}{2\alpha} H_n(\alpha^{1/2}x) + \frac{1}{4\alpha} H_{n+2}(\alpha^{1/2}x)
 \end{aligned}$$

After substitution of the above result into the integral $\int_{-\infty}^{\infty} H_m(\alpha^{1/2}x) x^2 H_n(\alpha^{1/2}x) e^{-\alpha x^2} dx$,

the integrals $\int_{-\infty}^{\infty} H_m(\alpha^{1/2}x) H_{n-2}(\alpha^{1/2}x) e^{-\alpha x^2} dx$, $\int_{-\infty}^{\infty} H_m(\alpha^{1/2}x) H_n(\alpha^{1/2}x) e^{-\alpha x^2} dx$, and

$\int_{-\infty}^{\infty} H_m(\alpha^{1/2}x) H_{n+2}(\alpha^{1/2}x) e^{-\alpha x^2} dx$ will arise. Because of the orthogonality of the

Hermite polynomials, the second integral is zero for $m \neq n$. The first and third integrals are nonzero only if $m = n + 2$ or $m = n - 2$. This result shows that additional peaks corresponding to $\Delta n = \pm 2$, corresponding to the first overtone, will appear in the vibrational spectrum due to the additional term in μ_x^{mn} .

P19.22) Show that the selection rule for the two-dimensional rotor in the dipole approximation is $\Delta m_l = \pm 1$. Use $A_{+\phi} e^{im_1 \phi}$ and $A_{+\phi} e^{im_2 \phi}$ for the initial and final states of the rotor and $\mu \cos \phi$ as the dipole moment element.

$$\int A_{+\phi} e^{-im_2\phi} \mu \cos \phi A_{+\phi} e^{im_1\phi} d\phi = \frac{\mu(A_{+\phi})^2}{2} \int e^{-im_2\phi} (e^{i\phi} + e^{-i\phi}) e^{im_1\phi} d\phi$$

$$= \frac{\mu(A_{+\phi})^2}{2} \int [e^{-i(m_2-m_1-1)\phi} + e^{-i(m_2-m_1+1)\phi}] d\phi$$

This integral only has a nonzero value if one of the exponents in the integrand is zero. Therefore, $m_2 = m_1 \pm 1$.

P19.23) Fill in the missing step in the derivation that led to the calculation in the spectral line shape in Figure 19.22. Starting from

$$a_2(t) = \mu_x^{21} \frac{E_0}{2} \left(\frac{1 - e^{\frac{i}{\hbar}(E_2 - E_1 + h\nu)t}}{E_2 - E_1 + h\nu} + \frac{1 - e^{-\frac{i}{\hbar}(E_2 - E_1 - h\nu)t}}{E_2 - E_1 - h\nu} \right)$$

and neglecting the first term in the parenthesis, show that

$$a_2^*(t) a_2(t) = \frac{E_0}{4} [\mu_x^{21}]^2 \frac{\sin^2 [(E_2 - E_1 - h\nu)t / 2\hbar]}{(E_2 - E_1 - h\nu)^2}$$

$$a_2^*(t) a_2(t) = [\mu_z^{21}]^2 E_0^2 \left(\frac{1 - e^{\frac{i}{\hbar}(E_2 - E_1 - h\nu)t}}{E_2 - E_1 - h\nu} \right) \left(\frac{1 - e^{-\frac{i}{\hbar}(E_2 - E_1 - h\nu)t}}{E_2 - E_1 - h\nu} \right)$$

$$= [\mu_z^{21}]^2 E_0^2 \frac{\left(2 - 2 \cos \left[(E_2 - E_1 - h\nu) \frac{t}{\hbar} \right] \right)}{(E_2 - E_1 - h\nu)^2}$$

$$\text{Using the identity } 1 - \cos x = 1 - \cos \left(\frac{x}{2} + \frac{x}{2} \right) = \cos^2 \frac{x}{2} + \sin^2 \frac{x}{2} - \left(\cos^2 \frac{x}{2} - \sin^2 \frac{x}{2} \right) = 2 \sin^2 \frac{x}{2}$$

$$a_2^*(t) a_2(t) = [\mu_z^{21}]^2 \frac{E_0^2}{4} \left(\frac{2 - 2 \cos \left[(E_2 - E_1 - h\nu) \frac{t}{\hbar} \right]}{(E_2 - E_1 - h\nu)^2} \right) = [\mu_z^{21}]^2 E_0^2 \frac{\sin^2 \left[(E_2 - E_1 - h\nu) \frac{t}{2\hbar} \right]}{(E_2 - E_1 - h\nu)^2}$$

P19.24) Selection rules in the dipole approximation are determined by the integral

$\mu_x^{mn} = \int \psi_m^*(\tau) \mu_x(\tau) \psi_n(\tau) d\tau$. If this integral is nonzero, the transition will be observed in an absorption spectrum. If the integral is zero, the transition is “forbidden” in the dipole approximation. It actually occurs with low probability because the dipole approximation is not exact. Consider the particle in the one-dimensional box and set $\mu_x = -ex$.

a) Calculate μ_x^{12} and μ_x^{13} in the dipole approximation. Can you see a pattern and discern a selection rule? You may need to evaluate a few more integrals of the type μ_x^{lm} . The standard integral

$$\int x \sin \frac{\pi x}{a} \sin \frac{n\pi x}{a} dx = \frac{1}{2} \left(\frac{a^2 \cos \frac{(n-1)\pi x}{a}}{(n-1)^2 \pi^2} + \frac{(n-1)a x \sin \frac{(n-1)\pi x}{a}}{(n-1)\pi} \right) - \frac{1}{2} \left(\frac{a^2 \cos \frac{(n+1)\pi x}{a}}{(n+1)^2 \pi^2} + \frac{a x \sin \frac{(n+1)\pi x}{a}}{(n+1)\pi} \right)$$

is useful for solving this problem.

b) Determine the ratio μ_x^{12}/μ_x^{14} . On the basis of your result, would you modify the selection rule that you determined in part (a)?

a) We first evaluate μ_x^{12} .

$$\begin{aligned} \mu_x^{12} &= -\frac{2e}{a} \int_0^a x \sin \frac{\pi x}{a} \sin \frac{2\pi x}{a} dx = \left[-\frac{e}{a} \left(\frac{a^2 \cos \frac{\pi x}{a}}{\pi^2} + \frac{a x \sin \frac{\pi x}{a}}{\pi} \right) + \frac{e}{a} \left(\frac{a^2 \cos \frac{3\pi x}{a}}{9\pi^2} + \frac{3a x \sin \frac{3\pi x}{a}}{9\pi} \right) \right]_0^a \\ &= -\frac{e}{a} \left(\frac{a^2 \cos \pi}{\pi^2} + \frac{a \sin \pi}{\pi} \right) + \frac{e}{a} \left(\frac{a^2 \cos 3\pi}{9\pi^2} + \frac{a \sin 3\pi}{3\pi} \right) + \frac{e}{a} \left(\frac{a^2 \cos 0}{\pi^2} + 0 \right) - \frac{e}{a} \left(\frac{a^2 \cos 0}{9\pi^2} - 0 \right) \\ &= -\frac{e}{a} \left(-\frac{a^2}{\pi^2} + 0 \right) - \frac{e}{a} \left(\frac{a^2}{9\pi^2} + 0 \right) + \frac{e}{a} \left(\frac{a^2}{\pi^2} + 0 \right) - \frac{e}{a} \left(\frac{a^2}{9\pi^2} + 0 \right) = 2 \frac{ea}{\pi^2} - \frac{2ea}{9\pi^2} = \frac{16ea}{9\pi^2} \end{aligned}$$

The result is $\mu_x^{12} = \frac{2e}{a} \frac{8a^2}{9\pi^2} = \frac{16ae}{9\pi^2}$

$$\begin{aligned}
 \mu_x^{13} &= -\frac{2e}{a} \int_0^a x \sin \frac{\pi x}{a} \sin \frac{3\pi x}{a} dx \\
 &= \left[-\frac{e}{a} \left(\frac{a^2 \cos \frac{2\pi x}{a}}{4\pi^2} + \frac{2ax \sin \frac{2\pi x}{a}}{4\pi} \right) + \frac{e}{a} \left(\frac{a^2 \cos \frac{4\pi x}{a}}{16\pi^2} + \frac{4ax \sin \frac{4\pi x}{a}}{16\pi} \right) \right]_0^a \\
 &= -\frac{e}{a} \left(\frac{a^2 \cos 2\pi}{4\pi^2} + \frac{2a^2 \sin 2\pi}{4\pi} \right) + \frac{e}{a} \left(\frac{a^2 \cos 4\pi}{16\pi^2} + \frac{4a^2 \sin 4\pi}{16\pi} \right) \\
 &\quad + \frac{e}{a} \left(\frac{a^2 \cos 0}{4\pi^2} + 0 \right) - \frac{e}{a} \left(\frac{a^2 \cos 0}{16\pi^2} + 0 \right) \\
 &= -\frac{e}{a} \left(\frac{a^2}{4\pi^2} + 0 \right) + \frac{e}{a} \left(\frac{a^2}{16\pi^2} + 0 \right) + \frac{e}{a} \left(\frac{a^2}{4\pi^2} + 0 \right) - \frac{e}{a} \left(\frac{a^2}{16\pi^2} + 0 \right) = 0
 \end{aligned}$$

The result is $\mu_x^{13} = 0$.

$$\begin{aligned}
 \mu_x^{14} &= -\frac{2e}{a} \int_0^a x \sin \frac{\pi x}{a} \sin \frac{4\pi x}{a} dx \\
 &= \left[-\frac{e}{a} \left(\frac{a^2 \cos \frac{3\pi x}{a}}{9\pi^2} + \frac{3ax \sin \frac{3\pi x}{a}}{9\pi} \right) + \frac{e}{a} \left(\frac{a^2 \cos \frac{5\pi x}{a}}{25\pi^2} + \frac{5ax \sin \frac{5\pi x}{a}}{25\pi} \right) \right]_0^a \\
 &= -\frac{e}{a} \left(\frac{a^2 \cos 3\pi}{9\pi^2} + \frac{3a^2 \sin 3\pi}{9\pi} \right) + \frac{e}{a} \left(\frac{a^2 \cos 5\pi}{25\pi^2} + \frac{5a^2 \sin 5\pi}{25\pi} \right) + \frac{e}{a} \left(\frac{a^2 \cos 0}{9\pi^2} + 0 \right) - \frac{e}{a} \left(\frac{a^2 \cos 0}{25\pi^2} + 0 \right) \\
 &= -\frac{e}{a} \left(-\frac{a^2}{9\pi^2} + 0 \right) + \frac{e}{a} \left(-\frac{a^2}{25\pi^2} + 0 \right) + \frac{e}{a} \left(\frac{a^2}{9\pi^2} + 0 \right) - \frac{e}{a} \left(\frac{a^2}{25\pi^2} + 0 \right) = \frac{2ea}{9\pi^2} - \frac{2ea}{25\pi^2} = \frac{32ea}{225\pi^2}
 \end{aligned}$$

The result is $\mu_x^{14} = \frac{32ea}{225\pi^2}$.

$$\begin{aligned}
\mu_x^{15} &= -\frac{2e}{a} \int_0^a x \sin \frac{\pi x}{a} \sin \frac{5\pi x}{a} dx \\
&= \left[-\frac{e}{a} \left(\frac{a^2 \cos \frac{4\pi x}{a}}{16\pi^2} + \frac{4ax \sin \frac{4\pi x}{a}}{16\pi} \right) + \frac{e}{a} \left(\frac{a^2 \cos \frac{6\pi x}{a}}{36\pi^2} + \frac{6ax \sin \frac{6\pi x}{a}}{36\pi} \right) \right]_0^a \\
&= -\frac{e}{a} \left(\frac{a^2 \cos 4\pi}{16\pi^2} + \frac{4a^2 \sin 4\pi}{16\pi} \right) + \frac{e}{a} \left(\frac{a^2 \cos 6\pi}{36\pi^2} + \frac{6a^2 \sin 6\pi}{36\pi} \right) \\
&\quad + \frac{e}{a} \left(\frac{a^2 \cos 0}{16\pi^2} + 0 \right) - \frac{e}{a} \left(\frac{a^2 \cos 0}{36\pi^2} + 0 \right) \\
&= -\frac{e}{a} \left(\frac{a^2}{16\pi^2} + 0 \right) + \frac{e}{a} \left(\frac{a^2}{36\pi^2} + 0 \right) + \frac{e}{a} \left(\frac{a^2}{16\pi^2} + 0 \right) - \frac{e}{a} \left(\frac{a^2}{36\pi^2} + 0 \right) = 0
\end{aligned}$$

The result is $\mu_x^{15} = 0$.

These results show that the $1 \rightarrow n$ transition is allowed only if n is even, or that the initial and final states have opposite parity with respect to reflection about the center of the box.

b) $\mu_x^{12}/\mu_x^{14} = \left(\frac{16ae}{9\pi^2} \right) / \left(\frac{32ea}{225\pi^2} \right) = 12.5$. It turns out that $\mu_x^{12}/\mu_x^{16} = 45.4$. This means that the transitions from $n = 1$ to $n = 4$ and 6 are much weaker than the transition from $n = 1$ to 2. Therefore, effectively, the selection rule is $\Delta n = 1$ for absorption.

Chapter 20: The Hydrogen Atom

Problem numbers in italics indicate that the solution is included in the *Student's Solutions Manual*.

Questions on Concepts

Q20.1) What are the units of the H atom total energy eigenfunctions? Why is $a_0^{3/2}R(r)$ graphed in Figure 20.6 rather than $R(r)$?

Because the probability $\int \psi^* \psi d\tau$ has no units, ψ has the units of $\frac{1}{\sqrt{\tau}}$. Therefore, the three dimensional wave functions for the hydrogen atom have the units $(\text{length})^{-\frac{3}{2}}$. We plot $a_0^{3/2}R(r)$ rather than $R(r)$ in Figure 20.6, because this product is unitless.

Q20.2) Use an analogy with the particle in the box to explain why the energy levels for the H atom are not equally spaced.

Given the functional form of the Coulomb potential, one can think of a “box” that is very narrow for low values of energy and very wide near the dissociation limit of zero energy. Therefore, by analogy with the particle in the box, we expect the low lying levels to be widely spaced, and the energy levels near the dissociation limit to be closely spaced.

Q20.3) What transition gives rise to the highest frequency spectral line in the Lyman series?

The transition $n \rightarrow 1$ to $n \rightarrow \infty$, effectively the dissociation limit, will have the highest frequency.

Q20.4) Why are the total energy eigenfunctions for the H atom not eigenfunctions of the kinetic energy?

They are not eigenfunctions of the kinetic energy operator because the total energy and kinetic operators do not commute with one another.

Q20.5) Explain why the radial distribution function rather than the square of the magnitude of the wave function should be used to make a comparison with the shell model of the atom.

The radial distribution function tells us what the probability is of finding the electron at a given radial distance from the nucleus regardless of its angular coordinates. This is what is needed to make a comparison with a shell model.

Q20.6) Is it always true that the probability of finding the electron in the H atom is greater in the interval $r - dr < r < r + dr$ than in the interval $r - dr < r < r + dr \quad \theta - d\theta < \theta < \theta + d\theta \quad \phi - d\phi < \phi < \phi + d\phi$?

The interval $r - dr < r < r + dr$ corresponds to a spherical shell, whereas the interval

$r - dr < r < r + dr \quad \theta - d\theta < \theta < \theta + d\theta \quad \phi - d\phi < \phi < \phi + d\phi$ corresponds to a small portion of the same spherical shell. Because the probability in any interval is a non-negative number, the total probability of finding the electron in the H atom must be bigger in the entire spherical shell than in a small portion of the same spherical shell.

Q20.7) What possible geometrical forms can the nodes in the angular function for p and d orbitals in the H atom have? What possible geometrical forms can the nodes in the radial function for s , p , and d orbitals in the H atom have?

The angular nodes for the p orbitals are planes, and the angular nodes for the d orbitals can be planes or cones. All spatial nodes for the H atom orbitals are spherical surfaces, corresponding to radial nodes.

Q20.8) If the probability density of finding the electron in the $1s$ orbital in the H atom has its maximum value for $r = 0$, does this mean that the proton and electron are located at the same point in space?

No, the probability is the product of the probability density and the volume over which the probability is being determined. Because the volume of the nucleus is very small, the probability of finding the electron in the volume corresponding to the nucleus is very small as shown in Example Problem 20.4.

Q20.9) Is the total energy wave function

$$\psi_{310}(r, \theta, \phi) = \frac{1}{81} \left(\frac{2}{\pi} \right)^{1/2} \left(\frac{1}{a_0} \right)^{3/2} \left(6 \frac{r}{a_0} - \frac{r^2}{a_0^2} \right) e^{-r/3a_0} \cos \theta \text{ an eigenfunction of any other operators? If so, which ones? What are the eigenvalues?}$$

Yes, it is an eigenfunction of the operator \hat{l}^2 with the eigenvalue $2\hbar^2$, and an eigenfunction of the operator \hat{l}_z with the eigenvalue zero.

Q20.10) What makes the z direction special so that we say that \hat{l}^2 , \hat{H} , and \hat{l}_z commute, whereas the individual angular momentum operators \hat{l}_z , \hat{l}_y and \hat{l}_x don't commute?

There is nothing special about the z direction. We choose the z direction because the angular momentum operator for this component has a simple form. We can rotate our coordinate system to make any direction that we choose to lie along the z axis. The important point is that we can know the magnitude of the angular momentum and only one of its components.

Problems

P20.1) Show by substitution that $\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$ is a solution of

$$\begin{aligned} & -\frac{\hbar^2}{2m_e} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi(r, \theta, \phi)}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi(r, \theta, \phi)}{\partial \theta} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial^2 \psi(r, \theta, \phi)}{\partial \phi^2} \right] \\ & -\frac{e^2}{4\pi\epsilon_0 r} \psi(r, \theta, \phi) = E\psi(r, \theta, \phi) \end{aligned}$$

What is the eigenvalue for total energy? Use the relation $a_0 = \epsilon_0 h^2 / (\pi m_e e^2)$.

Because the wavefunction does not depend on the angles, we need not consider the portion of the Schrödinger equation that involves partial derivatives with respect to θ and ϕ .

$$\begin{aligned} & -\frac{\hbar^2}{2m_e} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi(r, \theta, \phi)}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi(r, \theta, \phi)}{\partial \theta} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial^2 \psi(r, \theta, \phi)}{\partial \phi^2} \right] \\ & -\frac{e^2}{4\pi\epsilon_0 |\vec{r}|} \psi(r, \theta, \phi) \\ & = -\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial e^{-r/a_0}}{\partial r} \right) \right] - \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{e^2}{4\pi\epsilon_0 |\vec{r}|} e^{-r/a_0} \\ & -\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} e^{-r/a_0} \left(\frac{r^2}{a_0^2} - \frac{2r}{a_0} \right) \right] - \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{e^2}{4\pi\epsilon_0 |\vec{r}|} e^{-r/a_0} \\ & = -\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{\hbar^2}{2\mu a_0^2} \right) e^{-r/a_0} - \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left[-\frac{\hbar^2}{\mu a_0} + \frac{e^2}{4\pi\epsilon_0 r} \right] \frac{1}{r} e^{-r/a_0} \\ & = -\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{\hbar^2}{2\mu a_0^2} \right) e^{-r/a_0} - \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left[-\frac{\hbar^2 \pi \mu e^2}{\mu \epsilon_0 h^2} + \frac{e^2}{4\pi\epsilon_0 r} \right] \frac{1}{r} e^{-r/a_0} \\ & = -\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{\hbar^2}{2\mu a_0^2} \right) e^{-r/a_0} - \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left[-\frac{e^2}{4\pi\epsilon_0} + \frac{e^2}{4\pi\epsilon_0} \right] \frac{1}{r} e^{-r/a_0} \\ & = -\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{\hbar^2}{2\mu a_0} \frac{\pi \mu e^2}{4\pi^2 \hbar^2 \epsilon_0} \right) e^{-r/a_0} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{-e^2}{8\pi\epsilon_0 a_0} \right) e^{-r/a_0} \end{aligned}$$

The function is an eigenfunction of the Schrödinger equation with the eigenvalue

$$E = \frac{-e^2}{8\pi\epsilon_0 a_0}$$

P20.2) The total energy eigenvalues for the hydrogen atom are given by

$$E_n = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2}, \quad n = 1, 2, 3, 4, \dots, \text{ and the three quantum numbers associated with}$$

the total energy eigenfunctions are related by

$n = 1, 2, 3, 4, \dots; l = 0, 1, 2, 3, \dots, n-1$; and $m_l = 0, \pm 1, \pm 2, \pm 3, \dots \pm l$. Using the

nomenclature, list all eigenfunctions that have the following total energy eigenvalues

a) $E = -\frac{e^2}{32\pi\epsilon_0 a_0}$

b) $E = -\frac{e^2}{72\pi\epsilon_0 a_0}$

c) $E = -\frac{e^2}{128\pi\epsilon_0 a_0}$

d) What is the degeneracy of each of these energy levels?

a) $E = -\frac{e^2}{32\pi\epsilon_0 a_0}$ corresponds to $n = 2$. The total energy eigenfunctions are

$\psi_{200}, \psi_{210}, \psi_{211}, \psi_{21-1}$. The level has a degeneracy of 4.

b) $E = -\frac{e^2}{72\pi\epsilon_0 a_0}$ corresponds to $n = 3$. The total energy eigenfunctions are

$\psi_{300}, \psi_{310}, \psi_{311}, \psi_{31-1}, \psi_{320}, \psi_{321}, \psi_{32-1}, \psi_{322}, \psi_{32-2}$. The level has a degeneracy of 9.

c) $E = -\frac{e^2}{128\pi\epsilon_0 a_0}$ corresponds to $n = 4$. The total energy eigenfunctions are

$\psi_{400}, \psi_{410}, \psi_{411}, \psi_{41-1}, \psi_{420}, \psi_{421}, \psi_{42-1}, \psi_{422}, \psi_{42-2}, \psi_{43-2}, \psi_{43-1}, \psi_{430}, \psi_{431}, \psi_{432}, \psi_{433}, \psi_{43-3}$. The level has a degeneracy of 16.

P20.3) Show that the total energy eigenfunctions $\psi_{100}(r)$ and $\psi_{200}(r)$ are orthogonal.

$$\begin{aligned} \iiint \psi_{100}^*(\tau) \psi_{200}(\tau) d\tau &= \frac{1}{\sqrt{32}\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty r^2 e^{-r/a_0} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0} \\ &= \frac{1}{\sqrt{2}a_0^3} \times \left(\int_0^\infty 2r^2 e^{-3r/2a_0} dr - \int_0^\infty \frac{r^3}{a_0} e^{-3r/2a_0} dr \right) \end{aligned}$$

$$= \frac{1}{\sqrt{2} a_0^3} \times \left(\frac{4}{[3/2a_0]^3} - \frac{6}{a_0 [3/2a_0]^4} \right) = \frac{1}{\sqrt{2} a_0^3} \times \left(\frac{32a_0^3}{27} - \frac{96a_0^3}{81} \right) = 0$$

P20.4) Show that the total energy eigenfunctions $\psi_{210}(r, \theta, \phi)$ and $\psi_{211}(r, \theta, \phi)$ are orthogonal. Do you have to integrate over all three variables to show that the functions are orthogonal?

$$\iiint \psi_{210}^*(\tau) \psi_{211}(\tau) d\tau = \frac{1}{\sqrt{32} \sqrt{64} \pi a_0^3} \int_0^{2\pi} e^{+i\phi} d\phi \int_0^\pi \cos \theta \sin^2 \theta d\theta \int_0^\infty \left(\frac{r}{a_0} \right)^2 e^{-r/a_0} dr$$

This integral is zero because $\int_0^\pi \cos \theta \sin^2 \theta d\theta = \left[\frac{\sin^3 \theta}{3} \right]_0^\pi = 0 - 0 = 0$.

It is sufficient to evaluate the integral over θ .

P20.5) Locate the radial and angular nodes in the H orbitals $\psi_{3p_x}(r, \theta, \phi)$ and $\psi_{3p_z}(r, \theta, \phi)$.

$$\psi_{3p_x}(r, \theta, \phi) = \frac{1}{81\sqrt{2}\pi} \left(\frac{1}{a_0} \right)^{3/2} \left(6 \frac{r}{a_0} - \frac{r^2}{a_0^2} \right) e^{-r/3a_0} \sin \theta \cos \phi \text{ has radial nodes where}$$

$6 \frac{r}{a_0} - \frac{r^2}{a_0^2}$ has zeros. This is at $r = 0$, which does not count as a node, and $r = 6a_0$. The angular nodes correspond to the angles at which the function is zero, or $\theta = 0^\circ$ and $\phi = 90^\circ$, corresponding to the y-z plane.

$$\psi_{3p_z}(r, \theta, \phi) = \frac{1}{81} \left(\frac{2}{\pi} \right)^{1/2} \left(\frac{1}{a_0} \right)^{3/2} \left(6 \frac{r}{a_0} - \frac{r^2}{a_0^2} \right) e^{-r/3a_0} \cos \theta \text{ also has a radial node at } r = 6a_0. \text{ The angular node is for } \theta = 90^\circ, \text{ corresponding to the x-y plane.}$$

P20.6) How many radial and angular nodes are there in the following H orbitals set?

- a) $\psi_{2p_x}(r, \theta, \phi)$
- b) $\psi_{2s}(r)$
- c) $\psi_{3d_{xz}}(r, \theta, \phi)$
- d) $\psi_{3d_{x^2-y^2}}(r, \theta, \phi)$

The functions have $n-l-1$ radial nodes and l angular nodes. Therefore

a) $\psi_{2p_x}(r, \theta, \phi)$ has no radial nodes and one angular node.

b) $\psi_{2s}(r)$ has one radial node and no angular nodes.

c) $\psi_{3d_{xz}}(r, \theta, \phi)$ has no radial nodes and 2 angular nodes.

d) $\psi_{3d_{x^2-y^2}}(r, \theta, \phi)$ has no radial nodes and 2 angular nodes.

P20.7) In this problem, you will calculate the probability density of finding the electron within a sphere of radius r for the H atom in its ground state.

a) Show using integration by parts, $\int u dv = uv - \int v du$, that

$$\int r^2 e^{-\frac{r}{\alpha}} dr = e^{-\frac{r}{\alpha}} (-2\alpha^3 - 2\alpha^2 r - \alpha r^2)$$

Let $u = r^2$ and $dv = e^{-\frac{r}{\alpha}} dr$

$$\int r^2 e^{-\frac{r}{\alpha}} dr = -\alpha r^2 e^{-\frac{r}{\alpha}} + 2\alpha \int r e^{-\frac{r}{\alpha}} dr$$

Integrating by parts again,

$$\int r^2 e^{-\frac{r}{\alpha}} dr = -\alpha r^2 e^{-\frac{r}{\alpha}} + 2\alpha \left(-\alpha r e^{-\frac{r}{\alpha}} + \alpha \int e^{-\frac{r}{\alpha}} dr \right) = -\alpha r^2 e^{-\frac{r}{\alpha}} - 2\alpha \left(\alpha r e^{-\frac{r}{\alpha}} - \alpha^2 e^{-\frac{r}{\alpha}} \right)$$

$$\int r^2 e^{-\frac{r}{\alpha}} dr = e^{-\frac{r}{\alpha}} (-\alpha r^2 - 2\alpha^2 r - 2\alpha^3)$$

b) Using this result, show that the probability density of finding the electron within a sphere of radius r for the hydrogen atom in its ground state is $1 - e^{-\frac{2r}{a_0}} - \frac{2r}{a_0} \left(1 + \frac{r}{a_0} \right) e^{-\frac{2r}{a_0}}$.

Setting $\alpha = \frac{a_0}{2}$,

$$\begin{aligned} \frac{1}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^2 e^{-\frac{2r}{a_0}} dr &= \frac{4}{a_0^3} \left[e^{-\frac{2r}{a_0}} \left(-\frac{a_0}{2} r^2 - \frac{a_0^2}{2} r - \frac{a_0^3}{4} \right) \right]_0^r \\ &= \frac{4}{a_0^3} \left[e^{-\frac{2r}{a_0}} \left(-\frac{a_0}{2} r^2 - \frac{a_0^2}{2} r - \frac{a_0^3}{4} \right) + \frac{a_0^3}{4} \right] = -2 \frac{r^2}{a_0^2} e^{-\frac{2r}{a_0}} - 2 \frac{r}{a_0} e^{-\frac{2r}{a_0}} - e^{-\frac{2r}{a_0}} + 1 \\ &= 1 - e^{-\frac{2r}{a_0}} - 2 \frac{r}{a_0} \left(1 + \frac{r}{a_0} \right) e^{-\frac{2r}{a_0}} \end{aligned}$$

c) Evaluate this probability density for $r = 0.10 a_0$, $r = 1.0 a_0$, and $r = 4.0 a_0$.

The probability evaluated at $r = 0.10 a_0 = 1.1 \times 10^{-3}$. The probability evaluated at $r = 1.0 a_0 = 0.32$. The probability evaluated at $r = 4.0 a_0 = 0.99$.

P20.8) Using the result of Problem P20.7, calculate the probability of finding the electron in the 1s state outside a sphere of radius $0.5a_0$, $3a_0$, and $5a_0$.

The probability of finding the electron inside the sphere is $1 - e^{-\frac{2r}{a_0}} - \frac{2r}{a_0} \left(1 + \frac{r}{a_0}\right) e^{-\frac{2r}{a_0}}$. The

probability of finding it outside the sphere is

$1 - \left[1 - e^{-\frac{2r}{a_0}} - \frac{2r}{a_0} \left(1 + \frac{r}{a_0}\right) e^{-\frac{2r}{a_0}}\right] = e^{-\frac{2r}{a_0}} + \frac{2r}{a_0} \left(1 + \frac{r}{a_0}\right) e^{-\frac{2r}{a_0}}$. Evaluating this function at $0.5a_0$, $3a_0$, and $5a_0$ gives 0.920, 0.0620, and 2.77×10^{-3} , respectively.

P20.9) The d orbitals have the nomenclature d_{z^2} , d_{xy} , d_{xz} , d_{yz} , and $d_{x^2-y^2}$. Show how the d orbital $\psi_{3d_{yz}}(r, \theta, \phi) = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta \sin \phi$ can be written in the form $yzF(r)$.

In spherical coordinates, $x = r \sin \theta \cos \phi$, $y = r \sin \theta \sin \phi$, and $z = r \cos \theta$. Therefore,

$$\begin{aligned} \psi_{3d_{yz}}(r, \theta, \phi) &= \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta \sin \phi \\ &= \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{1}{a_0^2} e^{-r/3a_0} (r \cos \theta)(r \sin \theta \sin \phi) = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{1}{a_0^2} e^{-r/3a_0} (yz) \end{aligned}$$

P20.10) Show that the function $\frac{r}{a_0} e^{-r/2a_0}$ is a solution of the differential equation for

$R(r)$

$$-\frac{\hbar^2}{2m_e r^2} \frac{d}{dr} \left[r^2 \frac{dR(r)}{dr} \right] + \left[\frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right] R(r) = E R(r) \text{ for } l=1$$

What is the eigenvalue? Using this result, what is the value for the principal quantum number n for this function?

$$\begin{aligned} &-\frac{\hbar^2}{2m_e r^2} \frac{d}{dr} \left[r^2 \frac{d}{dr} \left[\frac{r}{a_0} e^{-r/2a_0} \right] \right] + \left[\frac{\hbar^2}{m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right] \frac{r}{a_0} e^{-r/2a_0} \\ &= -\frac{\hbar^2}{2m_e r^2} \frac{d}{dr} \left[\frac{r^2}{a_0} e^{-r/2a_0} - \frac{r^3}{2a_0^2} e^{-r/2a_0} \right] + \left[\frac{\hbar^2}{m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right] \frac{r}{a_0} e^{-r/2a_0} \\ &= -\frac{\hbar^2}{2m_e r^2} \left[-2 \frac{r^2}{a_0^2} e^{-r/2a_0} + \frac{r^3}{4a_0^3} e^{-r/2a_0} + 2 \frac{r}{a_0} e^{-r/2a_0} \right] + \left[\frac{\hbar^2}{m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right] \frac{r}{a_0} e^{-r/2a_0} \\ &= -\frac{\hbar^2}{2m_e r^2} \left[-2 \frac{r^2}{a_0^2} e^{-r/2a_0} + \frac{r^3}{4a_0^3} e^{-r/2a_0} \right] - \frac{e^2}{4\pi\epsilon_0 a_0} e^{-r/2a_0} \end{aligned}$$

$$\begin{aligned}
 &= -\frac{\hbar^2}{2m_e r^2} \left[-2 \frac{r^2 \pi m_e e^2}{a_0 \epsilon_0 \hbar^2} e^{-r/2a_0} + \frac{r^3}{4a_0^3} e^{-r/2a_0} \right] - \frac{e^2}{4\pi \epsilon_0 a_0} e^{-r/2a_0} \\
 &\text{where we have used the definition } a_0 = \frac{\epsilon_0 \hbar^2}{\pi m_e e^2} \\
 &= -\frac{\hbar^2}{2m_e r^2} \frac{r^3}{4a_0^3} e^{-r/2a_0} + \frac{e^2}{4\pi a_0 \epsilon_0} e^{-r/2a_0} - \frac{e^2}{4\pi \epsilon_0 a_0} e^{-r/2a_0} = -\frac{\hbar^2}{2m_e r^2} \frac{r^3}{4a_0^3} e^{-r/2a_0} \\
 &= -\frac{e^2}{32\pi a_0 \epsilon_0 a_0} \frac{r}{e^{-r/2a_0}}
 \end{aligned}$$

By comparison with $E_n = -\frac{e^2}{8\pi \epsilon_0 a_0 n^2}$, $n = 2$.

P20.11) Calculate the mean value of the radius $\langle r \rangle$ at which you would find the electron if the H atom wave function is $\psi_{100}(r)$.

$$\langle r \rangle = \frac{1}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^3 e^{-\frac{2r}{a_0}} dr$$

$$\langle r \rangle = \frac{4}{a_0^3} \int_0^\infty r^3 e^{-\frac{2r}{a_0}} dr$$

Using the standard integral $\int_0^\infty r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$

$$\langle r \rangle = \frac{4}{a_0^3} \frac{6a_0^4}{16} = \frac{3}{2} a_0$$

P20.12) Calculate the expectation value $(r - \langle r \rangle)^2$ if the H atom wave function is $\psi_{100}(r)$.

$$\langle (r - \langle r \rangle)^2 \rangle = \langle r^2 - 2r\langle r \rangle + \langle r \rangle^2 \rangle = \langle r^2 \rangle - 2\langle r \rangle^2 + \langle r \rangle^2 = \langle r^2 \rangle - \langle r \rangle^2$$

$$\langle r \rangle = \frac{1}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^3 e^{-\frac{2r}{a_0}} dr$$

$$\langle r \rangle = \frac{4}{a_0^3} \int_0^\infty r^3 e^{-\frac{2r}{a_0}} dr$$

Using the standard integral $\int_0^\infty r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$

$$\langle r \rangle = \frac{4}{a_0^3} \frac{6a_0^4}{16} = \frac{3}{2} a_0$$

$$\langle r^2 \rangle = \frac{1}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^4 e^{-\frac{2r}{a_0}} dr$$

$$\langle r^2 \rangle = \frac{4}{a_0^3} \int_0^\infty r^4 e^{-\frac{2r}{a_0}} dr$$

Using the standard integral $\int_0^\infty r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$

$$\langle r^2 \rangle = \frac{4}{a_0^3} \frac{4!}{(2/a_0)^5} = 3(a_0)^2$$

$$\text{Therefore, } (r - \langle r \rangle)^2 = \langle r^2 \rangle - \langle r \rangle^2 = 3(a_0)^2 - \left(\frac{3}{2}a_0\right)^2 = \frac{3}{4}(a_0)^2.$$

P20.13) Calculate the mean value of the radius $\langle r \rangle$ at which you would find the electron if the H atom wave function is $\psi_{210}(r, \theta, \phi)$.

$$\langle r \rangle = \frac{1}{32\pi a_0^5} \int_0^{2\pi} d\phi \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^\infty r^5 e^{-\frac{r}{a_0}} dr$$

$$\langle r \rangle = \frac{2\pi}{32\pi a_0^5} \left[-\frac{\cos^3 \theta}{3} \right]_0^\infty \int_0^\infty r^5 e^{-\frac{r}{a_0}} dr = \frac{2\pi}{32\pi a_0^5} \frac{2}{3} \int_0^\infty r^5 e^{-\frac{r}{a_0}} dr = \frac{1}{24 a_0^5} \int_0^\infty r^5 e^{-\frac{r}{a_0}} dr$$

Using the standard integral $\int_0^\infty r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$

$$\langle r \rangle = \frac{1}{24 a_0^5} 5! a_0^6 = 5a_0$$

P20.14) Ions with a single electron such as He^+ , Li^{2+} , and Be^{3+} are described by the H atom wave functions with $\frac{Z}{a_0}$ substituted for $\frac{1}{a_0}$. Z is the nuclear charge. The $1s$ wave

function becomes $\psi(r) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$. Using this result, compare the mean value of the radius $\langle r \rangle$ at which you would find the $1s$ electron in H, He^+ , Li^{2+} , and Be^{3+} .

$$\langle r \rangle = \frac{Z^3}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^3 e^{-\frac{2Zr}{a_0}} dr$$

$$\langle r \rangle = \frac{4Z^3}{a_0^3} \int_0^\infty r^3 e^{-\frac{2Zr}{a_0}} dr$$

Using the standard integral $\int_0^\infty r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$

$$\langle r \rangle = \frac{4Z^3}{a_0^3} \frac{6a_0^4}{16Z^4} = \frac{3}{2Z} a_0$$

$$\langle r \rangle_H = \frac{3}{2} a_0; \quad \langle r \rangle_{He^+} = \frac{3}{4} a_0; \quad \langle r \rangle_{Li^{2+}} = \frac{1}{2} a_0; \quad \langle r \rangle_{Be^{3+}} = \frac{3}{8} a_0$$

P20.15) The energy levels for ions with a single electron such as He^+ , Li^{2+} , and Be^{3+} are given by $E_n = -\frac{Z^2 e^2}{8\pi \epsilon_0 a_0 n^2}$, $n = 1, 2, 3, 4, \dots$. Calculate the ionization energies of H, He^+ , Li^{2+} , and Be^{3+} in their ground states in units of electron-volts (eV).

The ionization potential is the negative of the orbital energy.

$$I = \frac{Z^2 e^2}{8\pi \epsilon_0 a_0 n^2} = \frac{\frac{Z^2}{n^2} \times (1.602 \times 10^{-19} C)^2}{8\pi \times 8.854 \times 10^{-12} J^{-1} C^2 m^{-1} \times 5.292 \times 10^{-11} m} \times \frac{1 \text{ eV}}{1.602 \times 10^{-19} J}$$

$$I = 13.60 \frac{Z^2}{n^2} \text{ eV}$$

$$I_H = 13.60 \text{ eV}; \quad I_{He^+} = 54.42 \text{ eV}; \quad I_{Li^{2+}} = 122.4 \text{ eV}; \quad I_{Be^{3+}} = 217.7 \text{ eV}$$

P20.16) As we will be discussed in Chapter 10, core electrons shield valence electrons so that they experience an effective nuclear charge Z_{eff} rather than the full nuclear charge. Given that the first ionization energy of Li is 5.39 eV, use the formula in Problem P20.15 to estimate the effective nuclear charge experienced by the $2s$ electron in Li.

From the previous problem,

$$I = 13.60 \frac{Z^2}{n^2} \text{ eV}; \quad Z_{eff} = \sqrt{\frac{n^2 I}{13.60 \text{ eV}}} = \sqrt{\frac{4 \times 5.39 \text{ eV}}{13.60 \text{ eV}}} = 1.26$$

P20.17) In spherical coordinates, $z = r \cos \theta$. Calculate $\langle z \rangle$ and $\langle z^2 \rangle$ for the H atom in its ground state. Without doing the calculation, what would you expect for $\langle x \rangle$ and $\langle y \rangle$, $\langle x^2 \rangle$ and $\langle y^2 \rangle$? Why?

$$\langle z \rangle = \frac{1}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \cos \theta \sin \theta d\theta \int_0^\infty r^3 e^{-\frac{2r}{a_0}} dr$$

$$\langle z \rangle = \frac{2\pi}{\pi a_0^3} \left[-\frac{\cos^2 \theta}{2} \right]_0^\pi \int_0^\infty r^5 e^{-\frac{r}{a_0}} dr = 0 \text{ because the integral over } \theta \text{ is zero.}$$

$$\langle z^2 \rangle = \frac{1}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^\infty r^4 e^{-\frac{2r}{a_0}} dr$$

$$\langle z^2 \rangle = \frac{2\pi}{\pi a_0^3} \left[-\frac{\cos^3 \theta}{3} \right]_0^\pi \int_0^\infty r^4 e^{-\frac{2r}{a_0}} dr = \frac{4}{3a_0^3} \int_0^\infty r^4 e^{-\frac{2r}{a_0}} dr$$

Using the standard integral $\int_0^\infty r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$

$$\langle z^2 \rangle = \frac{4}{3a_0^3} \frac{24a_0^5}{32} = a_0^2$$

Because the H atom is spherically symmetrical, $\langle x \rangle$ and $\langle y \rangle$, $\langle x^2 \rangle$ and $\langle y^2 \rangle$ will have the same values as $\langle z \rangle$ and $\langle z^2 \rangle$.

P20.18) Calculate the average value of the kinetic and potential energies for the H atom in its ground state.

$$\langle E_{kinetic} \rangle = \int \psi^*(\tau) \hat{E}_{kinetic} \psi(\tau) d\tau$$

$$\langle E_{kinetic} \rangle = -\frac{\hbar^2}{2m_e} \frac{1}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty e^{-r/a_0} \left(\frac{1}{r^2} \frac{d}{dr} \left[r^2 \frac{d}{dr} e^{-r/a_0} \right] \right) r^2 dr$$

$$\langle E_{kinetic} \rangle = -\frac{\hbar^2}{2m_e} \frac{4}{a_0^3} \int_0^\infty \left[-\frac{2r}{a_0} e^{-2r/a_0} + \frac{r^2}{a_0^2} e^{-2r/a_0} \right] dr = \frac{\hbar^2}{m_e} \frac{4}{a_0^4} \int_0^\infty r e^{-2r/a_0} dr - \frac{\hbar^2}{m_e} \frac{2}{a_0^5} \int_0^\infty r^2 e^{-2r/a_0} dr$$

Using the standard integral $\int_0^\infty r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$

$$\langle E_{kinetic} \rangle = \frac{\hbar^2}{m_e} \frac{4}{a_0^4} \frac{a_0^2}{4} - \frac{\hbar^2}{m_e} \frac{2}{a_0^5} \frac{2a_0^3}{8} = \frac{\hbar^2}{2m_e a_0^2} = \frac{\hbar^2 \pi m_e e^2}{2m_e a_0 \epsilon_0 h^2} = \frac{e^2}{8\pi a_0 \epsilon_0}$$

$$\langle E_{potential} \rangle = \int \psi^*(\tau) \hat{E}_{potential} \psi(\tau) d\tau$$

$$\langle E_{potential} \rangle = -\frac{e^2}{4\pi \epsilon_0} \frac{1}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty \left[e^{-r/a_0} \right] \left(\frac{1}{r} \right) \left[e^{-r/a_0} \right] r^2 dr$$

$$\langle E_{potential} \rangle = -\frac{e^2}{4\pi \epsilon_0} \frac{4}{a_0^3} \int_0^\infty r e^{-2r/a_0} dr = -\frac{e^2}{4\pi \epsilon_0} \frac{4}{a_0^3} \frac{a_0^2}{4} = -\frac{e^2}{4\pi \epsilon_0 a_0}$$

P20.19) The force acting between the electron and the proton in the H atom is given by

$F = -\frac{e^2}{4\pi \epsilon_0 r^2}$. Calculate the expectation value $\langle F \rangle$ for the $1s$ and $2p_z$ states of the H

atom in terms of e , ϵ_0 , and a_0 .

$$\langle F \rangle_{1s} = -\frac{e^2}{4\pi \epsilon_0} \int \psi^*(\tau) \frac{1}{r^2} \psi(\tau) d\tau$$

$$\langle F \rangle_{1s} = -\frac{e^2}{4\pi \epsilon_0} \frac{1}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty \left[e^{-r/a_0} \right] \left(\frac{1}{r^2} \right) \left[e^{-r/a_0} \right] r^2 dr$$

$$\langle F \rangle_{1s} = -\frac{e^2}{4\pi \epsilon_0} \frac{4}{a_0^3} \int_0^\infty r e^{-2r/a_0} dr = -\frac{e^2}{4\pi \epsilon_0} \frac{4}{a_0^3} \left[-\frac{a_0}{2} e^{-2r/a_0} \right]_0^\infty = -\frac{e^2}{2\pi \epsilon_0 a_0^2}$$

$$\begin{aligned}\langle F \rangle_{2p_z} &= -\frac{e^2}{4\pi\epsilon_0} \int \psi^*(\tau) \frac{1}{r^2} \psi(\tau) d\tau \\ \langle F \rangle_{2p_z} &= -\frac{e^2}{4\pi\epsilon_0} \frac{1}{32\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^\infty \left(\frac{r}{a_0} \right)^2 \left[e^{-r/a_0} \right] \left(\frac{1}{r^2} \right) r^2 dr \\ \langle F \rangle_{2p_z} &= -\frac{e^2}{4\pi\epsilon_0} \frac{1}{16a_0^5} \left[\frac{\cos^3 \theta}{3} \right]_0^\pi \times \int_0^\infty r^2 e^{-r/a_0} dr \\ \langle F \rangle_{2p_z} &= -\frac{e^2}{4\pi\epsilon_0} \frac{1}{24a_0^3} \int_0^\infty r^2 e^{-r/a_0} dr\end{aligned}$$

Using the standard integral $\int_0^\infty r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$

$$\langle F \rangle_{2p_z} = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{24a_0^5} \times 2a_0^3 = -\frac{e^2}{48\pi\epsilon_0 a_0^2}$$

P20.20) Calculate the distance from the nucleus for which the radial distribution function for the $2p$ orbital has its main and subsidiary maxima.

$$r^2 R_{21}^2(r) = \frac{1}{\sqrt{24}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r^4}{a_0} e^{-r/a_0}$$

The maxima and minima are found by setting the derivative of this function equal to zero.

$$\frac{d}{dr} \left(\frac{r^4}{a_0} e^{-r/a_0} \right) = \frac{4r^3}{a_0} e^{-r/a_0} - \frac{r^4}{a_0^2} e^{-r/a_0} = \frac{r^3 e^{-r/a_0}}{a_0} \left(4 - \frac{r}{a_0} \right) = 0$$

The solutions are $r = 0$, $r = 0$, $r = 4a_0$.

There are no subsidiary maxima.

P20.21) Calculate $\langle r \rangle$ and the most probable value of r for the H atom in its ground state. Explain why they differ with a drawing.

$$\begin{aligned}\langle r \rangle &= \frac{1}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^3 e^{-\frac{2r}{a_0}} dr \\ \langle r \rangle &= \frac{4}{a_0^3} \int_0^\infty r^3 e^{-\frac{2r}{a_0}} dr\end{aligned}$$

Using the standard integral $\int_0^\infty r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$

$$\langle r \rangle = \frac{4}{a_0^3} \frac{6a_0^4}{16} = \frac{3}{2} a_0$$

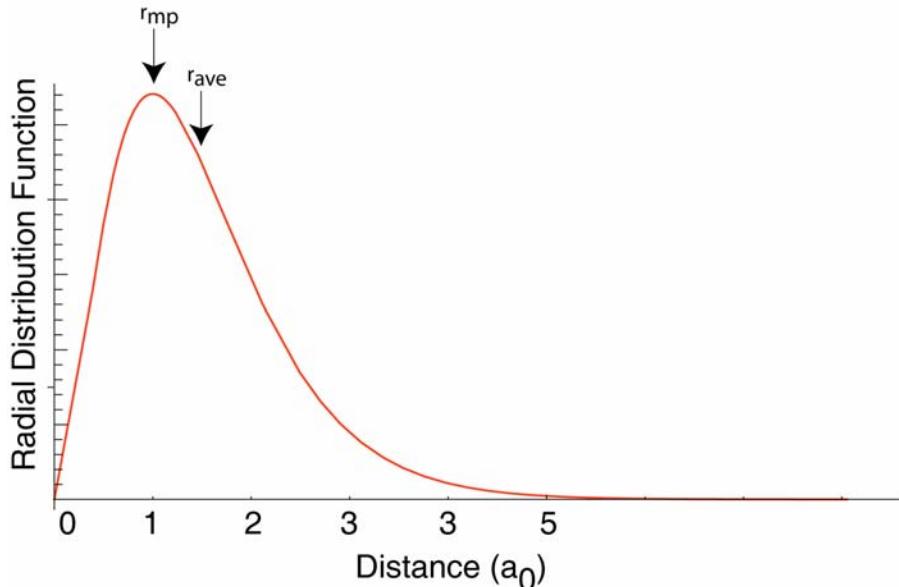
The most probable value of r is found by setting the derivative of the radial probability distribution equal to zero.

$$r^2 R_{10}^2(r) = 4 \left(\frac{1}{a_0} \right)^3 r^2 e^{-2r/a_0}$$

$$\frac{d}{dr} \left(r^2 e^{-2r/a_0} \right) = 2r e^{-2r/a_0} - \frac{2r^2}{a_0} e^{-2r/a_0} = 2e^{-2r/a_0} r \left(1 - \frac{r}{a_0} \right) = 0$$

The solutions are $r = 0$, $r = a_0$.

The mean and most probable values are not equal because $r^2 R_{10}^2(r)$ is not symmetric with respect to r about its maximum value as shown in the following figure.



P20.22) Calculate the expectation value of the moment of inertia of the H atom in the $2s$ and $2p_z$ states in terms of μ and a_0 .

For the $2s$ state,

$$\langle I \rangle = \langle \mu r^2 \rangle = \mu \frac{1}{32\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^4 \left(2 - \frac{r}{a_0} \right)^2 e^{-r/a_0} dr$$

$$= \mu \frac{1}{8a_0^3} \int_0^\infty \left(4r^4 - \frac{4r^5}{a_0} + \frac{r^6}{a_0^2} \right) e^{-r/a_0} dr = \mu \frac{1}{8a_0^3} \left(4 \int_0^\infty r^4 e^{-r/a_0} dr - \frac{4}{a_0} \int_0^\infty r^5 e^{-r/a_0} dr + \frac{1}{a_0^2} \int_0^\infty r^6 e^{-r/a_0} dr \right)$$

Using the standard integral $\int_0^\infty r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$

$$\langle I \rangle = \mu \frac{1}{8a_0^3} \left(4 \times 4! a_0^5 - \frac{4}{a_0} \times 5! \times a_0^6 + \frac{1}{a_0^2} \times 6! \times a_0^7 \right) = 42\mu a_0^2$$

For the $2p_z$ state,

$$\langle I \rangle = \langle \mu r^2 \rangle = \mu \frac{1}{32\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^\infty r^4 \left(\frac{r}{a_0} \right)^2 e^{-r/a_0} dr$$

$$= \mu \frac{1}{16a_0^5} \left[\frac{\cos^3 \theta}{3} \right]_0^\pi \times \int_0^\infty r^6 e^{-r/a_0} dr = \mu \frac{1}{24a_0^5} 6! a_0^7 = 30\mu a_0^2$$

P20.23) Calculate the wave number corresponding to the most and least energetic spectral lines in the Lyman, Balmer and Paschen series for the hydrogen atom.

$$\tilde{\nu} = 109,678 \left(\frac{1}{n_{initial}^2} - \frac{1}{n_{final}^2} \right) \text{cm}^{-1} \text{ and the most energetic line corresponds to } n \rightarrow \infty.$$

$n_{initial}$ is 1, 2, and 3 for the Lyman, Balmer and Paschen series, respectively.

$$\tilde{\nu} = 109,678 \text{ cm}^{-1} \text{ for the Lyman series,}$$

$$\tilde{\nu} = 109,678 \left(\frac{1}{4} \right) \text{cm}^{-1} = 27419 \text{ cm}^{-1} \text{ for the Balmer series, and}$$

$$\tilde{\nu} = 109,678 \left(\frac{1}{9} \right) \text{cm}^{-1} = 12186 \text{ cm}^{-1} \text{ for the Paschen series.}$$

The least energetic transition corresponds to $n_{initial} \rightarrow n_{initial} + 1$.

$$\tilde{\nu} = 109,678 \left(1 - \frac{1}{4} \right) \text{cm}^{-1} = 822583 \text{ cm}^{-1},$$

$$\tilde{\nu} = 109,678 \left(\frac{1}{4} - \frac{1}{9} \right) \text{cm}^{-1} = 15233.0 \text{ cm}^{-1}, \text{ and}$$

$$\tilde{\nu} = 109,678 \left(\frac{1}{9} - \frac{1}{16} \right) \text{cm}^{-1} = 5331.56 \text{ cm}^{-1} \text{ for the Lyman, Balmer, and Paschen series,}$$

respectively.

P20.24) As the principal quantum number n increases, the electron is more likely to be found far from the nucleus. It can be shown that for H and for ions with only one

electron such as He^+ , $\langle r \rangle_{nl} = \frac{n^2 a_0}{Z} \left[1 + \frac{1}{2} \left(1 - \frac{l(l+1)}{n^2} \right) \right]$. Calculate the value of n for an s

state in the hydrogen atom such that $\langle r \rangle = 1000 \text{ a}_0$. Round up to the nearest integer.

What is the ionization energy of the H atom in this state in electron-volts? Compare your answer with the ionization energy of the H atom in the ground state.

$$\langle r \rangle_{nl} = \frac{n^2 a_0}{Z} \left[1 + \frac{1}{2} \left(1 - \frac{l(l+1)}{n^2} \right) \right]$$

$$n = \sqrt{\frac{2Z \times \langle r \rangle_{n0}}{3a_0}} = \sqrt{\frac{2000a_0}{3a_0}} = 25.82 \approx 26$$

$$I = \frac{Z^2 e^2}{8\pi \epsilon_0 a_0 n^2} = \frac{\frac{Z^2}{n^2} \times (1.602 \times 10^{-19} \text{C})^2}{8\pi \times 8.854 \times 10^{-12} \text{J}^{-1} \text{C}^2 \text{m}^{-1} \times 5.292 \times 10^{-11} \text{m}} \times \frac{1 \text{eV}}{1.602 \times 10^{-19} \text{J}}$$

$$I = 13.6039 \frac{Z^2}{n^2} \text{eV} = 13.6039 \frac{1}{n^2} \text{eV} \text{ for the H atom.}$$

For the ground state, $I = 13.6039 \text{ eV}$ and for $n = 26$, $I = 0.0201 \text{ eV}$.

Chapter 21: Many-electron Atoms

Problem numbers in italics indicate that the solution is included in the *Student's Solutions Manual*.

Questions on Concepts

Q21.1) Show that the Slater determinant formalism automatically incorporates the Pauli exclusion principle by evaluating the He ground-state wave function of Equation (21.9), giving both electrons the same quantum numbers.

$$\psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\alpha(2) \end{vmatrix} = \frac{1}{\sqrt{2}} (1s(1)\alpha(1)1s(2)\alpha(2) - 1s(1)\alpha(1)1s(2)\alpha(2))$$
$$\psi(1,2) = 0$$

It is seen that the wave function is zero if two electrons have the same quantum numbers.

Q21.2) Would the trial wave function

$$\Phi(x) = \left(\frac{x}{a} - \frac{x^3}{a^3} \right) + \alpha \left(\frac{x^5}{a^5} - \frac{1}{2} \left(\frac{x^7}{a^7} \right) \right), \quad 0 < x < a$$

have been a suitable choice for the calculations carried out in Section 21.4? Justify your answer.

No, because it does not satisfy the boundary condition at $x = a$.

Q21.3) Why is the s, p, d, \dots nomenclature derived for the H atom also valid for many electron atoms?

The model assumes that the electron motion is not correlated, and that the potential felt by an electron is the spatial average of the electron distribution of the other electrons. Consequently, the potential is spherically symmetric, and the s, p, d, \dots nomenclature derived for the H atom is also valid for many electron atoms.

Q21.4) Why is the total energy of a many-electron atom not equal to the sum of the orbital energies for each electron?

In forming the sum of the orbital energies, the repulsive interactions between the electrons are counted twice. Therefore, this way to calculate the energy is not accurate.

Q21.5) Show using an example that the following two formulations of the Pauli exclusion principle are equivalent: Wave functions describing a many-electron system must change sign under the exchange of any two electrons, and no two electrons may have the same values for all four quantum numbers.

$$\frac{1}{\sqrt{2}}(1s(1)\alpha(1)1s(2)\beta(2)-1s(1)\beta(1)1s(2)\alpha(2))$$

is an example of a two electron wave function that changes sign when the electrons are interchanged. If the electrons have the same quantum numbers,

$$\frac{1}{\sqrt{2}}(1s(1)\alpha(1)1s(2)\alpha(2)-1s(1)\alpha(1)1s(2)\alpha(2))=0.$$

Therefore the antisymmetrized wave function automatically ensures that no two quantum numbers can be the same.

Q21.6) Is there a physical reality associated with the individual entries of a Slater determinant?

No. The Slater determinant merely provides a way to create an antisymmetric many electron wave function.

Q21.7) Explain why shielding is more effective by electrons in a shell of lower principal quantum number than by electrons having the same principal quantum number.

Electrons in a shell of lower principal quantum number have a higher probability of being found between the nucleus and the electrons having the same principal quantum number. Therefore, they are more effective in shielding.

Q21.8) Why does the effective nuclear charge ζ for the $1s$ orbital increase by 0.99 in going from oxygen to fluorine, but ζ for the $2p$ orbital only increases by 0.65?

Because the radial probability distribution of the $1s$ electrons are quite localized, there are no orbitals localized between the $1s$ and the nucleus, and no electrons are added to the atom in going from oxygen to fluorine, the $1s$ electron feels the full increase in the nuclear charge in going from oxygen to fluorine. By contrast, the $2p$ electrons are more delocalized. As an additional p electron is added in going from oxygen to fluorine, only a part of the increase in the nuclear charge is negated by shielding due to the additional $2p$ electron. Adding an electron in the same shell is not as effective in shielding as adding an electron in an inner shell.

Q21.9) Without invoking equations, explain why the energy of the triplet state is lower than that of the singlet state for He in the $1s^12s^1$ configuration.

The probability density is different in the singlet and triplet states. For the triplet state, the electrons are on average closer to the nucleus. This lowers the

electrostatic energy arising from the attractive interaction between the electrons and the nucleus. It also increases the energy arising from the electron-electron repulsion, but the net effect is to decrease the total energy of the atom in the triplet state.

Q21.10) Justify the statement that the Coulomb integral J defined in Equation (21.30) is positive by explicitly formulating the integral that describes the interaction between two negative classical charge clouds.

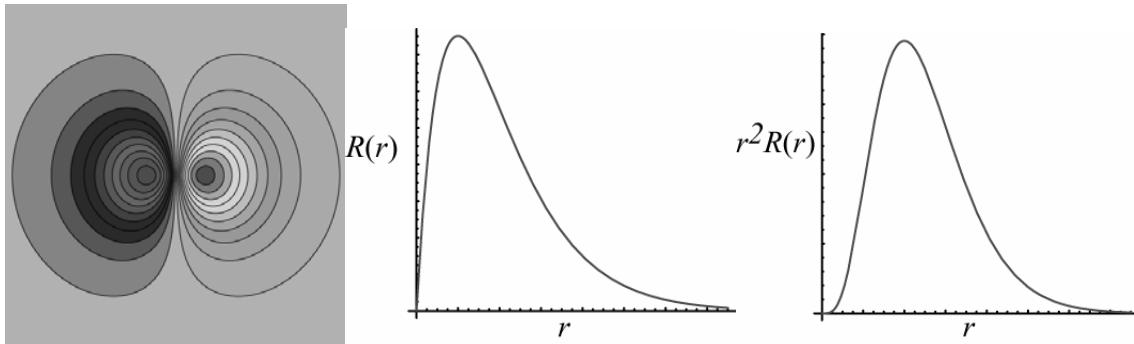
$$\begin{aligned} J_{12} &= \frac{e^2}{8\pi\varepsilon_0} \iint [1s(1)]^2 \left(\frac{1}{|\vec{r}_1 - \vec{r}_2|} \right) [2s(2)]^2 d\tau_1 d\tau_2 \\ &= \frac{1}{\sqrt{32}} \frac{e^2}{8\pi^2\varepsilon_0} \left(\frac{1}{a_0} \right)^6 \iint e^{-r_1/a_0} e \left(\frac{1}{|\vec{r}_1 - \vec{r}_2|} \right) \left(2 - \frac{r_2}{a_0} \right)^2 e^{-r_2/2a_0} d\tau_1 d\tau_2 \end{aligned}$$

The angular coordinates integrate to give a factor $16\pi^2$, leaving only the integration over r_1 and r_2 , which can vary between 0 and ∞ . The terms

$\frac{1}{|\vec{r}_1 - \vec{r}_2|}$, e^{-r_1/a_0} and $e^{-r_2/2a_0}$ are positive as r_1 and r_2 vary over their allowed ranges.

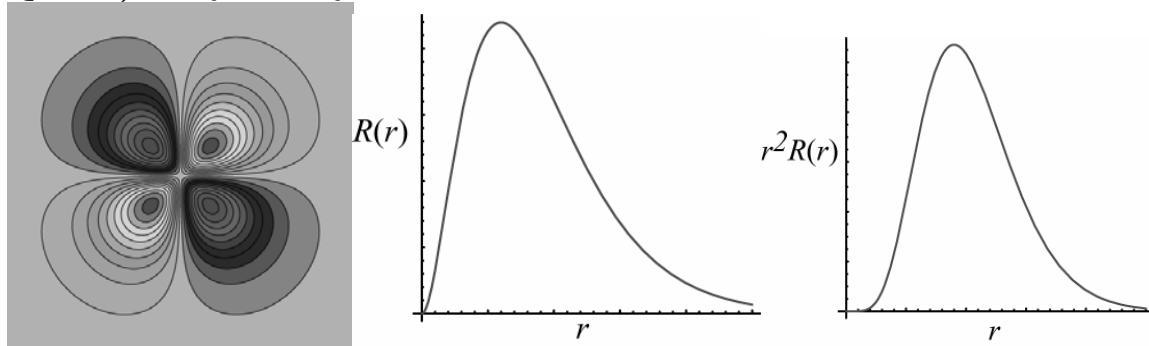
The only other factor involving r_1 or r_2 appears as the square, and is therefore always positive. Therefore, the integrand is always positive, and we can conclude that J_{12} must be positive.

Q21.11) The angular functions, $\Theta(\theta)\Phi(\phi)$, for the one-electron Hartree-Fock orbitals are the same as for the hydrogen atom, and the radial functions and radial probability functions are similar to those for the hydrogen atom. For this question, assume that the latter two functions are identical to those for the hydrogen atom. The following figure shows (a) a contour plot in the x - y plane with the y axis being the vertical axis, (b) the radial function, and (c) the radial probability distribution for a one-electron orbital. Identify the orbital ($2s$, $4dxz$, and so on). Apply the same conditions to Questions Q21.12 through Q21.18 and identify the orbitals as requested here.



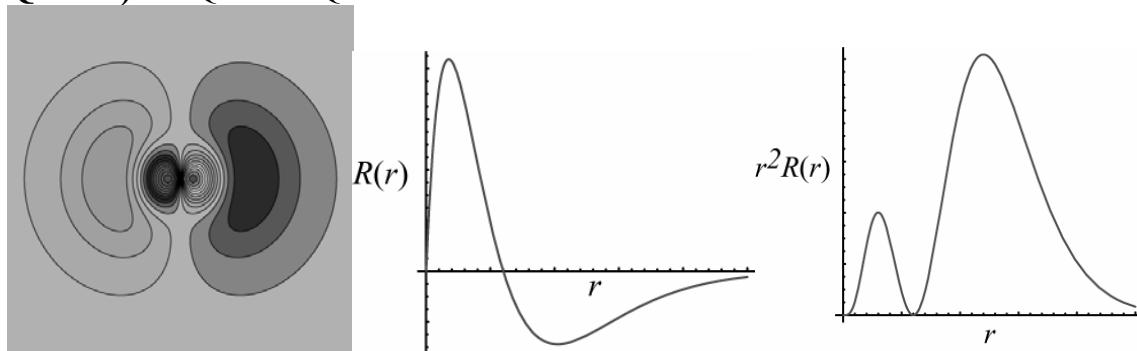
This orbital has no radial nodes and one angular node. It is therefore a $2p$ orbital.

Q21.12) See Question Q21.11.



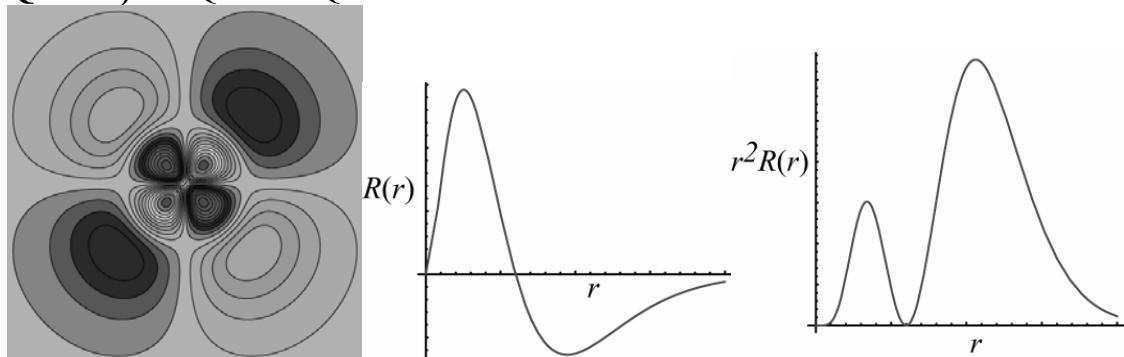
This orbital has no radial nodes and two angular nodes. It is therefore a $3d$ orbital.

Q21.13) See Question Q21.11.



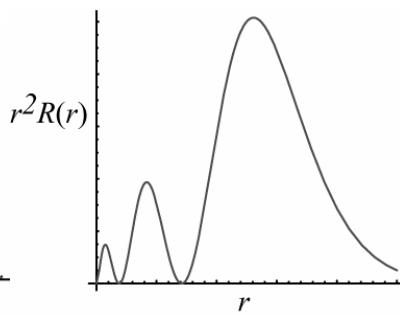
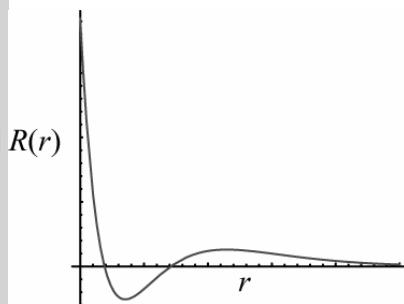
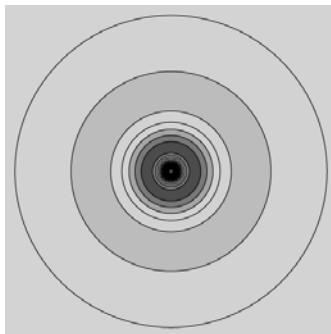
This orbital has one radial node and one angular node. It is therefore a $3p$ orbital.

Q21.14) See Question Q21.11.



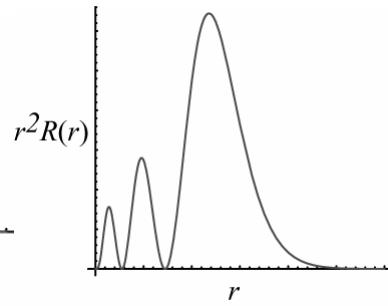
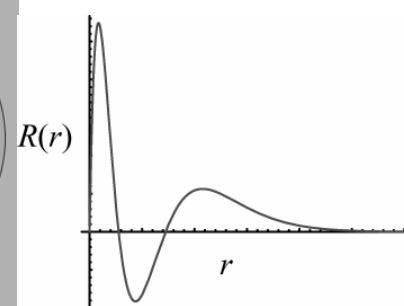
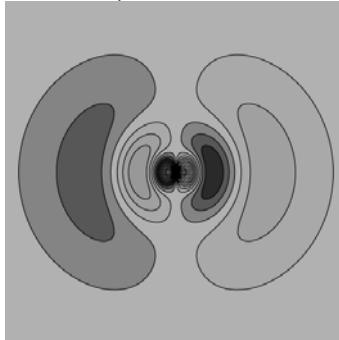
This orbital has one radial node and two angular nodes. It is therefore a $4d$ orbital.

Q21.15) See Question Q21.11.



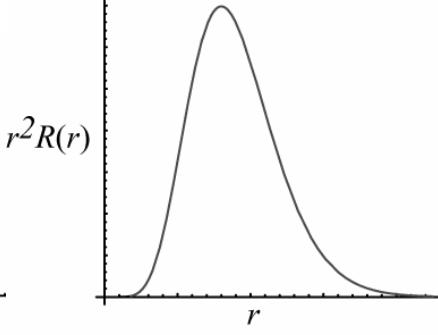
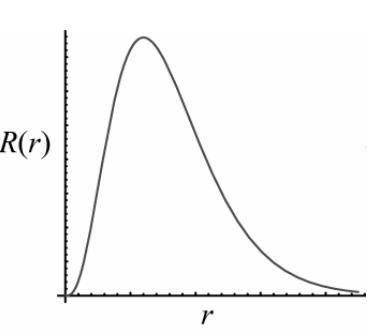
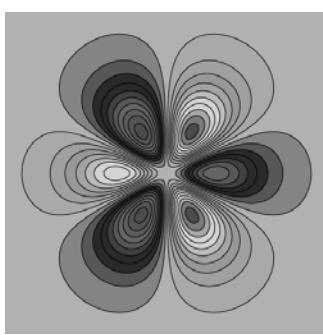
This orbital has two radial nodes and no angular nodes. It is therefore a 3s orbital.

Q21.16) See Question Q21.11.



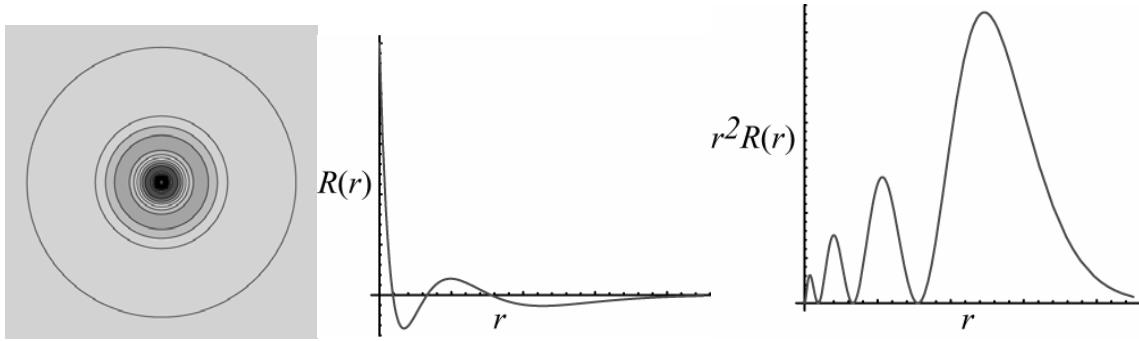
This orbital has two radial nodes and one angular node. It is therefore a 4p orbital.

Q21.17) See Question Q21.11.



This orbital has no radial nodes and three angular nodes. It is therefore a 4f orbital.

Q21.18) See Question Q21.11.



This orbital has three radial nodes and no angular nodes. It is therefore a 4s orbital.

Problems

P21.1) Calculate the angles that a spin angular momentum vector for an individual electron can make with the z axis.

The angle θ with the z axis is determined by

$$\cos \theta = \frac{s_z}{\sqrt{s(s+1)}} = \frac{\pm \frac{1}{2}}{\sqrt{\frac{1}{2}(\frac{1}{2}+1)}} = \frac{\pm 1}{\sqrt{3}}. \text{ This gives values for } \theta \text{ of } 54.7^\circ \text{ and } 125.3^\circ.$$

P21.2) Classify the following functions as symmetric, antisymmetric, or neither in the exchange of electrons 1 and 2:

a) $[1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

$$\begin{aligned} & [1s(2)2s(1) + 2s(2)1s(1)][\alpha(2)\beta(1) - \beta(2)\alpha(1)] = \\ & -[1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \end{aligned}$$

Therefore the function is antisymmetric in the exchange of electrons 1 and 2.

b) $[1s(1)2s(2) + 2s(1)1s(2)]\alpha(1)\alpha(2)$

$$[1s(2)2s(1) + 2s(2)1s(1)]\alpha(2)\alpha(1) = [1s(1)2s(2) + 2s(1)1s(2)]\alpha(1)\alpha(2)$$

Therefore the function is symmetric in the exchange of electrons 1 and 2.

c) $[1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) + \beta(1)\alpha(2)]$

$$\begin{aligned} & [1s(2)2s(1) + 2s(2)1s(1)][\alpha(2)\beta(1) + \beta(2)\alpha(1)] = \\ & [1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) + \beta(1)\alpha(2)] \end{aligned}$$

Therefore the function is symmetric in the exchange of electrons 1 and 2.

$$d) [1s(1)2s(2) - 2s(1)1s(2)][\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$[1s(2)2s(1) - 2s(2)1s(1)][\alpha(2)\beta(1) + \beta(2)\alpha(1)]$$

$$= -[1s(1)2s(2) - 2s(1)1s(2)][\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

Therefore the function is antisymmetric in the exchange of electrons 1 and 2.

$$e) [1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2) + \alpha(1)\alpha(2)]$$

$$[1s(1)2s(2) + 2s(1)1s(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2) + \alpha(1)\alpha(2)]$$

$$\neq \pm [1s(2)2s(1) + 2s(2)1s(1)][\alpha(2)\beta(1) - \beta(2)\alpha(1) + \alpha(2)\alpha(1)]$$

Therefore the function is neither symmetric or antisymmetric in the exchange of electrons 1 and 2.

P21.3) Is $\psi(1,2) = 1s(1)\alpha(1)1s(2)\beta(2) + 1s(2)\alpha(2)1s(1)\beta(1)$ an eigenfunction of the operator \hat{S}_z ? If so, what is its eigenvalue M_S ?

$$\begin{aligned} & \hat{S}_z [1s(1)\alpha(1)1s(2)\beta(2) + 1s(2)\alpha(2)1s(1)\beta(1)] \\ &= (\hat{s}_{z1} + \hat{s}_{z2}) [1s(1)\alpha(1)1s(2)\beta(2) + 1s(2)\alpha(2)1s(1)\beta(1)] \\ &= \frac{\hbar}{2} [1s(1)\alpha(1)1s(2)\beta(2) - 1s(2)\alpha(2)1s(1)\beta(1)] \\ &\quad + \frac{\hbar}{2} [-1s(1)\alpha(1)1s(2)\beta(2) + 1s(2)\alpha(2)1s(1)\beta(1)] \\ &= \frac{\hbar}{2}(0) \end{aligned}$$

The function is an eigenfunction of \hat{S}_z with the eigenvalue $M_S = 0$.

P21.4) The operator for the square of the total spin of two electrons is

$$\hat{S}_{total}^2 = (\hat{S}_1 + \hat{S}_2)^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2(\hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1z}\hat{S}_{2z}). \text{ Given that}$$

$$\hat{S}_x\alpha = \frac{\hbar}{2}\beta \quad \hat{S}_y\alpha = \frac{i\hbar}{2}\beta \quad \hat{S}_z\alpha = \frac{\hbar}{2}\alpha$$

$$\hat{S}_x\beta = \frac{\hbar}{2}\alpha \quad \hat{S}_y\beta = -\frac{i\hbar}{2}\alpha \quad \hat{S}_z\beta = -\frac{\hbar}{2}\beta$$

show that $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$ are eigenfunctions of the operator \hat{S}_{total}^2 . What is the eigenvalue in each case?

$$\begin{aligned}
 & \hat{S}_{\text{total}}^2 \alpha(1) \alpha(2) \\
 &= \hat{S}_1^2 \alpha(1) \alpha(2) + \hat{S}_2^2 \alpha(1) \alpha(2) + 2(\hat{S}_{1x} \hat{S}_{2x} \alpha(1) \alpha(2) + \hat{S}_{1y} \hat{S}_{2y} \alpha(1) \alpha(2) + \hat{S}_{1z} \hat{S}_{2z} \alpha(1) \alpha(2)) \\
 &= \alpha(2) \hat{S}_1^2 \alpha(1) + \alpha(1) \hat{S}_2^2 \alpha(2) + 2(\hat{S}_{1x} \alpha(1) \hat{S}_{2x} \alpha(2) + \hat{S}_{1y} \alpha(1) \hat{S}_{2y} \alpha(2) + \hat{S}_{1z} \alpha(1) \hat{S}_{2z} \alpha(2)) \\
 &= \frac{3\hbar^2}{4} \alpha(1) \alpha(2) + \frac{3\hbar^2}{4} \alpha(1) \alpha(2) + 2(\hat{S}_{1x} \alpha(1) \hat{S}_{2x} \alpha(2) + \hat{S}_{1y} \alpha(1) \hat{S}_{2y} \alpha(2) + \hat{S}_{1z} \alpha(1) \hat{S}_{2z} \alpha(2)) \\
 &= \frac{3\hbar^2}{4} \alpha(1) \alpha(2) + \frac{3\hbar^2}{4} \alpha(1) \alpha(2) + 2 \times \frac{\hbar}{2} (\hat{S}_{1x} \alpha(1) \beta(2) + i \hat{S}_{1y} \alpha(1) \beta(2) + \hat{S}_{1z} \alpha(1) \alpha(2)) \\
 &= \frac{3\hbar^2}{4} \alpha(1) \alpha(2) + \frac{3\hbar^2}{4} \alpha(1) \alpha(2) + 2 \times \left(\frac{\hbar}{2}\right)^2 (\beta(1) \beta(2) + i^2 \beta(1) \beta(2) + \alpha(1) \alpha(2)) \\
 &= \frac{3\hbar^2}{4} \alpha(1) \alpha(2) + \frac{3\hbar^2}{4} \alpha(1) \alpha(2) + \frac{2\hbar^2}{4} \alpha(1) \alpha(2) = 2\hbar^2 \alpha(1) \alpha(2)
 \end{aligned}$$

The eigenvalue is $2\hbar^2$.

$$\begin{aligned}
 & \hat{S}_{\text{total}}^2 \beta(1) \beta(2) \\
 &= \hat{S}_1^2 \beta(1) \beta(2) + \hat{S}_2^2 \beta(1) \beta(2) + 2(\hat{S}_{1x} \hat{S}_{2x} \beta(1) \beta(2) + \hat{S}_{1y} \hat{S}_{2y} \beta(1) \beta(2) + \hat{S}_{1z} \hat{S}_{2z} \beta(1) \beta(2)) \\
 &= \alpha(2) \hat{S}_1^2 \beta(1) + \beta(1) \hat{S}_2^2 \beta(2) + 2(\hat{S}_{1x} \beta(1) \hat{S}_{2x} \beta(2) + \hat{S}_{1y} \beta(1) \hat{S}_{2y} \beta(2) + \hat{S}_{1z} \beta(1) \hat{S}_{2z} \beta(2)) \\
 &= \frac{3\hbar^2}{4} \beta(1) \beta(2) + \frac{3\hbar^2}{4} \beta(1) \beta(2) + 2(\hat{S}_{1x} \beta(1) \hat{S}_{2x} \beta(2) + \hat{S}_{1y} \beta(1) \hat{S}_{2y} \beta(2) + \hat{S}_{1z} \beta(1) \hat{S}_{2z} \beta(2)) \\
 &= \frac{3\hbar^2}{4} \alpha(1) \alpha(2) + \frac{3\hbar^2}{4} \beta(1) \beta(2) + 2 \times \frac{\hbar}{2} (\hat{S}_{1x} \beta(1) \alpha(2) + i \hat{S}_{1y} \beta(1) \beta(2) - \hat{S}_{1z} \beta(1) \beta(2)) \\
 &= \frac{3\hbar^2}{4} \alpha(1) \alpha(2) + \frac{3\hbar^2}{4} \beta(1) \beta(2) + 2 \times \left(\frac{\hbar}{2}\right)^2 (\alpha(1) \alpha(2) - i^2 \beta(1) \beta(2) + \beta(1) \beta(2)) \\
 &= \frac{3\hbar^2}{4} \alpha(1) \alpha(2) + \frac{3\hbar^2}{4} \beta(1) \beta(2) + \frac{2\hbar^2}{4} \beta(1) \beta(2) = 2\hbar^2 \beta(1) \beta(2)
 \end{aligned}$$

The eigenvalue is $2\hbar^2$.

P21.5) Show that the functions $\frac{\alpha(1) \beta(2) + \beta(1) \alpha(2)}{\sqrt{2}}$ and $\frac{\alpha(1) \beta(2) - \beta(1) \alpha(2)}{\sqrt{2}}$

are eigenfunctions of \hat{S}_{total}^2 . What is the eigenvalue in each case?

Solve this equation by acting on $\alpha(1) \beta(2)$ and $\beta(1) \alpha(2)$ separately, and combining the results.

$$\begin{aligned}
& \hat{S}_{total}^2 \alpha(1) \beta(2) \\
&= \hat{S}_1^2 \alpha(1) \beta(2) + \hat{S}_2^2 \alpha(1) \beta(2) + 2(\hat{S}_{1x} \hat{S}_{2x} \alpha(1) \beta(2) + \hat{S}_{1y} \hat{S}_{2y} \alpha(1) \beta(2) + \hat{S}_{1z} \hat{S}_{2z} \alpha(1) \beta(2)) \\
&= \beta(2) \hat{S}_1^2 \alpha(1) + \alpha(1) \hat{S}_2^2 \beta(2) + 2(\hat{S}_{1x} \alpha(1) \hat{S}_{2x} \beta(2) + \hat{S}_{1y} \alpha(1) \hat{S}_{2y} \beta(2) + \hat{S}_{1z} \alpha(1) \hat{S}_{2z} \beta(2)) \\
&= \frac{3\hbar^2}{4} \alpha(1) \beta(2) + \frac{3\hbar^2}{4} \alpha(1) \beta(2) + 2(\hat{S}_{1x} \alpha(1) \hat{S}_{2x} \beta(2) + \hat{S}_{1y} \alpha(1) \hat{S}_{2y} \beta(2) + \hat{S}_{1z} \alpha(1) \hat{S}_{2z} \beta(2)) \\
&= \frac{3\hbar^2}{4} \alpha(1) \beta(2) + \frac{3\hbar^2}{4} \alpha(1) \beta(2) + 2 \times \frac{\hbar}{2} (\hat{S}_{1x} \alpha(1) \alpha(2) - i \hat{S}_{1y} \alpha(1) \alpha(2) - \hat{S}_{1z} \alpha(1) \beta(2)) \\
&= \frac{3\hbar^2}{4} \alpha(1) \beta(2) + \frac{3\hbar^2}{4} \alpha(1) \beta(2) + 2 \times \left(\frac{\hbar}{2}\right)^2 (\beta(1) \alpha(2) - i^2 \beta(1) \alpha(2) + \alpha(1) \beta(2)) \\
&= \frac{3\hbar^2}{2} \alpha(1) \beta(2) + \frac{\hbar^2}{2} (2 \beta(1) \alpha(2) + \alpha(1) \beta(2)) \\
&= \hbar^2 \alpha(1) \beta(2) + \hbar^2 \beta(1) \alpha(2)
\end{aligned}$$

$$\begin{aligned}
& \hat{S}_{total}^2 \beta(1) \alpha(2) \\
&= \hat{S}_1^2 \beta(1) \alpha(2) + \hat{S}_2^2 \beta(1) \alpha(2) + 2(\hat{S}_{1x} \hat{S}_{2x} \beta(1) \alpha(2) + \hat{S}_{1y} \hat{S}_{2y} \beta(1) \alpha(2) + \hat{S}_{1z} \hat{S}_{2z} \beta(1) \alpha(2)) \\
&= \alpha(2) \hat{S}_1^2 \beta(1) + \beta(1) \hat{S}_2^2 \alpha(2) + 2(\hat{S}_{1x} \beta(1) \hat{S}_{2x} \alpha(2) + \hat{S}_{1y} \beta(1) \hat{S}_{2y} \alpha(2) + \hat{S}_{1z} \beta(1) \hat{S}_{2z} \alpha(2)) \\
&= \frac{3\hbar^2}{4} \beta(1) \alpha(2) + \frac{3\hbar^2}{4} \beta(1) \alpha(2) + 2(\hat{S}_{1x} \beta(1) \hat{S}_{2x} \alpha(2) + \hat{S}_{1y} \beta(1) \hat{S}_{2y} \alpha(2) + \hat{S}_{1z} \beta(1) \hat{S}_{2z} \alpha(2)) \\
&= \frac{3\hbar^2}{4} \beta(1) \alpha(2) + \frac{3\hbar^2}{4} \beta(1) \alpha(2) + 2 \times \frac{\hbar}{2} (\hat{S}_{1x} \beta(1) \beta(2) + i \hat{S}_{1y} \beta(1) \beta(2) + \hat{S}_{1z} \beta(1) \alpha(2)) \\
&= \frac{3\hbar^2}{4} \beta(1) \alpha(2) + \frac{3\hbar^2}{4} \beta(1) \alpha(2) + 2 \times \left(\frac{\hbar}{2}\right)^2 (\alpha(1) \beta(2) - i^2 \alpha(1) \beta(2) - \beta(1) \alpha(2)) \\
&= \frac{3\hbar^2}{2} \beta(1) \alpha(2) + \frac{\hbar^2}{2} (2 \alpha(1) \beta(2) - \beta(1) \alpha(2)) \\
&= \hbar^2 \alpha(1) \beta(2) + \hbar^2 \beta(1) \alpha(2)
\end{aligned}$$

Therefore, \hat{S}_{total}^2 acting on $\frac{\alpha(1) \beta(2) + \beta(1) \alpha(2)}{\sqrt{2}}$ yields

$$\begin{aligned}
& \frac{1}{\sqrt{2}} [\hbar^2 \alpha(1) \beta(2) + \hbar^2 \beta(1) \alpha(2) + \hbar^2 \alpha(1) \beta(2) + \hbar^2 \beta(1) \alpha(2)] \\
&= \frac{2\hbar^2}{\sqrt{2}} [\alpha(1) \beta(2) + \beta(1) \alpha(2)]
\end{aligned}$$

The eigenvalue is $2\hbar^2$.

\hat{S}_{total}^2 acting on $\frac{\alpha(1) \beta(2) - \beta(1) \alpha(2)}{\sqrt{2}}$ yields

$$\begin{aligned} & \frac{1}{\sqrt{2}} [\hbar^2 \alpha(1) \beta(2) + \hbar^2 \beta(1) \alpha(2) - \hbar^2 \alpha(1) \beta(2) - \hbar^2 \beta(1) \alpha(2)] \\ &= \frac{1}{\sqrt{2}} \times 0 \times [\alpha(1) \beta(2) + \beta(1) \alpha(2)] \end{aligned}$$

The eigenvalue is 0.

P21.6) Write the Slater determinant for the ground-state configuration of Be.

$$\Psi_{Be} = \frac{1}{\sqrt{4!}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) & 2s(2)\beta(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) & 2s(3)\beta(3) \\ 1s(4)\alpha(4) & 1s(4)\beta(4) & 2s(4)\alpha(4) & 2s(4)\beta(4) \end{vmatrix}$$

P21.7) In this problem we represent the spin eigenfunctions and operators as vectors and matrices.

a) The spin eigenfunctions are often represented as the column vectors

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \text{ Show that } \alpha \text{ and } \beta \text{ are orthogonal using this representation.}$$

Using the rules of matrix multiplication, $\alpha\beta = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \end{pmatrix} = 1 \times 0 + 0 \times 1 = 0$. Therefore α and β are orthogonal.

b) If the spin angular momentum operators are represented by the matrices

$$\hat{s}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{s}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{s}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \text{ show that the commutation rule } [\hat{s}_x, \hat{s}_y] = i\hbar \hat{s}_z \text{ holds.}$$

$$\begin{aligned} \hat{s}_x \hat{s}_y - \hat{s}_y \hat{s}_x &= \left(\frac{\hbar}{2}\right)^2 \left\{ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right\} \\ &= \left(\frac{\hbar}{2}\right)^2 \left\{ \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} - \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} \right\} = 2i \left(\frac{\hbar}{2}\right)^2 \left\{ \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right\} = i\hbar \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = i\hbar \hat{s}_z \end{aligned}$$

$$c) \text{ Show that } \hat{s}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2 = \frac{\hbar^2}{4} \begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix}.$$

$$\begin{aligned} \hat{s}^2 &= \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2 = \frac{\hbar^2}{4} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \frac{\hbar^2}{4} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\ &= \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{\hbar^2}{4} \begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix} \end{aligned}$$

d) Show that α and β are eigenfunctions of \hat{s}_z and \hat{s}^2 . What are the eigenvalues?

$$\hat{s}_z \alpha = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } \hat{s}_z \beta = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{\hbar}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

The eigenvalues for α and β are $\frac{\hbar}{2}$ and $-\frac{\hbar}{2}$ respectively.

$$\hat{s}^2 \alpha = \frac{\hbar^2}{4} \begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3\hbar^2}{4} \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad \hat{s}^2 \beta = \frac{\hbar^2}{4} \begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{3\hbar^2}{4} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

The eigenvalues are $\frac{3\hbar^2}{4}$ in each case.

e) Show that α and β are not eigenfunctions of \hat{s}_x and \hat{s}_y .

$$\hat{s}_x \alpha = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2} \beta \neq c\alpha, \quad \hat{s}_x \beta = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \alpha \neq c\beta,$$

$$\hat{s}_y \alpha = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0 \\ i \end{pmatrix} = \frac{i\hbar}{2} \beta \neq c\alpha, \quad \hat{s}_y \beta = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} -i \\ 0 \end{pmatrix} = -\frac{i\hbar}{2} \alpha \neq c\beta$$

P21.8) In this problem you will prove that the ground-state energy for a system obtained using the variational method is greater than the true energy.

a) The approximate wave function Φ can be expanded in the true (but unknown) eigenfunctions ψ_n of the total energy operator in the form $\Phi = \sum_n c_n \psi_n$. Show that by

substituting $\Phi = \sum_n c_n \psi_n$ in the equation $E = \frac{\int \Phi^* \hat{H} \Phi d\tau}{\int \Phi^* \Phi d\tau}$, you obtain the result

$$E = \frac{\sum_n \sum_m \int (c_n^* \psi_n^*) \hat{H} (c_m \psi_m) d\tau}{\sum_n \sum_m \int (c_n^* \psi_n^*) (c_m \psi_m) d\tau}$$

$$E = \frac{\int \Phi^* \hat{H} \Phi d\tau}{\int \Phi^* \Phi d\tau} = \frac{\int \left(\Phi = \sum_n c_n \psi_n \right)^* \hat{H} \left(\Phi = \sum_m c_m \psi_m \right) d\tau}{\int \left(\Phi = \sum_n c_n \psi_n \right)^* \left(\Phi = \sum_m c_m \psi_m \right) d\tau} = \frac{\sum_n \sum_m \int (c_n^* \psi_n^*) \hat{H} (c_m \psi_m) d\tau}{\sum_n \sum_m \int (c_n^* \psi_n^*) (c_m \psi_m) d\tau}$$

b) Because the ψ_n are eigenfunctions of \hat{H} , they are orthogonal and $\hat{H} \psi_n = E_n \psi_n$.

Show that this information allows us to simplify the previous expression for E from

$$\text{part (a) to } E = \frac{\sum_m E_m c_m^* c_m}{\sum_m c_m^* c_m}$$

$$\begin{aligned}
 E &= \frac{\sum_{n} \sum_{m} \int (c_n^* \psi_n^*) \hat{H} (c_m \psi_m) d\tau}{\sum_{n} \sum_{m} \int (c_n^* \psi_n^*) (c_m \psi_m) d\tau} = \frac{\sum_{n} \sum_{m} E_m \int (c_n^* \psi_n^*) (c_m \psi_m) d\tau}{\sum_{n} \sum_{m} \int (c_n^* \psi_n^*) (c_m \psi_m) d\tau} \\
 &= \frac{\sum_{m} E_m c_m^* c_m \int \psi_m^* \psi_m d\tau}{\sum_{m} c_m^* c_m \int \psi_m^* \psi_m d\tau} = \frac{\sum_{m} E_m c_m^* c_m}{\sum_{m} c_m^* c_m}
 \end{aligned}$$

c) Arrange the terms in the summation such that the first energy is the true ground-state energy E_0 and the energy increases with the summation index m . Why can you conclude that $E - E_0 \geq 0$?

$$E - E_0 = \frac{\sum_{m} E_m c_m^* c_m}{\sum_{m} c_m^* c_m} - \frac{E_0 \sum_{m} c_m^* c_m}{\sum_{m} c_m^* c_m} = \frac{\sum_{m} (E_m - E_0) c_m^* c_m}{\sum_{m} c_m^* c_m} \geq 0. \text{ Both } (E_m - E_0) \text{ and } c_m^* c_m \text{ are greater than zero. Therefore, } E - E_0 \geq 0.$$

P21.9) In this problem, you will use the variational method to find the optimal $1s$ wave function for the hydrogen atom starting from the trial function $\Phi(r) = e^{-\alpha r}$ with α as the variational parameter. You will minimize

$$E(\alpha) = \frac{\int \Phi^* \hat{H} \Phi d\tau}{\int \Phi^* \Phi d\tau}$$

with respect to α .

a) Show that

$$\hat{H}\Phi = -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Phi(r)}{\partial r} \right) - \frac{e^2}{4\pi\epsilon_0 r} \Phi(r) = \frac{\alpha\hbar^2}{2m_e r^2} (2r - \alpha r^2) e^{-\alpha r} - \frac{e^2}{4\pi\epsilon_0 r} e^{-\alpha r}$$

We start with $\frac{\partial e^{-\alpha r}}{\partial r} = -\alpha e^{-\alpha r}$ and $\frac{\partial (r^2 e^{-\alpha r})}{\partial r} = 2re^{-\alpha r} - \alpha r^2 e^{-\alpha r}$. Using these results,

$$\hat{H}\Phi = -\frac{\hbar^2}{2m_e} \frac{1}{r^2} (2re^{-\alpha r} - \alpha r^2 e^{-\alpha r}) - \frac{e^2}{4\pi\epsilon_0 r} e^{-\alpha r} = \frac{\alpha\hbar^2}{2m_e r^2} (2r - \alpha r^2) e^{-\alpha r} - \frac{e^2}{4\pi\epsilon_0 r} e^{-\alpha r}$$

b) Obtain the result $\int \Phi^* \hat{H} \Phi d\tau = 4\pi \int_0^\infty r^2 \Phi^* \hat{H} \Phi dr = \frac{\pi\hbar^2}{2m_e \alpha} - \frac{e^2}{4\epsilon_0 \alpha^2}$ using the standard integrals in the Math Supplement.

$$\begin{aligned}
\int \Phi^* \hat{H} \Phi d\tau &= \frac{\alpha \hbar^2}{2m_e} \left(2 \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r e^{-2\alpha r} dr - \alpha \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^2 e^{-2\alpha r} dr \right) \\
&\quad - \frac{e^2}{4\pi\epsilon_0} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r e^{-2\alpha r} dr \\
&= \frac{4\pi\alpha\hbar^2}{2m_e} \left(2 \int_0^\infty r e^{-2\alpha r} dr - \alpha \int_0^\infty r^2 e^{-2\alpha r} dr \right) - \frac{e^2}{\epsilon_0} \int_0^\infty r e^{-2\alpha r} dr \\
&= \frac{2\pi\alpha\hbar^2}{m_e} \left(2 \frac{1!}{2^2 \alpha^2} - \alpha \frac{2!}{2^3 \alpha^3} \right) - \frac{e^2}{\epsilon_0} \frac{1!}{2^2 \alpha^2} = \frac{\pi\hbar^2}{2m_e \alpha} - \frac{e^2}{4\epsilon_0 \alpha^2}
\end{aligned}$$

c) Show that $\int \Phi^* \Phi d\tau = 4\pi \int_0^\infty r^2 \Phi^* \Phi dr = \frac{\pi}{\alpha^3}$ using the standard integrals in the Math

Supplement.

$$\begin{aligned}
\int \Phi^* \Phi d\tau &= \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^2 e^{-2\alpha r} dr \\
&= 4\pi \int_0^\infty r^2 e^{-2\alpha r} dr = 4\pi \frac{2!}{2^3 \alpha^3} = \frac{\pi}{\alpha^3}
\end{aligned}$$

d) You now have the result $E(\alpha) = \frac{\hbar^2 \alpha^2}{2m_e} - \frac{e^2 \alpha}{4\pi\epsilon_0}$. Minimize this function with respect to α and obtain the optimal value of α .

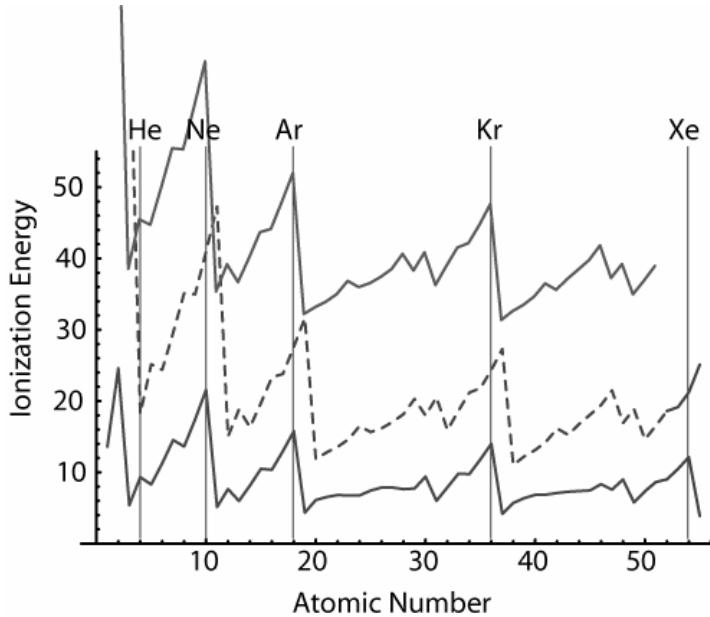
$$\begin{aligned}
\frac{d}{d\alpha} \left(\frac{\hbar^2 \alpha^2}{2m_e} - \frac{e^2 \alpha}{4\pi\epsilon_0} \right) &= -\frac{e^2}{4\pi\epsilon_0} + \frac{\hbar^2 \alpha}{m_e} = 0 \\
\alpha_{optimal} &= \frac{m_e e^2}{4\pi\epsilon_0 \hbar^2}
\end{aligned}$$

e) Is $E(\alpha_{optimal})$ equal to or greater than the true energy? Why?

$$E(\alpha) = \frac{\hbar^2 \alpha^2}{2m_e} - \frac{e^2 \alpha}{4\pi\epsilon_0} = \frac{\hbar^2}{2m_e} \left(\frac{m_e e^2}{4\pi\epsilon_0 \hbar^2} \right)^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{m_e e^2}{4\pi\epsilon_0 \hbar^2} \right) = -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2}.$$

$E(\alpha_{optimal})$ is equal to the true energy because our trial wave function has the same form as the true wave function.

P21.10) You have commissioned a measurement of the second ionization energy from two independent research teams. You find that they do not agree and decide to plot the data together with known values of the first ionization energy. The results are shown here.



The lowest curve is for the first ionization energy and the upper two curves are the results for the second ionization energy from the two research teams. The uppermost curve has been shifted vertically to avoid an overlap with the other new data set. On the basis of your knowledge of the periodic table, you suddenly know which of the two sets of data is correct and the error that one of the teams of researchers made. Which data set is correct? Explain your reasoning.

The data set shown by the dashed line is correct. Although the alkali atoms have the lowest ionization energies, they must have the highest ionization energy for the second ionization potential because the singly charged positive ions have the rare gas filled shell configuration. The experimenters that produced the data set shown by the gray line had assigned atomic numbers that were too low by one.

P21.11) In this problem you will show that the charge density of the filled $n = 2$, $l = 1$ subshell is spherically symmetrical and that therefore $\mathbf{L} = 0$. The angular distribution of the electron charge is simply the sum of the squares of the magnitude of the angular part of the wave functions for $l = 1$ and $m_l = -1, 0$, and 1 .

a) Given that the angular part of these wave functions is

$$Y_1^0(\theta, \phi) = \left(\frac{3}{4\pi} \right)^{1/2} \cos \theta$$

$$Y_1^1(\theta, \phi) = \left(\frac{3}{8\pi} \right)^{1/2} \sin \theta e^{i\phi}$$

$$Y_1^{-1}(\theta, \phi) = \left(\frac{3}{8\pi} \right)^{1/2} \sin \theta e^{-i\phi}$$

write an expression for $|Y_1^0(\theta, \phi)|^2 + |Y_1^1(\theta, \phi)|^2 + |Y_1^{-1}(\theta, \phi)|^2$.

$$|Y_1^0(\theta, \phi)|^2 + |Y_1^1(\theta, \phi)|^2 + |Y_1^{-1}(\theta, \phi)|^2 = \frac{3}{4\pi} \cos^2 \theta + \frac{3}{8\pi} \sin^2 \theta + \frac{3}{8\pi} \sin^2 \theta$$

b) Show that $|Y_1^0(\theta, \phi)|^2 + |Y_1^1(\theta, \phi)|^2 + |Y_1^{-1}(\theta, \phi)|^2$ does not depend on θ and ϕ .

$$\frac{3}{4\pi} \cos^2 \theta + \frac{3}{8\pi} \sin^2 \theta + \frac{3}{8\pi} \sin^2 \theta = \frac{3}{4\pi} (\cos^2 \theta + \sin^2 \theta) = \frac{3}{4\pi}$$

This is not a function of θ and ϕ .

c) Why does this result show that the charge density for the filled $n = 2, l = 1$ subshell is spherically symmetrical?

If a function is independent of θ and ϕ , then it has the same value for all θ and ϕ . This is what we mean by being spherically symmetrical.

P21.12) List the quantum numbers L and S that are consistent with the terms

a) 4S , b) 4G , c) 3P , and d) 2D

a) ${}^4S: L = 0, 2S + 1 = 4, S = 3/2$

b) ${}^4G: L = 4, 2S + 1 = 4, S = 3/2$

c) ${}^3P: L = 1, 2S + 1 = 3, S = 1$

d) ${}^2D: L = 2, 2S + 1 = 2, S = 1/2$

P21.13) List the allowed quantum numbers m_l and m_s for the following subshells and determine the maximum occupancy of the subshells.

a) $2p$ b) $3d$ c) $4f$ d) $5g$

a) $2p: 1, 0, -1$ for m_l and $1/2$ and $-1/2$ for m_s for each of the m_l values.

Subshell occupancy = 6.

b) $3d: 2, 1, 0, -1, -2$ for m_l and $1/2$ and $-1/2$ for m_s for each of the m_l values.

Subshell occupancy = 10.

c) $4f: 3, 2, 1, 0, -1, -2, -3$ for m_l and $1/2$ and $-1/2$ for m_s for each of the m_l values.

Subshell occupancy = 14.

d) $5g: 4, 3, 2, 1, 0, -1, -2, -3, -4$ for m_l and $1/2$ and $-1/2$ for m_s for each of the m_l values.

Subshell occupancy = 18.

P21.14) Two angular momenta with quantum numbers $j_1 = 3/2$ and $j_2 = 5/2$ are added together. What are the possible values of J for the resultant angular momentum states?

$J = |J_1 + J_2|, |J_1 + J_2 - 1|, |J_1 + J_2 - 2|, \dots, |J_1 - J_2|$ giving possible J values of 4, 3, 2, and 1.

P21.15) Calculate the terms that can arise from the configuration $np^1n'p^1, n \neq n'$. Compare your results with those derived in the text for np^2 . Which configuration has more terms and why?

Because the principle quantum number is different, any combination of m_l and m_s is allowed. Therefore, $S = 0, 1$ and $L = 0, 1$, and 2 . Any combination of the two quantum numbers is allowed. This leads to 1S , 1P , and 1D terms as well as 3S , 3P , and 3D terms. The $np^1n'p^1, n \neq n'$ configuration has more terms because some of the possible terms listed above are not allowed if $n = n'$ because of the Pauli principle.

P21.16) A general way to calculate the number of states that arise from a given configuration is as follows. Calculate the combinations of m_l and m_s for the first electron, and call that number n . The number of combinations used is the number of electrons which we call m . The number of unused combinations is $n - m$. According to probability theory, the number of distinct permutations that arise from distributing the m electrons among the n combinations is $\frac{n!}{m!(n-m)!}$. For example, the

number of states arising from a p^2 configuration is $\frac{6!}{2!4!} = 15$, which is the result obtained in Section 21.8. Using this formula, calculate the number of possible ways to place five electrons in a d subshell. What is the ground-state term for the d^5 configuration and how many states does the term include?

The first electrons can have any combination of 5 m_l and 2 m_s values so that $n = 10$ and $m = 5$. Using the formula, the calculated number of states is $\frac{10!}{5!(10-5)!} = 252$. The number of states in a term is $(2L+1)(2S+1)$. The terms from Table 21.5 are listed here, with the number of states in each term in square brackets following the term designation: $^6S[6 \times 1]$, $^4G[4 \times 9]$, $^4F[4 \times 7]$, $^4D[4 \times 5]$, $^4P[4 \times 3]$, $^2I[2 \times 13]$, $^2H[2 \times 11]$, $^2G(2)[2 \times 2 \times 9]$, $^2F(2)[2 \times 2 \times 7]$, $^2D(3)[3 \times 2 \times 5]$, $^2P[2 \times 3]$, and $^2S[2 \times 1]$. The number of states in these terms is $6 + 36 + 28 + 20 + 12 + 26 + 22 + 36 + 28 + 30 + 6 + 2 = 252$, showing consistency.

The ground state is that with the maximum multiplicity which according to Table 21.5 is the 6S term. The number of states in the term = $(2L + 1)(2S + 1) = 6$.

P21.17) How many ways are there to place three electrons into an f subshell? What is the ground-state term for the f^3 configuration, and how many states are associated with this term? See Problem P21.16.

The first electrons can have any combination of 7 m_l and 2 m_s values so that $n = 14$ and $m = 3$. The number of states is $\frac{14!}{3!(14-3)!} = 364$.

Using the method discussed in Example Problem 21.7, $M_{Lmax} = 6$ and $M_{Smax} = 3/2$. Therefore the ground state term is ^4I , which has $(2L + 1)(2S + 1) = (2 \times 6 + 1)(4) = 52$ states.

P21.18) What atomic terms are possible for the following electron configurations?

Which of the possible terms has the lowest energy?

- a) ns^1np^1 b) ns^1nd^1 c) ns^2np^1 d) ns^1np^2

a) ns^1np^1 L can only have the value 1, and S can have the values 0 and 1. The possible terms are ^1P and ^3P . Hund's Rules predict that the ^3P term will have the lower energy.

b) ns^1nd^1 L can only have the value 2, and S can have the values 0 and 1. The possible terms are ^1D and ^3D . Hund's Rules predict that the ^3D term will have the lower energy.

c) ns^2np^1 L can only have the value 1, and S can only have the value $1/2$. The only possible term is ^2P .

d) ns^1np^2 A table such as the table in the text for the p^2 configuration will have three columns, one for each of the electrons, for M_L and M_S . Each of the fifteen states for the p^2 configuration can be combined with $m_s = \pm \frac{1}{2}$ for the ns electron. This gives a total of 30 states. Working through the table gives ^2D , ^4P , ^2P , and ^2S terms. Hund's Rules predict that the ^4P term will have the lowest energy.

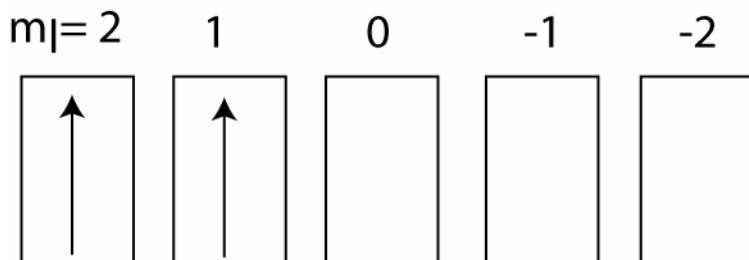
P21.19) The ground-state level for the phosphorus atom is $^4\text{S}_{3/2}$. List the possible values of L , M_L , S , M_S , J , and M_J consistent with this level.

$S = 3/2$ and $L = 0$. M_L can range from $-L$ to $+L$ and can only have the value zero in this case. M_S can range from $-S$ to $+S$ and can have the values $-3/2$, $-1/2$, $1/2$, and $3/2$ in this case. J lies between $|L + S|$ and $|L - S|$ and can only have the value $3/2$ for this case. M_J can range from $-J$ to $+J$ and can have the values $-3/2$, $-1/2$, $1/2$, and $3/2$ in this case.

P21.20) Derive the ground-state term symbols for the following configurations: a) d^2 , b) f^9 , c) f^{14}

The method illustrated in Example Problem 21.7 is used for all parts.

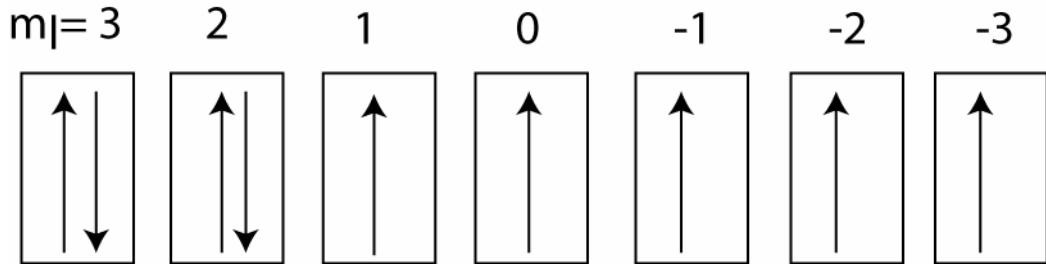
a)



Chapter 21/Multielectron Atoms

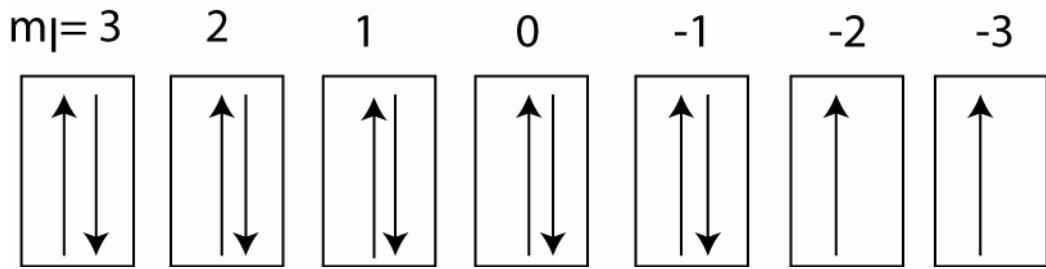
$M_{Lmax} = 3$ and $M_{Smax} = 1$. Therefore, the ground state term is 3F .

b)



$M_{Lmax} = 5$ and $M_{Smax} = 2.5$. Therefore, the ground state term is 6H .

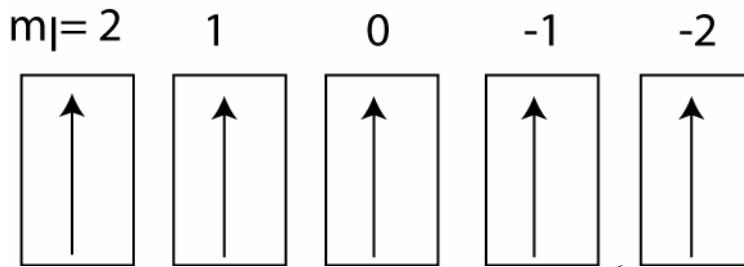
c)



$M_{Lmax} = 5$ and $M_{Smax} = 1$. Therefore, the ground state term is 3H .

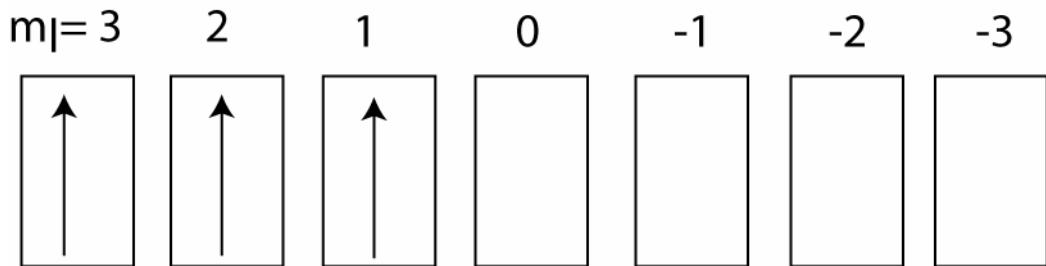
P21.21) Derive the ground-state term symbols for the following configurations:
 a) d^5 , b) f^3 , c) p^4

a) d^5



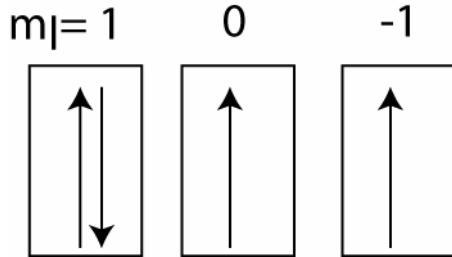
$M_{Lmax} = 0$ and $M_{Smax} = 5/2$. Therefore, the ground state term is 6S .

b) f^3



$M_{Lmax} = 6$ and $M_{Smax} = 3/2$. Therefore, the ground state term is 4I .

c) p^4



$M_{Lmax} = 1$ and $M_{Smax} = 1$. Therefore, the ground state term is 3P .

P21.22) What are the levels that arise from a 4F term? How many states are there in each level?

$S = 3/2$ and $L = 3$. M_L can range from $-L$ to $+L$ and can have the values $-3, -2, -1, 0, 1, 2$, and 3 in this case. M_S can range from $-S$ to $+S$ and can have the values $-3/2, -1/2, 1/2$, and $3/2$ in this case. J lies between $|L + S|$ and $|L - S|$ and can have the values $9/2, 7/2, 5/2$, and $3/2$ for this case.

For $J = 9/2$, M_J can range from $-J$ to $+J$ and can have the values $-9/2, -7/2, -5/2, -3/2, -1/2, 1/2, 3/2, 5/2, 7/2$, and $9/2$. There 10 states in this level.

For $J = 7/2$, M_J can range from $-J$ to $+J$ and can have the values $-7/2, -5/2, -3/2, -1/2, 1/2, 3/2, 5/2$, and $7/2$. There 8 states in this level.

For $J = 5/2$, M_J can range from $-J$ to $+J$ and can have the values $-5/2, -3/2, -1/2, 1/2, 3/2$, and $5/2$. There 6 states in this level.

For $J = 3/2$, M_J can range from $-J$ to $+J$ and can have the values $-3/2, -1/2, 1/2$, and $3/2$. There 4 states in this level.

P21.23) Using Table 21.5, which lists the possible terms that arise from a given configuration, and Hund's rules, write the term symbols for the ground state of the atoms H through F in the form $^{(2S+1)}L_J$.

We use Hund's rule that the term with the highest multiplicity is the lowest in energy to get the left superscript. For the right subscript, if there are several choices for J , the lowest J value gives the lowest energy if the subshell is less than half full, and the highest J value gives the lowest energy if the subshell is exactly or more than half full. Applying these rules gives rise to the following term symbols.

Chapter 21/Multielectron Atoms

Atom	Configuration	Ground state term symbol
H	$1s^1$	$^2S_{1/2}$
He	$1s^2$	1S_0
Li	$1s^2 2s^1$	$^2S_{1/2}$
Be	$1s^2 2s^2$	1S_0
B	$1s^2 2s^2 2p^1$	$^2P_{1/2}$
C	$1s^2 2s^2 2p^2$	3P_0
N	$1s^2 2s^2 2p^3$	$^4S_{3/2}$
O	$1s^2 2s^2 2p^4$	3P_2
F	$1s^2 2s^2 2p^5$	$^2P_{3/2}$

P21.24) Using Table 21.5, which lists the possible terms that arise from a given configuration, and Hund's rules, write the term symbols for the ground state of the atoms K through Cu, excluding Cr, in the form $^{(2S+1)}L_J$.

We use Hund's rule that the term with the highest multiplicity is the lowest in energy to get the left superscript. For the right subscript, if there are several choices for J , the lowest J value gives the lowest energy if the subshell is less than half full, and the highest J value gives the lowest energy if the subshell is exactly or more than half full. Applying these rules gives rise to the following term symbols.

Atom	Configuration	Ground state term symbol
K	$4s^1$	$^2S_{1/2}$
Ca	$4s^2$	1S_0
Sc	$3d^1$	$^2D_{3/2}$
Ti	$3d^2$	3F_2
V	$3d^3$	$^4F_{3/2}$
Mn	$3d^5$	$^6S_{5/2}$
Fe	$3d^6$	5D_4
Co	$3d^7$	$^4F_{9/2}$
Ni	$3d^8$	3F_4
Cu	$4s^1 3d^{10}$	$^2S_{1/2}$

P21.25) Using Table 21.5, which lists the possible terms that arise from a given configuration, and Hund's rules, write the configurations and term symbols for the ground state of the ions F⁻ and Ca²⁺ in the form $^{(2S+1)}L_J$.

We use Hund's rule that the term with the highest multiplicity is the lowest in energy to get the left superscript. For the right subscript, if there are several choices for J , the lowest J value gives the lowest energy if the subshell is less than half full, and the highest

J value gives the lowest energy if the subshell is exactly or more than half full. Applying these rules gives rise to the following term symbols.



P21.26) Derive the ground-state term symbols for the following atoms or ions: a) H, b) F, c) F^- , d) Na, e) Na^+ , f) P, g) Sc

We use Hund's rule that the term with the highest multiplicity is the lowest in energy to get the left superscript. For the right subscript, if there are several choices for J , the lowest J value gives the lowest energy if the subshell is less than half full, and the highest J value gives the lowest energy if the subshell is exactly or more than half full. Applying these rules gives rise to the following term symbols.

Atom	Configuration	Ground state term symbol
H	$1s^1$	${}^2\text{S}_{1/2}$
F	$2s^2 2p^5$	${}^2\text{P}_{3/2}$
F^-	$2s^2 2p^6$	${}^1\text{S}_0$
Na	$3s^1$	${}^2\text{S}_{1/2}$
Na^+	$2s^2 2p^6$	${}^1\text{S}_0$
P	$3p^3$	${}^4\text{S}_{3/2}$
Sc	$3d^1$	${}^2\text{D}_{3/2}$

P21.27) What J values are possible for a ${}^6\text{H}$ term? Calculate the number of states associated with each level and show that the total number of states is the same as calculated from $(2S + 1)(2L + 1)$.

$$S = 5/2, L = 5.$$

J lies between $|L + S|$ and $|L - S|$ and can have the values $15/2, 13/2, 11/2, 9/2, 7/2$, and $5/2$. The number of states is $2J + 1$ or $16, 14, 12, 10, 8$, and 6 , respectively.

This gives a total number of states of $16 + 14 + 12 + 10 + 8 + 6 = 66$.
 $(2S + 1)(2L + 1) = 6 \times 11 = 66$ also.

P21.28) Given that the levels in the ${}^3\text{P}$ term for carbon have the relative energies (expressed in wave numbers) of ${}^3\text{P}_1 - {}^3\text{P}_0 = 16.4 \text{ cm}^{-1}$ and ${}^3\text{P}_2 - {}^3\text{P}_1 = 27.1 \text{ cm}^{-1}$, calculate the ratio of the number of C atoms in the ${}^3\text{P}_2$ and ${}^3\text{P}_0$ levels at 200 and 1000 K.

Because ${}^3\text{P}_1 - {}^3\text{P}_0 = 16.4 \text{ cm}^{-1}$ and ${}^3\text{P}_2 - {}^3\text{P}_1 = 27.1 \text{ cm}^{-1}$, ${}^3\text{P}_2 - {}^3\text{P}_0 = 43.5 \text{ cm}^{-1}$.

$$\frac{n_{3p_2}}{n_{3p_0}} = \frac{g_{3p_2}}{g_{3p_0}} e^{-\frac{\epsilon_{3p_2} - \epsilon_{3p_0}}{kT}} = \frac{g_{3p_2}}{g_{3p_0}} e^{-\frac{hc(\tilde{v}_{3p_2} - \tilde{v}_{3p_0})}{kT}}$$

$$= \frac{5}{1} \exp\left(-\frac{6.634 \times 10^{-34} \text{ J s} \times 2.998 \times 10^{10} \text{ cm s}^{-1} \times 43.5 \text{ cm}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 200 \text{ K}}\right) = 3.65$$

At 1000 K, the ratio is 4.70.

P21.29) The first ionization potential of ground-state He is 24.6 eV. The wavelength of light associated with the $1s2p^1P$ term is 58.44 nm. What is the ionization energy of the He atom in this excited state?

The photon energy is

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{58.44 \times 10^{-9} \text{ m}} \times \frac{1 \text{ J}}{1.602 \times 10^{-19} \text{ J}} = 21.2 \text{ eV}$$

Therefore, the ionization energy of the He atom in this state is $24.6 \text{ eV} - 21.2 \text{ eV} = 3.4 \text{ eV}$.

P21.30) In this problem you will supply the missing steps in the derivation of the formula $E_{\text{singlet}} = E_{1s} + E_{2s} + J + K$ for the singlet level of the $1s^12s^1$ configuration of He.

a) Expand Equation (21.27) to obtain

$$E_{\text{singlet}} = \frac{1}{2} \int [1s(1)2s(2) + 2s(1)1s(2)] (\hat{H}_1) [1s(1)2s(2) + 2s(1)1s(2)] d\tau_1$$

$$+ \frac{1}{2} \int [1s(1)2s(2) + 2s(1)1s(2)] (\hat{H}_2) [1s(1)2s(2) + 2s(1)1s(2)] d\tau_2$$

$$+ \frac{1}{2} \iint [1s(1)2s(2) + 2s(1)1s(2)] \left(\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right) [1s(1)2s(2) + 2s(1)1s(2)] d\tau_1 d\tau_2$$

The integral

$$E_{\text{singlet}} = \frac{1}{2} \iint [1s(1)2s(2) + 2s(1)1s(2)] \left(\hat{H}_1 + \hat{H}_2 + \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right) [1s(1)2s(2) + 2s(1)1s(2)] d\tau_1 d\tau_2$$

can be expressed as the sum of three integrals, each containing one of the three operators. This gives the desired result.

b) Starting from the equations $\hat{H}_i 1s(i) = E_{1s} 1s(i)$ and $\hat{H}_i 2s(i) = E_{2s} 2s(i)$, show that

$$E_{\text{singlet}} = E_{1s} + E_{2s} + \frac{1}{2} \iint [1s(1)2s(2) + 2s(1)1s(2)] \left(\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right) [1s(1)2s(2) + 2s(1)1s(2)] d\tau_1 d\tau_2$$

$$\begin{aligned}
E_{\text{singlet}} &= \frac{1}{2} \iint [1s(1)2s(2) + 2s(1)1s(2)] \left[\hat{H}_1 + \hat{H}_2 + \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right] [1s(1)2s(2) + 2s(1)1s(2)] d\tau_1 d\tau_2 \\
&= \frac{1}{2} \iint [1s(1)2s(2) + 2s(1)1s(2)] (\hat{H}_1) [1s(1)2s(2) + 2s(1)1s(2)] d\tau_1 d\tau_2 \\
&\quad + \frac{1}{2} \iint [1s(1)2s(2) + 2s(1)1s(2)] (\hat{H}_2) [1s(1)2s(2) + 2s(1)1s(2)] d\tau_1 d\tau_2 \\
&\quad + \frac{1}{2} \iint [1s(1)2s(2) + 2s(1)1s(2)] \left[\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right] [1s(1)2s(2) + 2s(1)1s(2)] d\tau_1 d\tau_2
\end{aligned}$$

Letting the operators act on the following wave function gives

$$\begin{aligned}
E_{\text{singlet}} &= \frac{1}{2} \iint [1s(1)2s(2) + 2s(1)1s(2)] [E_{1s}1s(1)2s(2) + E_{2s}2s(1)1s(2)] d\tau_1 d\tau_2 \\
&\quad + \frac{1}{2} \iint [1s(1)2s(2) + 2s(1)1s(2)] [E_{2s}1s(1)2s(2) + E_{1s}2s(1)1s(2)] d\tau_1 d\tau_2 \\
&\quad + \frac{1}{2} \iint [1s(1)2s(2) + 2s(1)1s(2)] \left[\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right] [1s(1)2s(2) + 2s(1)1s(2)] d\tau_1 d\tau_2
\end{aligned}$$

Expanding the previous expression gives

$$\begin{aligned}
E_{\text{singlet}} &= \frac{1}{2} E_{1s} \iint [1s(1)2s(2) + 2s(1)1s(2)] [1s(1)2s(2)] d\tau_1 d\tau_2 \\
&\quad + \frac{1}{2} E_{1s} \iint [1s(1)2s(2) + 2s(1)1s(2)] [2s(1)1s(2)] d\tau_1 d\tau_2 \\
&\quad + \frac{1}{2} E_{2s} \iint [1s(1)2s(2) + 2s(1)1s(2)] [1s(1)2s(2)] d\tau_1 d\tau_2 \\
&\quad + \frac{1}{2} E_{2s} \iint [1s(1)2s(2) + 2s(1)1s(2)] [2s(1)1s(2)] d\tau_1 d\tau_2 \\
&\quad + \frac{1}{2} \iint [1s(1)2s(2) + 2s(1)1s(2)] \left[\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right] [1s(1)2s(2) + 2s(1)1s(2)] d\tau_1 d\tau_2
\end{aligned}$$

Chapter 21/Multielectron Atoms

Each of the first four integrals of the previous expression can be expanded into the sum of two integrals. For example,

$$\begin{aligned} & \frac{1}{2} E_{1s} \iint [1s(1)2s(2) + 2s(1)1s(2)] [1s(1)2s(2)] d\tau_1 d\tau_2 \\ &= \frac{1}{2} E_{1s} \iint [1s(1)2s(2)] [1s(1)2s(2)] d\tau_1 d\tau_2 + \frac{1}{2} E_{1s} \iint [2s(1)1s(2)] [1s(1)2s(2)] d\tau_1 d\tau_2 \end{aligned}$$

Because the orbitals are orthogonal and normalized, the first integral has the value one, and the second has the value zero.

Therefore, the previous expression can be simplified to

$$\begin{aligned} E_{\text{singlet}} &= +\frac{1}{2} E_{1s} + \frac{1}{2} E_{1s} + \frac{1}{2} E_{2s} + \frac{1}{2} E_{2s} \\ &\quad + \frac{1}{2} \iint [1s(1)2s(2) + 2s(1)1s(2)] \left(\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right) [1s(1)2s(2) + 2s(1)1s(2)] d\tau_1 d\tau_2 \\ E_{\text{singlet}} &= E_{1s} + E_{2s} + \frac{1}{2} \iint [1s(1)2s(2) + 2s(1)1s(2)] \left(\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right) [1s(1)2s(2) + 2s(1)1s(2)] d\tau_1 d\tau_2 \end{aligned}$$

This is the desired result.

c) Expand the previous equation using the definitions

$$J = \frac{e^2}{8\pi\epsilon_0} \iint [1s(1)]^2 \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) [2s(2)]^2 d\tau_1 d\tau_2 \text{ and}$$

$$K = \frac{e^2}{8\pi\epsilon_0} \iint [1s(1)2s(2)] \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) [1s(2)2s(1)] d\tau_1 d\tau_2$$

to obtain the desired result, $E_{\text{singlet}} = E_{1s} + E_{2s} + J + K$.

We expand the term involving the operator $\left(\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right)$

Because the operator involves only multiplication, the order of the terms is unimportant, giving

$$\begin{aligned} & \frac{1}{2} \iint [1s(1)2s(2) + 2s(1)1s(2)] \left(\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right) [1s(1)2s(2) + 2s(1)1s(2)] d\tau_1 d\tau_2 \\ &= \frac{1}{2} \iint [1s(1)2s(2)]^2 \left(\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right) d\tau_1 d\tau_2 + \frac{1}{2} \iint [2s(1)1s(2)]^2 \left(\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right) d\tau_1 d\tau_2 \\ &+ \iint [1s(1)2s(2)] \left(\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right) [2s(1)1s(2)] d\tau_1 d\tau_2 \end{aligned}$$

Because the labels in the first two terms are irrelevant to the value for the integral, we can switch the labels 1 and 2 in the second integral.

$$\begin{aligned} &= \iint [1s(1)2s(2)]^2 \left(\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right) d\tau_1 d\tau_2 + \iint [1s(1)2s(2)] \left(\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right) [2s(1)1s(2)] d\tau_1 d\tau_2 \\ &= J + K \end{aligned}$$

Adding $E_{1s} + E_{2s}$ to this result gives the desired answer.

P21.31) For a closed-shell atom, an antisymmetric wave function can be represented by a single Slater determinant. For an open-shell atom, more than one determinant is needed. Show that the wave function for the $M_S = 0$ triplet state of He $1s^12s^1$ is a linear combination of two of the Slater determinants of Example Problem 21.2. Which of the two are needed, and what is the linear combination?

$$\begin{aligned} \psi_{\text{triplet}} &= \frac{1}{\sqrt{2}} [1s(1)2s(2) - 2s(1)1s(2)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ &= \frac{1}{2} [1s(1)2s(2)\alpha(1)\beta(2) + 1s(1)2s(2)\beta(1)\alpha(2) - 2s(1)1s(2)\alpha(1)\beta(2) - 2s(1)1s(2)\beta(1)\alpha(2)] \end{aligned}$$

We next expand the individual determinants $\psi_1(1,2), \psi_2(1,2), \psi_3(1,2)$, and $\psi_4(1,2)$.

$$\begin{aligned} \psi_1(1,2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 2s(2)\beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}} [1s(1)2s(2)\alpha(1)\beta(2) - 2s(1)1s(2)\beta(1)\alpha(2)] \\ \psi_2(1,2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix} = \frac{1}{\sqrt{2}} [1s(1)2s(2)\alpha(1)\alpha(2) - 2s(1)1s(2)\alpha(1)\alpha(2)] \\ \psi_3(1,2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\beta(1) & 2s(1)\beta(1) \\ 1s(2)\beta(2) & 2s(2)\beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}} [1s(1)2s(2)\beta(1)\beta(2) - 2s(1)1s(2)\beta(1)\beta(2)] \\ \psi_4(1,2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\beta(2) & 2s(2)\alpha(2) \end{vmatrix} = \frac{1}{\sqrt{2}} [1s(1)2s(2)\beta(1)\alpha(2) - 2s(1)1s(2)\alpha(1)\beta(2)] \end{aligned}$$

By comparing the first term in the expanded equation for ψ_{triplet} with the eight terms of the same type generated by expanding $\psi_1(1,2), \psi_2(1,2), \psi_3(1,2)$, and $\psi_4(1,2)$, we see

that $\psi_1(1,2)$ must be one component of ψ_{triplet} . By comparing the second term in the expanded equation for ψ_{triplet} with the eight terms of the same type generated by expanding $\psi_1(1,2)$, $\psi_2(1,2)$, $\psi_3(1,2)$, and $\psi_4(1,2)$, we see that $\psi_4(1,2)$ must be the other component of ψ_{triplet} . Because both of the first two terms of ψ_{triplet} are positive,

$$\psi_{\text{triplet}} = \frac{1}{\sqrt{2}} [\psi_1(1,2) + \psi_4(1,2)].$$

Chapter 22: Examples of Spectroscopy Involving Atoms

Problem numbers in italics indicate that the solution is included in the *Student's Solutions Manual*.

Questions on Concepts:

Q22.1) Write an equation giving the relationship between the Rydberg constant for H and for Li²⁺.

Because the Rydberg constant varies as the reduced mass, μ , the ratio $\frac{R_H}{R_{Li^{2+}}}$ is given by
$$\frac{R_H}{R_{Li^{2+}}} = \frac{m_{nuclear}^H}{m_{nuclear}^{Li^{2+}}} \frac{m_{electron} + m_{nuclear}^{Li^{2+}}}{m_{electron} + m_{nuclear}^H}$$

Q22.2) Why is atomic absorption spectroscopy more sensitive in many applications than atomic emission spectroscopy?

Absorption spectra rely on the population of low-lying whereas emission spectroscopy relies on the population of excited states. The low-lying states have a higher population, with few exceptions. Therefore absorption spectroscopy generally has a better signal to noise ratio than emission spectroscopy.

Q22.3) Why does the Doppler Effect lead to a shift in the wavelength of a star, but to a broadening of a transition in a gas?

The wavelength of a star is shifted because all the photon emitters are moving in the same direction with respect to the observer. In a gas, the atoms move randomly and with equal probability in all directions with respect to the observer. This leads to a broadening of the frequency rather than a shift.

Q22.4) How can the width of a laser line be less than that determined by the Doppler broadening?

The laser line is narrowed further than what arises from Doppler broadening as a result of the action of the optical resonator. Not all lasing frequencies are enhanced through the resonator, thereby leading to a narrowing of the frequencies emitted.

Q22.5) Why does one need to put a sample in a vacuum chamber to study it with XPS or AES?

Chapter 22/Examples of Spectroscopy Involving Atoms

The electrons will contain the information on the atom from which they were ejected only if they do not undergo inelastic collisions with gas phase atoms. Therefore, the sample needs to be in a vacuum.

Q22.6) Why is XPS a surface-sensitive technique?

XPS is a surface-sensitive technique because only electrons that do not undergo inelastic collisions before they exit into the vacuum have an energy characteristic of the atom from which they were ejected. Because the inelastic mean free path is on the order of a nanometer, the surface sensitivity is very high.

Q22.7) What is the origin of the chemical shift in XPS?

The origin of the chemical shift in XPS is shielding. If electrons are withdrawn from the atom of interest, the binding energy of the remaining electrons will increase because the orbital is less shielded. This leads to a decrease in the kinetic energy of the emitted electron.

Q22.8) Explain the direction of the chemical shifts for Fe(0), Fe(II), and Fe(III) in Figure 22.14.

As electrons are removed from Fe to form Fe^{2+} or Fe^{3+} , the Fe 2p electrons are less well shielded from the nuclear charge. Therefore, they will experience a higher binding energy. Because the shielding is less effective for Fe^{3+} , it will exhibit the greatest binding energy.

Q22.9) Why is an electronically excited atom more reactive than the same ground-state atom?

It is more reactive because it contains excess energy in the form of electronic energy that can be used to overcome an activation barrier.

Q22.10) Why are two medium-energy photons rather than one high-energy photon used in laser isotope separation?

One high energy photon would ionize all atoms, regardless of their mass. Two photons are needed to utilize the fact that the excited state energies are different for the various isotopes.

Problems

P22.1) Calculate the wavelengths of the first three lines of the Lyman, Balmer, and Paschen series, and the series limit (the shortest wavelength) for each series.

$$\text{Lyman Series: } E_n = R_H \left(\frac{1}{1^2} - \frac{1}{n^2} \right)$$

$$n = 2 \quad E_2 = R_H \left(1 - \frac{1}{4} \right) = \frac{3}{4} R_H = 82258 \text{ cm}^{-1} \quad \lambda = 121.6 \text{ nm}$$

$$n = 3 \quad E_2 = R_H \left(1 - \frac{1}{9} \right) = \frac{8}{9} R_H = 97491 \text{ cm}^{-1} \quad \lambda = 102.6 \text{ nm}$$

$$n = 4 \quad E_2 = R_H \left(1 - \frac{1}{16} \right) = \frac{15}{16} R_H = 102823 \text{ cm}^{-1} \quad \lambda = 97.3 \text{ nm}$$

$$n = \infty \quad E_2 = R_H \left(1 - \frac{1}{\infty} \right) = R_H = 109677 \text{ cm}^{-1} \quad \lambda = 91.2 \text{ nm}$$

$$\text{Balmer Series: } E_n = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

$$n = 3 \quad E_2 = R_H \left(\frac{1}{4} - \frac{1}{9} \right) = \frac{5}{36} R_H = 15233 \text{ cm}^{-1} \quad \lambda = 656.5 \text{ nm}$$

$$n = 3 \quad E_2 = R_H \left(\frac{1}{4} - \frac{1}{16} \right) = \frac{3}{16} R_H = 20565 \text{ cm}^{-1} \quad \lambda = 486.3 \text{ nm}$$

$$n = 4 \quad E_2 = R_H \left(\frac{1}{4} - \frac{1}{25} \right) = \frac{21}{100} R_H = 23032 \text{ cm}^{-1} \quad \lambda = 434.2 \text{ nm}$$

$$n = \infty \quad E_2 = R_H \left(\frac{1}{4} - \frac{1}{\infty} \right) = \frac{1}{4} R_H = 27419 \text{ cm}^{-1} \quad \lambda = 364.7 \text{ nm}$$

$$\text{Paschen Series: } E_n = R_H \left(\frac{1}{3^2} - \frac{1}{n^2} \right)$$

$$n = 4 \quad E_2 = R_H \left(\frac{1}{9} - \frac{1}{16} \right) = \frac{7}{144} R_H = 5331.5 \text{ cm}^{-1} \quad \lambda = 1876 \text{ nm}$$

$$n = 5 \quad E_2 = R_H \left(\frac{1}{9} - \frac{1}{25} \right) = \frac{16}{225} R_H = 7799.3 \text{ cm}^{-1} \quad \lambda = 1282 \text{ nm}$$

$$n = 6 \quad E_2 = R_H \left(\frac{1}{9} - \frac{1}{36} \right) = \frac{1}{12} R_H = 9139.8 \text{ cm}^{-1} \quad \lambda = 1094 \text{ nm}$$

$$n = \infty \quad E_2 = R_H \left(\frac{1}{9} - \frac{1}{\infty} \right) = \frac{1}{9} R_H = 12186.4 \text{ cm}^{-1} \quad \lambda = 820.6 \text{ nm}$$

P22.2) As discussed in Chapter 20, in a more exact solution of the Schrödinger equation for the hydrogen atom, the coordinate system is placed at the center of mass of the atom rather than at the nucleus. In that case, the energy levels for a one-electron atom or ion of nuclear charge Z are given by

$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}$$

Chapter 22/Examples of Spectroscopy Involving Atoms

where μ is the reduced mass of the atom. The masses of an electron, a proton, and a tritium (${}^3\text{H}$ or T) nucleus are given by $9.1094 \times 10^{-31} \text{ kg}$, $1.6726 \times 10^{-27} \text{ kg}$ and $5.0074 \times 10^{-27} \text{ kg}$, respectively. Calculate the frequency of the $n = 1 \rightarrow n = 4$ transition in H and T to five significant figures. Which of the transitions, $1s \rightarrow 4s$, $1s \rightarrow 4p$, $1s \rightarrow 4d$, could the frequencies correspond to?

The frequencies differ because the reduced mass is different for H and T.

$$\mu_H = \frac{m_{proton} \times m_{electron}}{m_{proton} + m_{electron}} = \frac{(1.6726 \times 10^{-27} \text{ kg})(9.1094 \times 10^{-31} \text{ kg})}{1.6726 \times 10^{-27} \text{ kg} + 9.1094 \times 10^{-31} \text{ kg}} = 9.10444 \times 10^{-31} \text{ kg}$$

$$\mu_T = \frac{m_{tritium+} \times m_{electron}}{m_{tritium+} + m_{electron}} = \frac{(5.0074 \times 10^{-27} \text{ kg})(9.1094 \times 10^{-31} \text{ kg})}{5.0074 \times 10^{-27} \text{ kg} + 9.1094 \times 10^{-31} \text{ kg}} = 9.10774 \times 10^{-31} \text{ kg}$$

$$E_H(n) = -\frac{Z^2 \mu_H e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} = \frac{9.10444 \times 10^{-31} \text{ kg} \times (1.6021773 \times 10^{-19} \text{ C})^4}{32\pi^2 \times (8.8541878 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1})^2 \times (1.054573 \times 10^{-34} \text{ J s})^2 \times n^2}$$

$$E_H(n) = \frac{2.17869 \times 10^{-18} \text{ J}}{n^2}. \text{ Similarly,}$$

$$E_T(n) = \frac{2.17948 \times 10^{-18} \text{ J}}{n^2}$$

$$\nu_H = \frac{2.17869 \times 10^{-18} \text{ J}}{6.6260755 \times 10^{-34} \text{ Js}} \left(1 - \frac{1}{4^2}\right) = 3.08255 \times 10^{15} \text{ s}^{-1}$$

$$\nu_T = \frac{2.17948 \times 10^{-18} \text{ J}}{6.6260755 \times 10^{-34} \text{ Js}} \left(1 - \frac{1}{4^2}\right) = 3.08367 \times 10^{15} \text{ s}^{-1}$$

Of the transitions $1s \rightarrow 4s$, $1s \rightarrow 4p$, $1s \rightarrow 4d$, only the transition $1s \rightarrow 4p$ is allowed.

P22.3) The Lyman series in the hydrogen atom corresponds to transitions that originate from the $n = 1$ level in absorption or that terminate in the $n = 1$ level for emission. Calculate the energy, frequency (in inverse seconds and inverse centimeters), and wavelength of the least and most energetic transition in this series.

$$\tilde{\nu} = R_H \left(\frac{1}{n_{initial}^2} - \frac{1}{n_{final}^2} \right)$$

$$\tilde{\nu}_{max} = R_H \left(\frac{1}{1} - \frac{1}{\infty} \right) = 109677 \text{ cm}^{-1}$$

$$E_{max} = hc\tilde{\nu}_{max} = 6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^{10} \text{ cm s}^{-1} \times 109677 \text{ cm}^{-1} = 2.178 \times 10^{-18} \text{ J}$$

$$\nu_{max} = c\tilde{\nu}_{max} = 2.998 \times 10^{10} \text{ cm s}^{-1} \times 109677 \text{ cm}^{-1} = 3.288 \times 10^{15} \text{ s}^{-1}$$

$$\lambda_{max} = \frac{1}{\tilde{\nu}_{max}} = 91.18 \text{ nm}$$

$$\tilde{\nu}_{min} = R_H \left(\frac{1}{1} - \frac{1}{2^2} \right) = \frac{3 \times 109677 \text{ cm}^{-1}}{4} = 82257 \text{ cm}^{-1}$$

$$E_{min} = hc\tilde{\nu}_{min} = 6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^{10} \text{ cm s}^{-1} \times 82257 \text{ cm}^{-1} = 1.634 \times 10^{-18} \text{ J}$$

$$\nu_{min} = c\tilde{\nu}_{min} = 2.998 \times 10^{10} \text{ cm s}^{-1} \times 82257 \text{ cm}^{-1} = 2.466 \times 10^{15} \text{ s}^{-1}$$

$$\lambda_{min} = \frac{1}{\tilde{\nu}_{min}} = 121.6 \text{ nm}$$

P22.4) The spectrum of the hydrogen atom reflects the splitting of the $1s^2 S$ and $2p^2 P$ terms into levels. The energy difference between the levels in each term is much smaller than the difference in energy between the terms. Given this information, how many spectral lines are observed in the $1^2S \rightarrow 2^2P$ transition? Are the frequencies of these transitions very similar or quite different?

The 2S term has a single level, $^2S_{1/2}$. The 2P term splits into two levels, $^2P_{1/2}$ and $^2P_{3/2}$. Therefore, there will be two closely spaced lines in the spectrum corresponding to the transitions $^2S_{1/2} \rightarrow ^2P_{1/2}$ and $^2S_{1/2} \rightarrow ^2P_{3/2}$. The energy spacing between the lines will be much smaller than the energy of the transition.

P22.5) The Grotrian diagram in Figure 22.1 shows a number of allowed electronic transitions for He. Which of the following transitions shows multiple spectral peaks due to a splitting of terms into levels? How many peaks are observed in each case? Are any of the following transitions between energy levels forbidden by the selection rules?

- a) $1s^2 \ ^1S \rightarrow 1s2p \ ^1P$ b) $1s2p \ ^1P \rightarrow 1s3s \ ^1S$ c) $1s2s \ ^3S \rightarrow 1s2p \ ^3P$ d) $1s2p \ ^3P \rightarrow 1s3d \ ^3D$

a) $1s^2 \ ^1S \rightarrow 1s2p \ ^1P$ No splitting because each term consists of a single level.

b) $1s2p \ ^1P \rightarrow 1s3s \ ^1S$ No splitting because each term consists of a single level.

c) $1s2s \ ^3S \rightarrow 1s2p \ ^3P$ The 3P term is split into 3 levels, 3P_2 , 3P_1 , and 3P_0 and the 3S term has one level. The selection rule is $\Delta J = 0, \pm 1$. Therefore there will be three peaks corresponding to the $^3S \rightarrow ^3P_2$, $^3S \rightarrow ^3P_1$, and $^3S \rightarrow ^3P_0$ transitions.

d) $1s2p\ ^3P \rightarrow 1s3d\ ^3D$ The 3P term is split into 3 levels, 3P_2 , 3P_1 , and 3P_0 , and the 3D term is split into 3 levels, 3D_3 , 3D_2 , and 3D_1 . The selection rule is $\Delta J = 0, \pm 1$. The allowed transitions are $^3P_2 \rightarrow ^3D_3$, $^3P_2 \rightarrow ^3D_2$, and $^3P_2 \rightarrow ^3D_1$; $^3P_1 \rightarrow ^3D_2$ and $^3P_1 \rightarrow ^3D_1$; $^3P_0 \rightarrow ^3D_2$, $^3P_0 \rightarrow ^3D_1$. Therefore there will be six peaks.

P22.6) Use the transition frequencies shown in Example Problem 22.2 to calculate the energy (in joules and electron-volts) of the six levels relative to the $3s\ ^2S_{1/2}$ level. State your answers with the correct number of significant figures.

$$E\left(3p\ ^2P_{1/2}\right) = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{589.6 \times 10^{-9} \text{ m}} = 3.369 \times 10^{-19} \text{ J} = 2.102 \text{ eV}$$

$$E\left(3p\ ^2P_{3/2}\right) = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{589.0 \times 10^{-9} \text{ m}} = 3.373 \times 10^{-19} \text{ J} = 2.105 \text{ eV}$$

$$E\left(4s\ ^2S_{1/2}\right) = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{589.6 \times 10^{-9} \text{ m}} + \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{1183.3 \times 10^{-9} \text{ m}} \\ = 5.048 \times 10^{-19} \text{ J} = 3.150 \text{ eV}$$

$$E\left(5s\ ^2S_{1/2}\right) = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{589.0 \times 10^{-9} \text{ m}} + \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{616.0 \times 10^{-9} \text{ m}} \\ = 6.597 \times 10^{-19} \text{ J} = 4.118 \text{ eV}$$

$$E\left(3d\ ^2D_{3/2}\right) = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{589.6 \times 10^{-9} \text{ m}} + \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{818.3 \times 10^{-9} \text{ m}} \\ = 5.797 \times 10^{-19} \text{ J} = 3.618 \text{ eV}$$

$$E\left(4d\ ^2D_{3/2}\right) = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{589.0 \times 10^{-9} \text{ m}} + \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{568.2 \times 10^{-9} \text{ m}} \\ = 6.869 \times 10^{-19} \text{ J} = 4.287 \text{ eV}$$

P22.7) The absorption spectrum of the hydrogen atom shows lines at 5334, 7804, 9145, 9953, and $10,478 \text{ cm}^{-1}$. There are no lower frequency lines in the spectrum. Use the graphical methods discussed in Example Problem 22.1 to determine $n_{initial}$ and the ionization energy of the hydrogen atom in this state. Assume values for $n_{initial}$ of 1, 2, and 3.

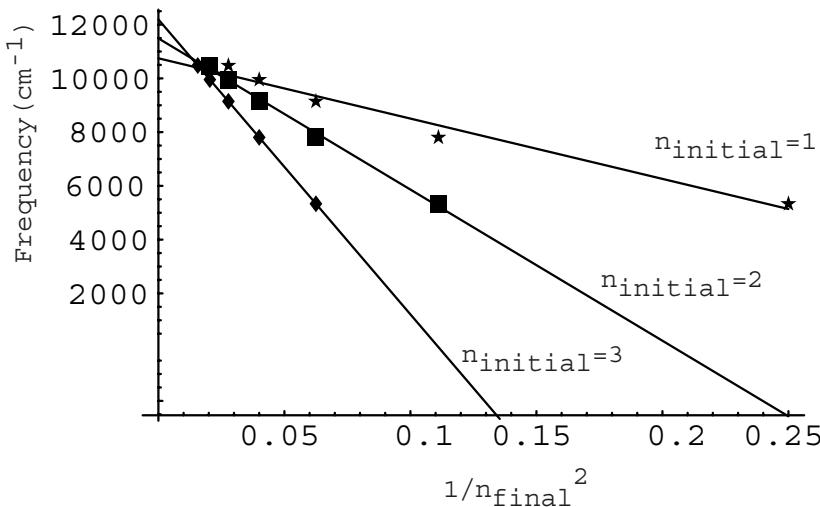
The slope of a plot of $\tilde{\nu}$ versus assumed values of $\frac{1}{n_{final}^2}$ will have a slope of $-R_H$ and an

intercept with the frequency axis of $\frac{R_H}{n_{initial}^2}$. However, both $n_{initial}$ and n_{final} are unknown,

so that in plotting the data, we have to assign n_{final} values to the observed frequencies. Because there are no lower frequency lines in the spectrum, we know that the lowest value for n_{final} is $n_{initial} + 1$. We try different combinations of n_{final} values and see if the

slope and intercept are consistent with the expected values of $-R_H$ and $\frac{R_H}{n_{initial}^2}$. In this case,

we assume that the sequence of spectral lines corresponds to $n_{final} = 2, 3, 4, 5$, and 6 for an assumed value of $n_{initial} = 1$, $n_{final} = 3, 4, 5, 6$, and 7 for an assumed value of $n_{initial} = 2$, and $n_{final} = 4, 5, 6, 7$, and 8 for an assumed value of $n_{initial} = 3$. The plots are shown below.



The slopes and intercepts calculated for these assumed values of $n_{initial}$ are:

Assumed $n_{initial}$	Slope (cm^{-1})	Intercept (cm^{-1})
1	-2.24×10^4	1.07×10^4
2	-5.63×10^4	1.15×10^4
3	-1.09×10^5	1.22×10^4

By examining the consistency of these values with the expected values, we conclude that $n_{initial} = 3$. The ionization energy of the hydrogen atom in this state is $\frac{hcR_H}{3^2}$, corresponding to $n_{final} \rightarrow \infty$, or $2.42 \times 10^{-19} \text{ J}$.

P22.8) Calculate the transition dipole moment,

$\mu_z^{mn} = \int \psi_m^*(\tau) \mu_z \psi_n(\tau) d\tau$ where $\mu_z = -er \cos \theta$ for a transition from the 1s level to the 2s level in H. Show that this transition is forbidden. The integration is over r , θ , and ϕ .

$$\mu_z^{21} = -\frac{\mu_z E_0}{2} \int \psi_2^* \mu_z \psi_1 d\tau = -\frac{\mu_z E_0}{2} 2\pi \int_0^\pi \sin \theta d\theta \int_0^\infty r^2 \psi_{2s}^*(r) r \cos \theta \psi_{1s}(r) dr$$

We need to show that the integral

$$\int_0^\pi \sin \theta d\theta \int_0^\infty r^2 \psi_{2s}^*(r) r \cos \theta \psi_{1s}(r) dr = 0.$$

This can be shown by carrying out the integration over θ .

$$\int_0^\pi \sin \theta \cos \theta d\theta = \frac{1}{2} [\sin^2 \theta]_0^\pi = 0$$

P22.9) Calculate the transition dipole moment,

$\mu_z^{mn} = \int \psi_m^*(\tau) \mu_z \psi_n(\tau) d\tau$ where $\mu_z = -er \cos \theta$ for a transition from the 1s level to the $2p_z$ level in H. Show that this transition is allowed. The integration is over r , θ , and ϕ .

Use $\psi_{210}(r, \theta, \phi) = \frac{1}{\sqrt{32\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$ for the $2p_z$ wave function.

$$\begin{aligned}\mu_z^{21} &= -e \int \psi_2^* \mu_z \psi_1 d\tau = -e 2\pi \int_0^\pi \sin \theta d\theta \int_0^\infty r^2 \psi_{2p_z}^*(r) r \cos \theta \psi_{1s}(r) dr \\ &= -e 2\pi \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \int_0^\pi \sin \theta \cos^2 \theta d\theta \int_0^\infty r^2 (e^{-r/2a_0} r \cos \theta) (e^{-r/a_0}) dr \\ &= -e \frac{1}{2\sqrt{2}} \left(\frac{1}{a_0}\right)^3 \int_0^\pi \sin \theta \cos^2 \theta d\theta \int_0^\infty r^2 (e^{-r/2a_0}) r \cos \theta (e^{-r/a_0}) dr \\ &= -e \frac{1}{2\sqrt{2}} \left(\frac{1}{a_0}\right)^3 \left(-\frac{1}{3} [\cos^3 \theta]_0^\pi\right) \int_0^\infty r^3 \left(e^{-\frac{3r}{2a_0}}\right) dr \\ &= -e \frac{1}{2\sqrt{2}} \left(\frac{1}{a_0}\right)^3 \times \frac{2}{3} \times \frac{3!}{\left(\frac{3}{2a_0}\right)^4} = -\frac{e}{2\sqrt{2}} \times \frac{2}{3} \times \frac{3! 2^4}{3^4} \left(\frac{1}{a_0}\right)^3 a_0^4 = -\frac{16\sqrt{2} e}{81} a_0\end{aligned}$$

Because the transition dipole moment is different from zero, the transition is allowed.

P22.10) In the Na absorption spectrum, the following transitions are observed:

$$\begin{aligned}4p\ ^2P - 3s\ ^2S &\quad \lambda = 330.26 \text{ nm} \\ 3p\ ^2P - 3s\ ^2S &\quad \lambda = 589.593 \text{ nm}, 588.996 \text{ nm} \\ 5s\ ^2S - 3p\ ^2P &\quad \lambda = 616.073 \text{ nm}, 615.421 \text{ nm}\end{aligned}$$

Calculate the energies of the $4p\ ^2P$ and $5s\ ^2S$ states with respect to the $3s\ ^2S$ ground state.

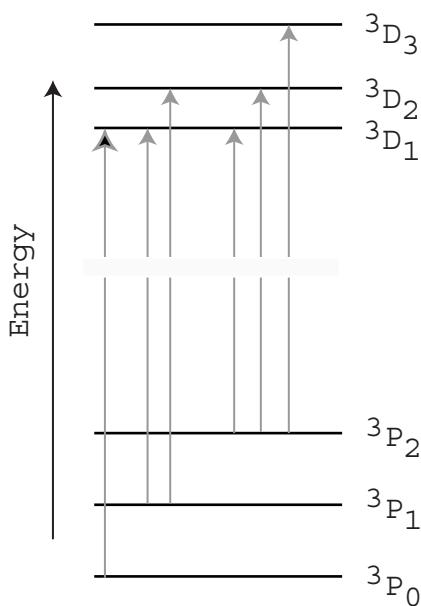
$$E(4p\ ^2P) = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ ms}^{-1}}{330.26 \times 10^{-9} \text{ m}} = 6.015 \times 10^{-19} \text{ J} = 3.754 \text{ eV}$$

By looking at the Grotrian diagram of Example Problem 22.2, it is seen that the $5s\ ^2S$ state is accessed by absorption of the photons of wavelength 588.996 nm and 616.073 nm.

$$\begin{aligned}E(5s\ ^2S) &= \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ ms}^{-1}}{5888.996 \times 10^{-9} \text{ m}} + \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ ms}^{-1}}{616.073 \times 10^{-9} \text{ m}} \\ &= 6.597 \times 10^{-19} \text{ J} = 4.117 \text{ eV}\end{aligned}$$

P22.11) Consider the $1s\ np\ ^3P \rightarrow 1s\ nd\ ^3D$ transition in He. Draw an energy-level diagram, taking the spin-orbit coupling that splits terms into levels into account. Into how many levels does each term split? The selection rule for transitions in this case is $\Delta J = 0, \pm 1$. How many transitions will be observed in an absorption spectrum? Show the allowed transitions in your energy diagram.

For the 3P term, $L = 1$, $S = 1$, and J can have the values 2, 1, and 0. There will be three levels. For the 3D term, $L = 2$, $S = 1$, and J can have the values 3, 2, and 1. There will be three levels. For the given selection rules, there will be 6 transitions as indicated in the figure below.



P22.12) Atomic emission experiments of a mixture show a calcium line at 422.673 nm corresponding to a $^1P_1 \rightarrow ^1S_0$ transition and a doublet due to potassium $^2P_{3/2} \rightarrow ^2S_{1/2}$ and $^2P_{1/2} \rightarrow ^2S_{1/2}$ transitions at 764.494 nm and 769.901 nm, respectively.

- Calculate the ratio $\frac{g_{upper}}{g_{lower}}$ for each of these transitions.
- Calculate $\frac{n_{upper}}{n_{lower}}$ for a temperature of 1600°C for each transition.
- Calculate the ratio $\frac{g_{upper}}{g_{lower}}$ for each of these transitions.

Chapter 22/Examples of Spectroscopy Involving Atoms

$$\frac{g_{upper}}{g_{lower}} = \frac{2J_{upper} + 1}{2J_{lower} + 1}$$

$$^1P_1 \rightarrow ^1S_0: \frac{g_{upper}}{g_{lower}} = \frac{3}{1} \quad ^2P_{3/2} \rightarrow ^2S_{1/2}: \frac{g_{upper}}{g_{lower}} = \frac{4}{2} = 2$$

$$^2P_{1/2} \rightarrow ^2S_{1/2}: \frac{g_{upper}}{g_{lower}} = \frac{2}{2} = 1$$

b) Calculate $\frac{n_{upper}}{n_{lower}}$ for each transition at a temperature of 1600°C.

$$\frac{n_{upper}}{n_{lower}} = \frac{g_{upper}/kT}{g_{lower}} = \frac{g_{upper}}{g_{lower}} e^{-\frac{hc\tilde{\nu}}{kT}}$$

$$^1P_1 \rightarrow ^1S_0: \frac{n_{upper}}{n_{lower}} = \frac{g_{upper}}{g_{lower}} e^{-\frac{hc\tilde{\nu}}{kT}} = 3 \exp\left(-\frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ ms}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 1873 \text{ K} \times 422.673 \times 10^{-9} \text{ m}}\right) = 3.86 \times 10^{-8}$$

$$^2P_{3/2} \rightarrow ^2S_{1/2}: \frac{n_{upper}}{n_{lower}} = \frac{g_{upper}}{g_{lower}} e^{-\frac{hc\tilde{\nu}}{kT}} = 2 \exp\left(-\frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ ms}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 1873 \text{ K} \times 764.494 \times 10^{-9} \text{ m}}\right) = 8.67 \times 10^{-5}$$

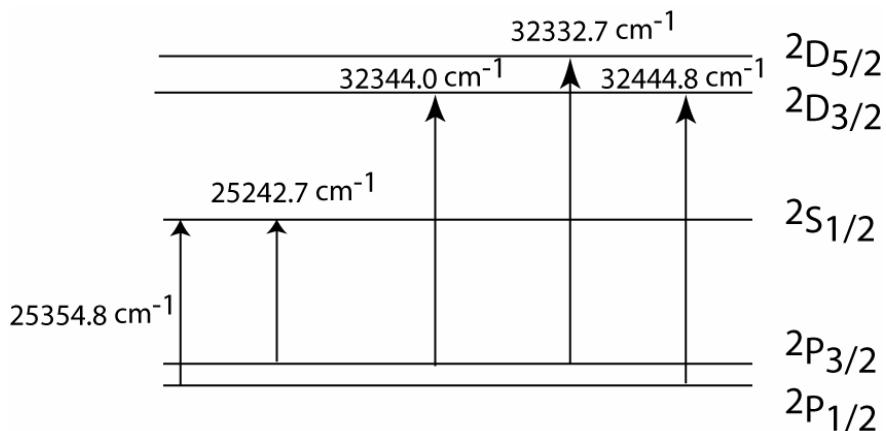
$$^2P_{1/2} \rightarrow ^2S_{1/2}: \frac{n_{upper}}{n_{lower}} = \frac{g_{upper}}{g_{lower}} e^{-\frac{hc\tilde{\nu}}{kT}} = \exp\left(-\frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ ms}^{-1}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 1873 \text{ K} \times 769.901 \times 10^{-9} \text{ m}}\right) = 4.65 \times 10^{-5}$$

P22.13) The principal line in the emission spectrum of sodium is violet. On close examination, the line is seen to be a doublet with wavelengths 393.366 and 396.487 nm. Explain the source of this doublet.

The lower lying state is the level and state $^2S_{1/2}$, and the upper level is 2P , which contains the states $^2P_{1/2}$ and $^2P_{3/2}$. Both transitions are allowed, and the 589.0 nm wavelength corresponds to the transition between the ground state and $^2P_{3/2}$ because states with higher J lie lower in energy. The 589.6 nm wavelength corresponds to the transition between the ground state and $^2P_{1/2}$.

P22.14) The transition $\text{Al}[\text{Ne}](3s)^2(3p)^1 \rightarrow \text{Al}[\text{Ne}](3s)^2(4s)^1$ has two lines given by $\tilde{\nu} = 25354.8 \text{ cm}^{-1}$ and $\tilde{\nu} = 25242.7 \text{ cm}^{-1}$. The transition $\text{Al}[\text{Ne}](3s)^2(3p)^1 \rightarrow \text{Al}[\text{Ne}](3s)^2(3d)^1$ has three lines given by $\tilde{\nu} = 32444.8 \text{ cm}^{-1}$, $\tilde{\nu} = 32334.0 \text{ cm}^{-1}$, and $\tilde{\nu} = 32332.7 \text{ cm}^{-1}$. Sketch an energy-level diagram of the states involved and explain the source of all lines. [Hint: The lowest energy levels are P levels and the highest are D levels. The energy spacing between the D levels is greater than for the P levels.]

The $\text{Al}[\text{Ne}](3s)^2(4s)^1$ configuration corresponds to a $^2S_{1/2}$ state. The $\text{Al}[\text{Ne}](3s)^2(3p)^1$ configuration contains two levels, $^2P_{1/2}$ and $^2P_{3/2}$. The $\text{Al}[\text{Ne}](3s)^2(3d)^1$ configuration contains two levels, $^2D_{3/2}$ and $^2D_{5/2}$. The relative order of these levels is $^2P_{1/2} < ^2S_{1/2} < ^2D_{3/2} < ^2D_{5/2}$. In each case, the level with the smaller J value has the lower energy. The levels are sketched below (not to scale). With the information given, the most energetic transition must be $^2P_{3/2} \rightarrow ^2D_{5/2}$, and the least energetic $^2P_{3/2} \rightarrow ^2S_{1/2}$. The rest of the transitions can be assigned on the basis of the level spacings.



P22.15) The Doppler broadening in a gas can be expressed as $\Delta\nu = \frac{2\nu_0}{c} \sqrt{\frac{2RT \ln 2}{M}}$,

where M is the molar mass. For the sodium $3p\ ^2P_{3/2} \rightarrow 3s\ ^2P_{1/2}$ transition,

$\nu_0 = 5.0933 \times 10^{14} \text{ s}^{-1}$. Calculate $\Delta\nu$ and $\Delta\nu/\nu_0$ at 500 K.

$$\Delta\nu = \frac{2\nu}{c} \sqrt{\frac{2kT \ln 2}{m}} = \frac{2 \times 5.0933 \times 10^{14} \text{ s}^{-1}}{2.998 \times 10^8 \text{ m s}^{-1}} \times \sqrt{\frac{2 \ln 2 \times 1.381 \times 10^{-23} \text{ J K}^{-1} \times 500 \text{ K}}{22.99 \text{ amu} \times \frac{1.661 \times 10^{-27} \text{ kg}}{\text{amu}}}} = 1.70 \times 10^9 \text{ s}^{-1}$$

$$\frac{\Delta\nu}{\nu} = \frac{1.70 \times 10^9 \text{ s}^{-1}}{5.0933 \times 10^{14} \text{ s}^{-1}} = 3.33 \times 10^{-6}$$

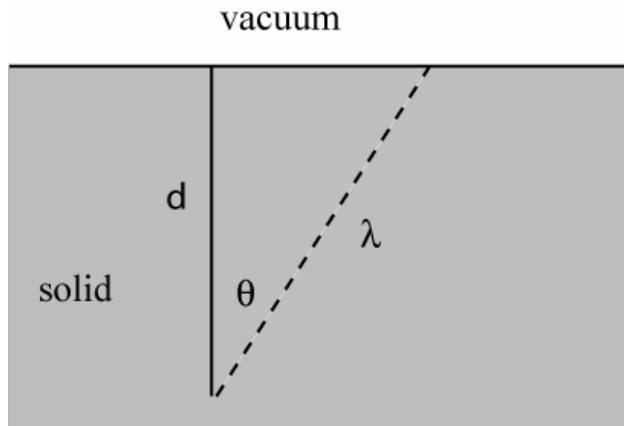
P22.16) The inelastic mean free path of electrons in a solid, λ , governs the surface sensitivity of techniques such as AES and XPS. The electrons generated below the surface must make their way to the surface without losing energy in order to give elemental and chemical shift information. An empirical expression for elements that gives λ as a function of the kinetic energy of the electron generated in AES or XPS is $\lambda = 538E^{-2} + 0.41(lE)^{0.5}$. The units of λ are monolayers, E is the kinetic energy of the electron, and l is the monolayer thickness in nanometers. On the basis of this equation, what kinetic energy maximizes the surface sensitivity for a monolayer thickness of 0.3 nm? An equation solver would be helpful in obtaining the answer.

$$\frac{d}{dE} (538E^{-2} + 0.41(lE)^{0.5}) = -\frac{1076}{E^3} + \frac{0.1123}{\sqrt{E}}$$

Setting the derivative equal to zero and solving for E gives two complex roots and $E = 39 \text{ eV}$.

P22.17) The effective path length that an electron travels before being ejected into the vacuum is related to the depth below the surface at which it is generated and the exit angle by $d = \lambda \cos \theta$, where λ is the inelastic mean free path and θ is the angle between the surface normal and the exit direction.

- a) Justify this equation based on a sketch of the path that an electron travels before exiting into the vacuum.



If the electron emerges other than normal to the surface, its path is longer and given by $d = \lambda \cos \theta$.

- b) The XPS signal from a thin layer on a solid surface is given by $I = I_0 \left(1 - e^{-d/\lambda \cos \theta}\right)$.

I_0 is the signal that would be obtained from an infinitely thick layer and d and λ were defined in Problem P22.16. Calculate the ratio $\frac{I}{I_0}$ at $\theta = 0$ for $\lambda = 2d$. Calculate the exit angle required to increase $\frac{I}{I_0}$ to 0.50.

$$I = I_0 \left(1 - e^{-d/\lambda \cos \theta}\right); \frac{I}{I_0} = 1 - e^{-d/\lambda \cos \theta} = 1 - e^{-\frac{d}{2d}} = 0.39.$$

$$\cos \theta = -\frac{1}{2 \ln \left(\frac{I}{I_0}\right)} = -\frac{1}{2 \ln (0.50)} = 0.721$$

$$\theta = 44^\circ$$

Chapter 23: Chemical Bonding in H_2^+ and H_2

Q23.1) Justify the Born-Oppenheimer approximation based on vibrational frequencies and electron relaxation times.

Atoms are much more massive than electrons. Therefore, the vibrational period (inverse frequency) of a molecule is significantly longer than the relaxation time needed for the much less massive electrons to adjust to the periodic changes in the nuclear positions. For this reason, the nuclear motion can be decoupled from the electron motion.

Q23.2) Why are the magnitudes of the coefficients c_a and c_b in the H_2^+ wavefunctions ψ_g and ψ_u equal?

H_2 is a homonuclear diatomic molecule. Therefore $\psi^*\psi$ must be independent of which nucleus is called a , and which is called b . Expressed mathematically,

$$(c_a \phi_{H1s_a} + c_b \phi_{H1s_b})^* (c_a \phi_{H1s_a} + c_b \phi_{H1s_b}) = (c_a \phi_{H1s_b} + c_b \phi_{H1s_a})^* (c_a \phi_{H1s_b} + c_b \phi_{H1s_a}) \text{ only if } |c_a| = |c_b|.$$

Q23.3) If there is a node in ψ_u , is the electron in this wave function really delocalized? How does it get from one side of the node to the other?

This same problem arose in discussing the particle in the box, and is only a problem if wave particle duality is ignored. A vibrating guitar string has a node in the first harmonic, but this doesn't prevent both parts of the string from emitting sound waves. Similarly, the electron already has a probability of being on both sides of the node. Therefore, it doesn't need to get from one side of the node to the other.

Q23.4) For the case of two $\text{H}1s$ AOs in an H_2 molecule, the value of the overlap integral S_{ab} is never exactly zero. Explain this statement.

This is the case because amplitude of the atomic wave functions falls off exponentially. Therefore the amplitude never reaches zero. Therefore, S_{ab} will be greater than zero, although very small, when the atoms are widely separated.

Q23.5) For H_2^+ , explain why H_{aa} is the total energy of an undisturbed hydrogen atom separated from a bare proton by the distance R .

Imagine an undisturbed hydrogen atom separated from a bare proton by the distance R .

The energy of the total system is the energy of the atom, E_{1s} , plus the interaction energy between the two nuclei, $\frac{e^2}{4\pi\epsilon_0 R}$ and the energy of the electron on the H atom interacting with the bare proton. Treating the electron as a diffuse electron charge, the last term is J . The sum of these three terms is H_{aa} .

Q23.6) By considering each term in the integrand why the values of J and K are positive for H_2^+ .

For J , the integrand is $\phi_{H1s_a}^* \left(\frac{e^2}{4\pi\epsilon_0 r_b} \right) \phi_{H1s_a}$. Because all three factors in this expression are positive everywhere, the integrand is positive everywhere. Therefore, the value of the integral is greater than zero. Exactly the same argument can be made for K .

Q23.7) Why can you conclude that the energy of the antibonding MO in H_2^+ is raised more than the energy of the bonding MO is lowered?

ΔE_g and ΔE_u have the same expressions in the numerator. However, ΔE_g has $1 + S_{ab}$ in the denominator, whereas ΔE_u has $1 - S_{ab}$ in the denominator. Because $S_{ab} > 0$, $1 + S_{ab} > 1$, and $1 - S_{ab} < 1$. Therefore, $\Delta E_u > \Delta E_g$.

Q23.8) Using Figures 23.8 and 23.9, explain why $\psi_g^2 < 0$ and $\psi_u^2 > 0$ outside of the bonding region of H_2^+ .

The solid curve is the difference between ψ^2 for the molecular wave function and for two noninteracting H atoms. Therefore, it represents the shift in the electron density for forming a molecule in the u and g states. Because the solid curve is negative in the bonding region for the u state, charge must be shifted outside of the bonding region. This is the case because the total probability density ψ^2 is conserved. Similarly, because the solid curve is positive in the bonding region for the g state, charge must be shifted into the bonding region.

Q23.9) Why is it necessary to include some ionic character in the wave function for the ground state of H_2 to better approximate the true wave function?

The calculated energy is lower after the inclusion of the ionic terms in the wave function. Because the variational theorem states that a lowering of the energy occurs as a result of an improvement in the wave function, we can conclude that the ionic terms are necessary to adequately describe bonding in H_2 .

Q23.10) How can you conclude that the molecular wave function for H_2 in the molecular orbital model given in Equation (23.20) does not describe dissociation correctly?

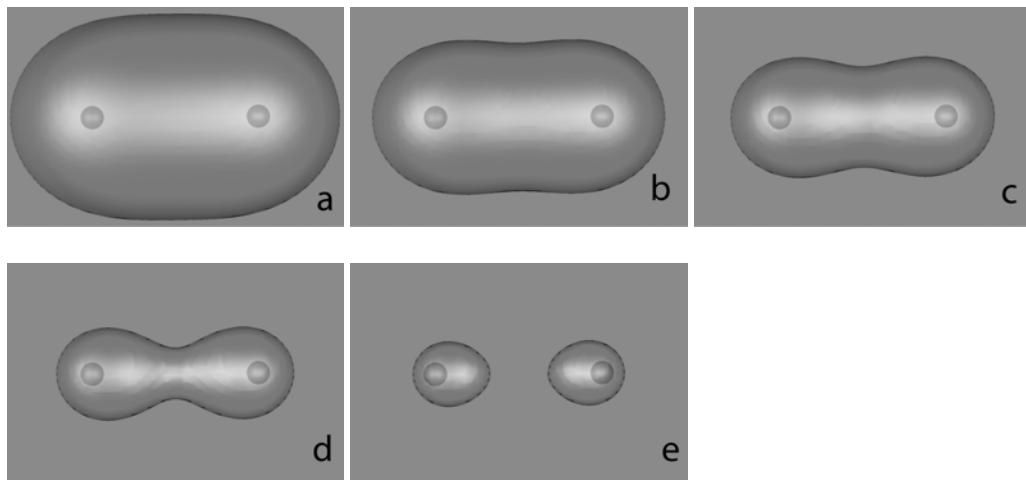
Each of the four terms,

$1s_a(1)1s_b(2)$, $1s_b(1)1s_a(2)$, $1s_a(1)1s_a(2)$, and $1s_b(1)1s_b(2)$ represents a possible outcome of an individual experiment in which the charge on the hydrogen atoms is measured after dissociation. This wave function therefore predicts that 50% of the dissociation events will lead to H^+ and H^- rather than 100% of the dissociation events will lead to two neutral H atoms as is actually observed.

Q23.11) What is the difference between a molecular orbital and a molecular wave function?

A molecular orbital is a one electron wave function that is delocalized over the whole molecule. A molecular wave function is an n electron wave function that is delocalized over the whole molecule.

Q23.12) The following images show contours of constant electron density for H_2 calculated using the methods described in Chapter 27. The values of electron density are (a) 0.10, (b) 0.15, (c) 0.20, (d) 0.25, (e) 0.30 electrons/ a_0^3 .



a) Explain why the apparent size of the H_2 molecule as approximated by the volume inside the contour varies in the sequence a–e.

The amplitude of the wave function and therefore the probability density falls off as the distance from the nuclei increases. Therefore, contours of higher electron density lie closer to the molecule and will appear smaller in a contour plot.

b) Notice the neck that forms between the two hydrogen atoms in contours c and d. What does neck formation tell you about the relative density in the bonding region and in the region near the nuclei?

The neck shows that the electron density in the bonding region is smaller than the electron density near the nuclei.

- c) Explain the shape of the contours in image e by comparing this image with Figures 23.8 and 23.9.

This image shows the distortion of the electron density from a spherically symmetric shape at a density greater than that found in the bonding region. It corresponds to one of the contours close to the nucleus in the image for the bonding MO in Figure 23.9. The same information is contained in Figure 23.8 where it is seen that for a given distance from a proton, the probability density is higher on the side of the proton towards the bond than on the side of the proton corresponding to the outside of the molecule.

- d) Estimate the electron density in the bonding region midway between the H atoms by estimating the value of the electron density at which the neck disappears.

The density lies between 0.25 and 0.30 electrons/ a_0^3 because the neck is still visible at 0.25 electrons/ a_0^3 , but not at 0.30 electrons/ a_0^3 .

Problems

- P23.1)** Follow the procedure outlined in Section 23.3 to determine c_u in Equation (23.4).

$$\begin{aligned} 1 &= \int c_u^* (\psi_{H1s_a}^* - \psi_{H1s_b}^*) c_u (\psi_{H1s_a} - \psi_{H1s_b}) d\tau \\ &= c_u^2 \left(\int \psi_{H1s_a}^* \psi_{H1s_a} d\tau + \int \psi_{H1s_b}^* \psi_{H1s_b} d\tau - 2 \int \psi_{H1s_b}^* \psi_{H1s_a} d\tau \right) \\ &= c_u^2 (2 - 2S_{ab}) \quad \text{and} \\ c_u &= \frac{1}{\sqrt{2 - 2S_{ab}}} \end{aligned}$$

- P23.2)** Show that calculating E_u in the manner described by Equation (23.6) gives the

$$\text{result } E_u = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}.$$

$$\begin{aligned}
E_u &= \frac{\int \psi_u^* \hat{H} \psi_u d\tau}{\int \psi_u^* \psi_u d\tau} \\
&= \frac{1}{2(1-S_{ab})} \left(\int \psi_{H1s_a}^* \hat{H} \psi_{H1s_a} d\tau + \int \psi_{H1s_b}^* \hat{H} \psi_{H1s_b} d\tau - \int \psi_{H1s_b}^* \hat{H} \psi_{H1s_a} d\tau - \int \psi_{H1s_a}^* \hat{H} \psi_{H1s_b} d\tau \right) \\
&= \frac{1}{2(1-S_{ab})} (H_{aa} + H_{bb} - H_{ba} - H_{ab}) \\
&= \frac{H_{aa} - H_{ab}}{1 + S_{ab}}
\end{aligned}$$

P23.3) Using ζ as a variational parameter in the normalized function

$\psi_{H1s} = \frac{1}{\sqrt{\pi}} \left(\frac{\zeta}{a_0} \right)^{\frac{3}{2}} e^{-\frac{\zeta r}{a_0}}$ allows one to vary the size of the orbital. Show this by calculating

the probability of finding the electron inside a sphere of radius $2 a_0$ for different values of ζ using the standard integral

$$\int x^2 e^{-ax} dx = -e^{-ax} \left(\frac{2}{a^3} + 2 \frac{x}{a^2} + \frac{x^2}{a} \right)$$

a) Obtain an expression for the probability as a function of ζ .

$$\text{Using the standard integral } \int x^2 e^{-ax} dx = -e^{-ax} \left(\frac{2}{a^3} + 2 \frac{x}{a^2} + \frac{x^2}{a} \right)$$

$$\int \psi_{H1s}^* \psi_{H1s} d\tau = \frac{4\pi}{\pi} \left(\frac{\zeta}{a_0} \right)^3 \int_0^{2a_0} r^2 e^{-\frac{2\zeta r}{a_0}} = -e^{-\frac{2\zeta r}{a_0}} \left(1 + 2 \frac{r\zeta}{a_0} + 2 \left(\frac{r\zeta}{a_0} \right)^2 \right)$$

Evaluating this expression between the limits $r = 0$ and $r = 2 a_0$ gives

$$\int_0^{2a_0} \psi_{H1s}^* \psi_{H1s} d\tau = -e^{-4\zeta} (1 + 4\zeta + 8\zeta^2) + 1 = 1 - e^{-4\zeta} (1 + 4\zeta + 8\zeta^2)$$

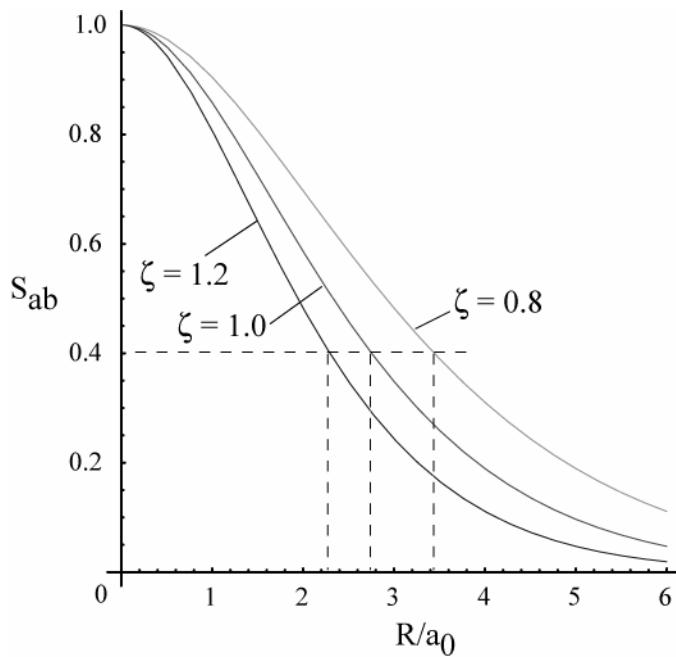
b) Evaluate the probability for $\zeta = 1, 2$, and 3 .

$$1 - e^{-4\zeta} (1 + 4\zeta + 8\zeta^2) = 0.762 \text{ for } \zeta = 1; \quad 0.986 \text{ for } \zeta = 2; \quad 0.999 \text{ for } \zeta = 3$$

P23.4) The overlap integral for ψ_g and ψ_u as defined in Section 23.3 is given

by $S_{ab} = e^{-\zeta \frac{R}{a_0}} \left(1 + \zeta \frac{R}{a_0} + \frac{1}{3} \zeta^2 \frac{R^2}{a_0^2} \right)$. Plot S_{ab} as a function of $\frac{R}{a_0}$ for $\zeta = 0.8, 1.0$, and 1.2 .

Estimate the value of $\frac{R}{a_0}$ for which $S_{ab} = 0.4$ for each of these values of ζ .



S_{ab} has the value of 0.4 at $R/a_0 = 3.42$, 2.68, and 2.25 for $\zeta = 0.8$, 1.0, and 1.2, respectively.

P23.5) By evaluating the appropriate integral, show that the normalization constant for the H_2 VB wave function is $N = \frac{1}{\sqrt{2 + 2S_{ab}^2}}$.

The VB wave function is given by

$$\psi_{bonding}^{VB}(1,2) = N \left[\phi_{H1s_a}(1)\phi_{H1s_b}(2) + \phi_{H1s_b}(1)\phi_{H1s_a}(2) \right] \left[\frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \alpha(2)\beta(1)) \right]$$

In normalizing this function we consider only the spatial part, because the spin part is already normalized.

$$1 = \int (\psi_{bonding}^{VB})^* \psi_{bonding}^{VB} d\tau$$

$$1 = N^2 \int [\phi_{H1s_a}(1)\phi_{H1s_b}(2) + \phi_{H1s_b}(1)\phi_{H1s_a}(2)]^2 d\tau$$

$$\begin{aligned} 1 &= N^2 \left\{ \int \phi_{H1s_a}(1)\phi_{H1s_b}(2)\phi_{H1s_a}(1)\phi_{H1s_b}(2) d\tau + \int \phi_{H1s_a}(1)\phi_{H1s_b}(2)\phi_{H1s_b}(1)\phi_{H1s_a}(2) \right\} \\ &\quad + \int N^2 \left\{ \int \phi_{H1s_b}(1)\phi_{H1s_a}(2)\phi_{H1s_a}(1)\phi_{H1s_b}(2) d\tau + \int \phi_{H1s_b}(1)\phi_{H1s_a}(2)\phi_{H1s_b}(1)\phi_{H1s_a}(2) \right\} \end{aligned}$$

Because the second and third integrals and the first and fourth give the same result

$$1 = 2N^2 \left\{ \int \phi_{H1s_a}(1)\phi_{H1s_b}(2)\phi_{H1s_a}(1)\phi_{H1s_b}(2) d\tau + \int \phi_{H1s_a}(1)\phi_{H1s_b}(2)\phi_{H1s_b}(1)\phi_{H1s_a}(2) \right\}$$

$$1 = 2N^2 \left\{ \int \phi_{H1s_a}(1)\phi_{H1s_a}(1) \int \phi_{H1s_b}(2)\phi_{H1s_b}(2) d\tau_2 + \int \phi_{H1s_a}(1)\phi_{H1s_b}(1) d\tau_1 \int \phi_{H1s_a}(2)\phi_{H1s_b}(2) d\tau_2 \right\}$$

These integrals can be simplified because $\int \phi_{H1s_a}(1)\phi_{H1s_a}(1) d\tau_i = 1$ and $\int \phi_{H1s_a}(1)\phi_{H1s_b}(1) d\tau_i = S_{ab}$

$$1 = 2N^2 (1 + S_{ab}^2)$$

$$N = \frac{1}{\sqrt{2 + 2S_{ab}^2}}$$

P23.6) By simplifying Equation (23.23), show that $\langle E_{electronic} \rangle = \frac{1}{1 + S_{ab}^2} [2E_{1s}(1 + S^2) + J + K]$

for H₂ in the VB model.

$$\begin{aligned}
 \langle E_{\text{electronic}} \rangle &= \frac{1}{2+2S_{ab}^2} \int \left[\begin{array}{c} \phi_{H1s_a}(1) \phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \end{array} \right] \left[\begin{array}{c} \hat{H}_a(1) + \hat{H}_b(2) \\ - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \end{array} \right] \left[\begin{array}{c} \phi_{H1s_a}(1) \phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \end{array} \right] d\tau \\
 &= \frac{1}{2+2S_{ab}^2} \int \left[\begin{array}{c} \phi_{H1s_a}(1) \phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \end{array} \right] (\hat{H}_a(1)) \left[\begin{array}{c} \phi_{H1s_a}(1) \phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \end{array} \right] d\tau \\
 &\quad + \frac{1}{2+2S_{ab}^2} \int \left[\begin{array}{c} \phi_{H1s_a}(1) \phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \end{array} \right] (\hat{H}_b(2)) \left[\begin{array}{c} \phi_{H1s_a}(1) \phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \end{array} \right] d\tau \\
 &\quad - \frac{1}{2+2S_{ab}^2} \int \left[\begin{array}{c} \phi_{H1s_a}(1) \phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \end{array} \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\begin{array}{c} \phi_{H1s_a}(1) \phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \end{array} \right] d\tau
 \end{aligned}$$

Because $\phi_{H1s_a}(1, 2)$ is an eigenfunction of $\hat{H}_a(1, 2)$ with eigenvalue E_{1s} ,

and the same holds for $\phi_{H1s_b}(1, 2)$ and $\hat{H}_b(1, 2)$,

$$\begin{aligned}
 \langle E_{\text{electronic}} \rangle &= \frac{2E_{1s}}{2+2S_{ab}^2} \int \left[\begin{array}{c} \phi_{H1s_a}(1) \phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \end{array} \right] \left[\begin{array}{c} \phi_{H1s_a}(1) \phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \end{array} \right] d\tau \\
 &\quad - \frac{1}{2+2S_{ab}^2} \int \left[\begin{array}{c} \phi_{H1s_a}(1) \phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \end{array} \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\begin{array}{c} \phi_{H1s_a}(1) \phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \end{array} \right] d\tau \\
 \langle E_{\text{electronic}} \rangle &= \frac{2E_{1s}}{2+2S_{ab}^2} \left\{ \begin{array}{l} \int [\phi_{H1s_a}(1) \phi_{H1s_a}(1)] d\tau_1 \int [\phi_{H1s_b}(2) \phi_{H1s_b}(2)] d\tau_2 \\ + \int [\phi_{H1s_a}(1) \phi_{H1s_b}(1)] d\tau_1 \int [\phi_{H1s_a}(2) \phi_{H1s_b}(2)] d\tau_2 \\ \int [\phi_{H1s_b}(1) \phi_{H1s_a}(1)] d\tau_1 \int [\phi_{H1s_b}(2) \phi_{H1s_a}(2)] d\tau_2 \\ + \int [\phi_{H1s_b}(1) \phi_{H1s_b}(1)] d\tau_1 \int [\phi_{H1s_a}(2) \phi_{H1s_a}(2)] d\tau_2 \end{array} \right\} \\
 &\quad - \frac{1}{2+2S_{ab}^2} \int \left[\begin{array}{c} \phi_{H1s_a}(1) \phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \end{array} \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\begin{array}{c} \phi_{H1s_a}(1) \phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \end{array} \right] d\tau
 \end{aligned}$$

The first and fourth integrals have the value 1, and the second and third integrals have the value S_{ab}^2 .

$$\begin{aligned}
 \langle E_{\text{electronic}} \rangle &= \frac{4E_{1s}(1+S_{ab}^2)}{2+2S_{ab}^2} \\
 &\quad - \frac{1}{2+2S_{ab}^2} \int \left[\begin{array}{c} \phi_{H1s_a}(1) \phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \end{array} \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\begin{array}{c} \phi_{H1s_a}(1) \phi_{H1s_b}(2) \\ + \phi_{H1s_b}(1) \phi_{H1s_a}(2) \end{array} \right] d\tau
 \end{aligned}$$

$$\langle E_{electronic} \rangle = \frac{4E_{1s}(1+S_{ab}^2)}{2+2S_{ab}^2}$$

$$-\frac{1}{2+2S_{ab}^2} \int \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ +\phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\begin{array}{l} \phi_{H1s_a}(1)\phi_{H1s_b}(2) \\ +\phi_{H1s_b}(1)\phi_{H1s_a}(2) \end{array} \right] d\tau$$

$$\langle E_{electronic} \rangle = \frac{4E_{1s}(1+S_{ab}^2)}{2+2S_{ab}^2}$$

$$-\frac{1}{2+2S_{ab}^2} \left\{ \begin{array}{l} \int \left[\phi_{H1s_a}(1)\phi_{H1s_b}(2) \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\phi_{H1s_a}(1)\phi_{H1s_b}(2) \right] d\tau \\ + \int \left[\phi_{H1s_a}(1)\phi_{H1s_b}(2) \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\phi_{H1s_b}(1)\phi_{H1s_a}(2) \right] d\tau \\ + \int \left[\phi_{H1s_b}(1)\phi_{H1s_a}(2) \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\phi_{H1s_a}(1)\phi_{H1s_b}(2) \right] d\tau \\ + \int \left[\phi_{H1s_b}(1)\phi_{H1s_a}(2) \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\phi_{H1s_b}(1)\phi_{H1s_a}(2) \right] d\tau \end{array} \right\}$$

The first and fourth as well as the second and third integrals give the same value because the *a* and *b* orbitals are identical.

$$\langle E_{electronic} \rangle = \frac{4E_{1s}(1+S_{ab}^2)}{2+2S_{ab}^2}$$

$$-\frac{1}{2+2S_{ab}^2} \left\{ \begin{array}{l} 2 \int \left[\phi_{H1s_a}(1)\phi_{H1s_b}(2) \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\phi_{H1s_a}(1)\phi_{H1s_b}(2) \right] d\tau \\ + 2 \int \left[\phi_{H1s_a}(1)\phi_{H1s_b}(2) \right] \left(\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}} \right) \right) \left[\phi_{H1s_b}(1)\phi_{H1s_a}(2) \right] d\tau \end{array} \right\}$$

Using the definitions of *J* and *K* in Equation (23.25),

$$\langle E_{electronic} \rangle = \frac{4E_{1s}(1+S_{ab}^2)}{2+2S_{ab}^2} + \frac{1}{2+2S_{ab}^2} (2J+2K)$$

$$\langle E_{electronic} \rangle = \frac{1}{1+S_{ab}^2} [2E_{1s}(1+S_{ab}^2) + J + K]$$

Chapter 24: Chemical Bonding in Diatomic Molecules

Questions on Concepts

Q24.1) What is the justification for saying that, in expanding MOs in terms of AOs, the equality $\sigma_j(l) = \sum_i c_{ij} \phi_i(l)$ can in principle be satisfied?

The set of all AOs on an atom is a complete set, meaning that any well-behaved function can be expanded in terms of the AOs. However, because the set is infinite in size, it must be truncated to carry out calculations.

Q24.2) Distinguish between the following concepts used to describe chemical bond formation: basis set, minimal basis set, atomic orbital, molecular orbital, and molecular wave function.

Basis set: the set of AOs used to construct the MOs

Minimal basis set: the smallest set of AOs that is meaningful to carry out a calculation. Generally, this includes the core AOs and both occupied and unoccupied valence AOs.

Atomic orbital: a one electron wave function for an atom, generally obtained using the Hartree-Fock theory.

Molecular orbital: a one electron wave function that is usually expressed as a linear combination of atomic orbitals.

Molecular wave function: an n electron wave function that is expressed in terms of the molecular orbitals.

Q24.3) Give examples for AOs for which the overlap reaches its maximum value only as the internuclear separation approaches zero in a diatomic molecule. Also give examples of AOs for which the overlap goes through a maximum value and then decreases as the internuclear separation approaches zero.

For a diatomic molecule with the bond along the z axis, the overlap of p_x or p_y AOs reaches its maximum value only as the internuclear separation approaches zero. The overlap of an s AO with a p_z AO goes through a maximum value, and decreases as the internuclear separation approaches zero.

Q24.4) Why is it reasonable to approximate H_{11} and H_{22} by the appropriate ionization energy of the corresponding neutral atom?

If the AOs were eigenfunctions of the Hartree-Fock total energy operator, the ionization energy would be exactly H_{11} and H_{22} . Because the actual wave function is dominated by the atomic AO, it is reasonable to approximate H_{11} and H_{22} by the appropriate ionization energy of the corresponding neutral atom.

Q24.5) Does the total energy of a molecule rise or fall when an electron is put in an antibonding orbital?

The total energy of a molecule is lowered if the orbital energy of the antibonding MO is negative, and raised if the orbital energy of the antibonding MO is positive. The zero of energy is the electron and the molecule with $n-1$ electrons at infinite separation.

Q24.6) Are the coefficients of the AOs of different atoms in MOs responsible for bonding in an ionically bonded diatomic molecule similar or different in magnitude?

They will be very different because the probability of finding the electron on an atom in an ionically bonded diatomic molecule is very different on the two atoms.

Q24.7) Explain why $s-p$ mixing is more important in Li_2 than in F_2 .

Atomic orbitals mix to a greater degree if the difference of their orbital energies is small. The difference in the $2s$ and $2p$ orbital energies increases in the sequence $\text{Li} \rightarrow \text{F}$, so the degree of mixing decreases along this sequence.

Q24.8) Why are MOs on heteronuclear diatomics not labeled with g and u subscripts?

Heteronuclear diatomic molecules lack a center of inversion. Therefore, the g and u labels do not apply.

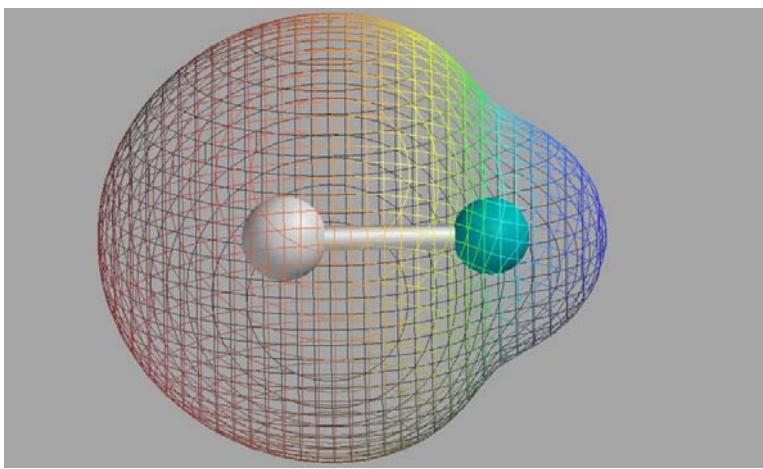
Q24.9) Explain how the amplitude of the $1\sigma_g$ MO in H_2 and F_2 midway between the atoms differs.

The $1\sigma_g$ MO in H_2 and F_2 is constructed from the $1s$ AOs. These are the valence AOs in H_2 , but are core AOs in F_2 . Therefore, the overlap of the AOs is large for H_2 and nearly zero for F_2 . Therefore the $1\sigma_g$ MO has a vanishingly small amplitude between the F atoms, and a much larger amplitude between the H atoms.

Q24.10) Why do we neglect the bond length in He_2 when discussing the trends shown in Figure 24.11?

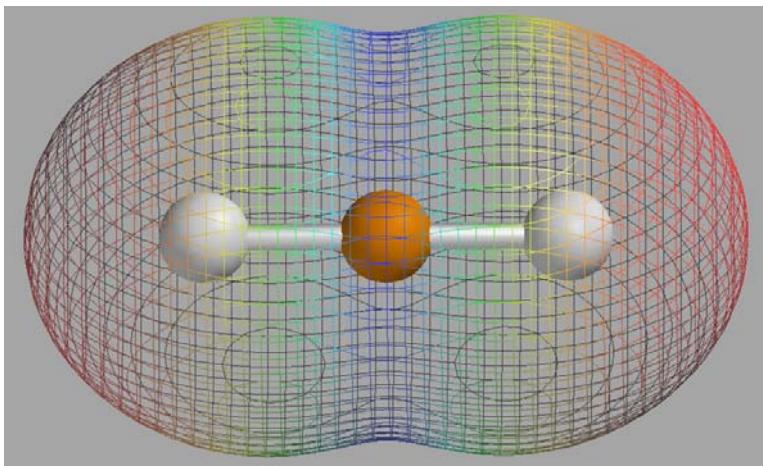
Because the bond in He_2 is not a chemical bond, but rather a van der Waals bond, it will be longer than a normal chemical bond. Therefore, it is reasonable to neglect the bond length in He_2 in discussing the trends shown in Figure 24.15.

Q24.11) Consider the molecular electrostatic potential map for the LiH molecule shown here. Is the hydrogen atom (shown as a white sphere) an electron acceptor or an electron donor in this molecule?



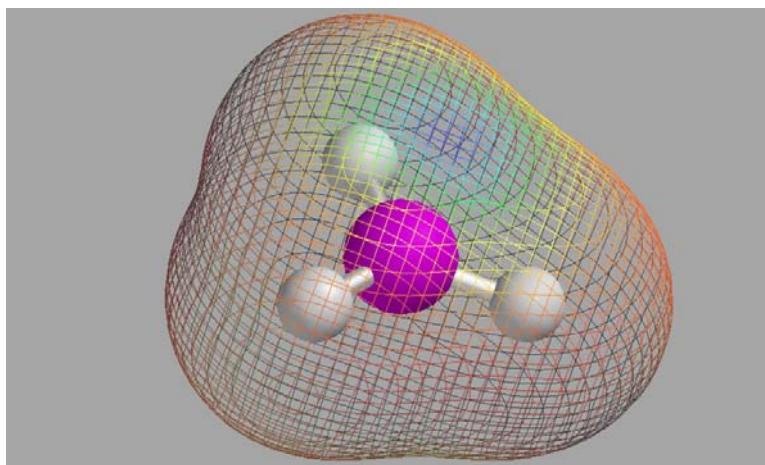
It is an electron acceptor, because the red color around the H indicates a negative value for the electrostatic potential which results from an excess of electron charge.

Q24.12) Consider the molecular electrostatic potential map for the BeH₂ molecule shown here. Is the hydrogen atom (shown as a white sphere) an electron acceptor or an electron donor in this molecule?



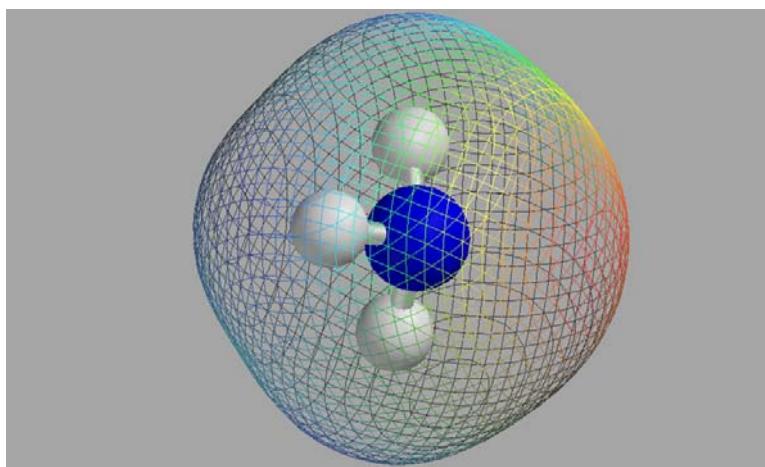
It is an electron acceptor, because the red color around the H indicates a negative value for the electrostatic potential which results from an excess of electron charge.

Q24.13) Consider the molecular electrostatic potential map for the BH₃ molecule shown here. Is the hydrogen atom (shown as a white sphere) an electron acceptor or an electron donor in this molecule?



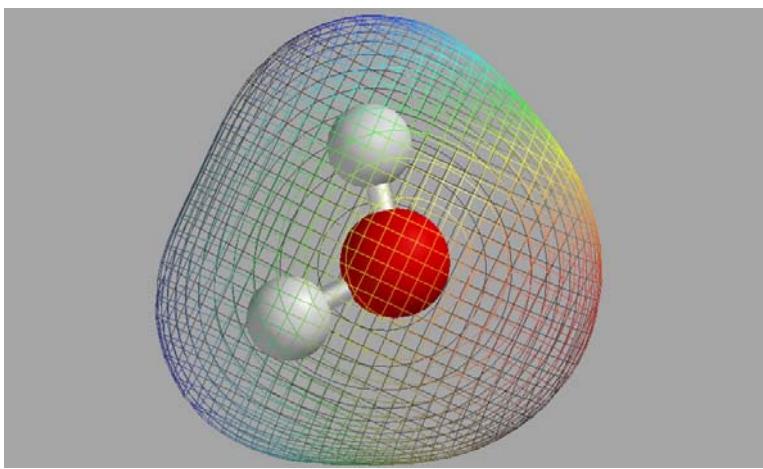
It is an electron acceptor, because the red color around the H indicates a negative value for the electrostatic potential which results from an excess of electron charge.

Q24.14) Consider the molecular electrostatic potential map for the NH₃ molecule shown here. Is the hydrogen atom (shown as a white sphere) an electron acceptor or an electron donor in this molecule?



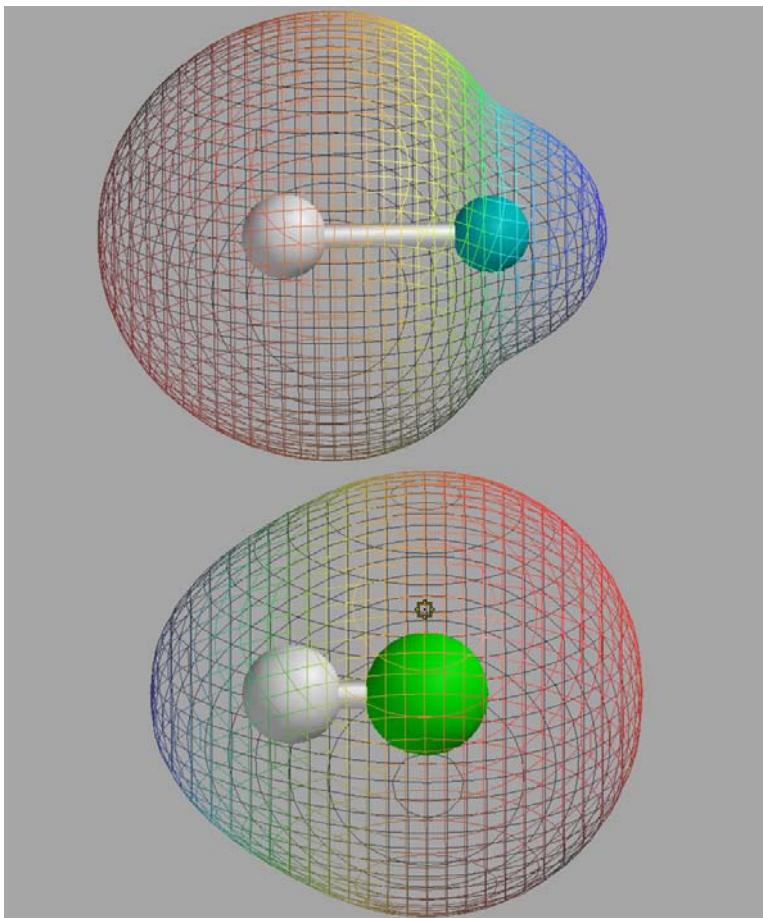
It is an electron donor, because the blue color around the H indicates a positive value for the electrostatic potential which results from a deficiency of electron charge.

Q24.15) Consider the molecular electrostatic potential map for the H₂O molecule shown here. Is the hydrogen atom (shown as a white sphere) an electron acceptor or an electron donor in this molecule?



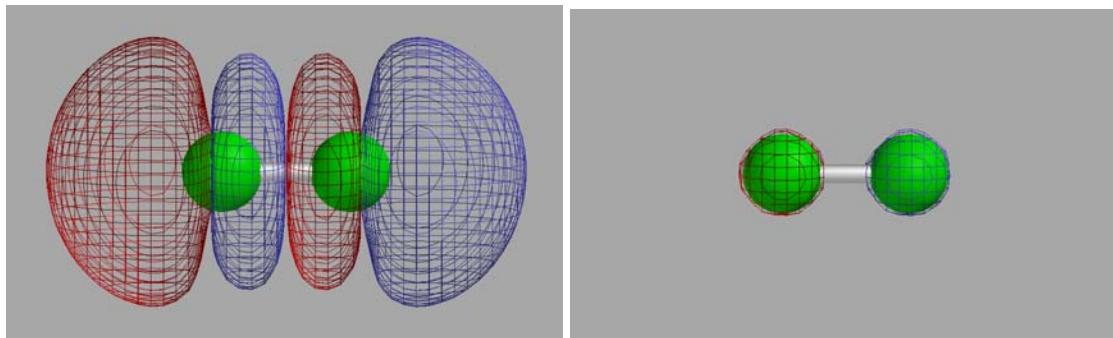
It is an electron donor, because the blue color around the H indicates a positive value for the electrostatic potential which results from a deficiency of electron charge.

Q24.16) The molecular electrostatic potential maps for LiH and HF are shown here. Does the apparent size of the hydrogen atom (shown as a white sphere) tell you whether it is an electron acceptor or an electron donor in these molecules?



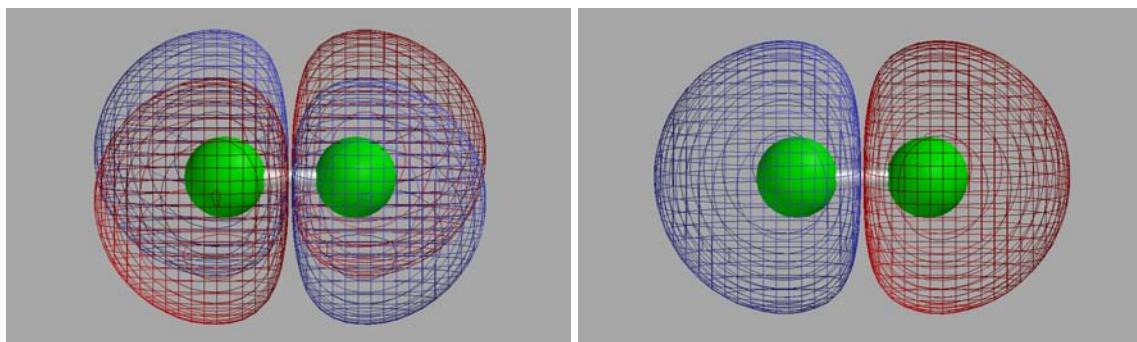
Yes, it does. The electrostatic potential is displayed on a total electron charge density contour. The excess electron charge around the H atom pushes the contour out and makes the H look bigger. In HF, electrons are withdrawn from the H, so that the contour is moved towards the H nucleus, making the H look smaller.

Q24.17) Identify the molecular orbitals for F₂ in the images shown here in terms of the two designations discussed in Section 24.4. The molecular axis is the z axis, and the y axis is tilted slightly out of the plane of the image.



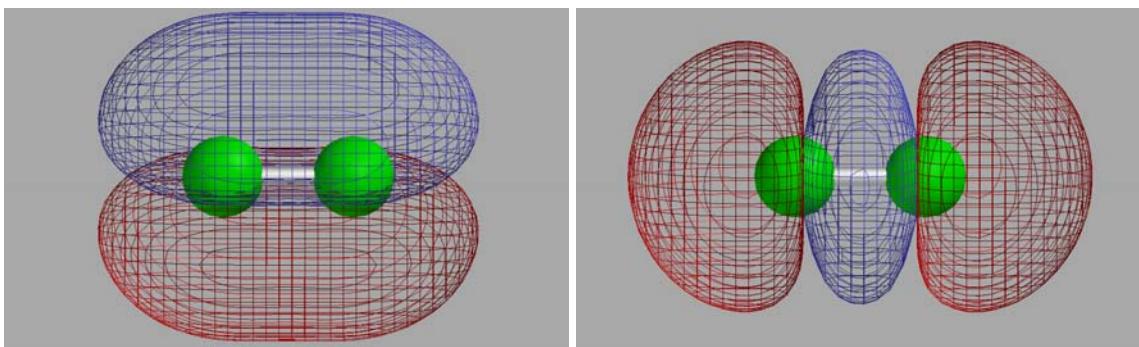
The left image has σ symmetry, the AOs are out of phase, and there is a single node between the atoms. Therefore it is the $3\sigma_u^*$ or $\sigma_u^*(2p_z)$ MO. The right image shows out of phase AOs with no overlap. Therefore it is the $1\sigma_u^*$ or $\sigma_u^*(1s)$ MO.

Q24.18) See Question Q24.17.



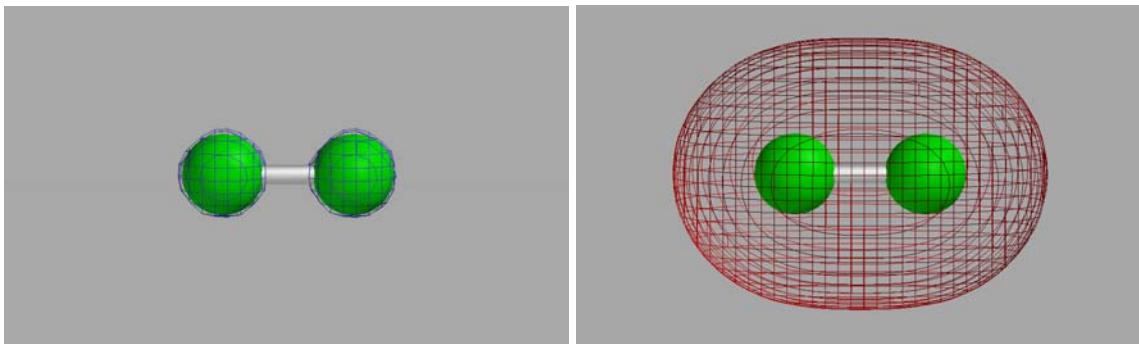
The left image has π symmetry and a single node in the bonding region. Because of the orientation of the coordinate system, the left image is the $1\pi_g^*$ or $\pi_g^*(2p_z)$ MO. The right image has σ symmetry and a single nodal plane perpendicular to the molecular axis. Therefore, it is the $2\sigma_u^*$ or $\sigma_u^*(2s)$ MO.

Q24.19) See Question Q24.17.



The left image is of π symmetry and has no node in the bonding region. It is the $1\pi_u$ or π_u ($2p_x$) MO. The right image has σ symmetry with no nodes in the bonding region. Therefore, it is the $3\sigma_g$ or σ_g ($2p_z$) MO.

Q24.20) See Question Q24.17.



The left image shows in phase AOs with no overlap. Therefore it is the $1\sigma_g$ or σ_g ($1s$) MO. The right image has σ symmetry and a no nodal plane perpendicular to the molecular axis. Therefore, it is the $2\sigma_g$ or σ_g ($2s$) MO.

Problems

P24.1) Evaluate the energy for the two MOs generated by combining two H_{1s} AOs. Use Equation (24.11) and carry out the calculation for $S_{12} = 0.1, 0.2$, and 0.6 to mimic the effect of decreasing the atomic separation in the molecule. Use the parameters $H_{11} = H_{22} = -13.6$ eV and $H_{12} = -1.75 S_{12} \sqrt{H_{11} H_{22}}$. Explain the trend that you observe in the results.

$$E_1 = \frac{H_{11} + H_{12}}{1 + S_{12}} \text{ and } E_2 = \frac{H_{11} - H_{12}}{1 - S_{12}}$$

S_{12}	H_{12} (eV)	ε_1 (eV)	ε_2 (eV)
0.1	-2.38	-14.5	-12.5
0.2	-4.76	-15.3	-11.1
0.6	-14.3	-17.4	+1.7

Chapter 24/Chemical Bonding in Diatomic Molecules

The increase in the overlap mimics a decrease in the bond length. As S_{12} increases, the orbitals overlap more and their interaction becomes greater. The result is that ε_1 becomes more strongly binding and ε_2 becomes more strongly antibonding.

P24.2) Evaluate the energy for the two MOs generated by combining a H1s and a F2p AO. Use Equation (24.11) and carry out the calculation for $S_{12} = 0.1, 0.2,$ and 0.6 to mimic the effect of increasing the atomic separation in the molecule. Use the parameters $H_{11} = -13.6 \text{ eV}$, $H_{22} = -18.6 \text{ eV}$, and $H_{12} = -1.75 S_{12} \sqrt{H_{11} H_{22}}$. Explain the trend that you observe in the results.

$$E = \frac{1}{2 - 2S_{12}^2} [H_{11} + H_{22} - 2S_{12}H_{12}]$$

$$\pm \frac{1}{2 - 2S_{12}^2} \left[\sqrt{(H_{11}^2 + 4H_{12}^2 + H_{22}^2 - 4S_{12}H_{12}H_{22} - 2H_{11}(H_{22} + 2S_{12}H_{12} - 2S_{12}^2H_{22}))} \right]$$

S_{12}	$H_{12}(\text{eV})$	$\varepsilon_{\text{antibonding}}(\text{eV})$	$\varepsilon_{\text{bonding}}(\text{eV})$
0.1	-2.78	-13.2	-18.8
0.2	-5.57	-12.1	-19.1
0.6	-16.7	+1.94	-20.9

As the overlap increases, mimicking the atoms getting closer, the interaction of the AOs increases, and the difference between the MO and the AO energies increases. For small values of the overlap, the energy of the bonding MO is only slightly lower than that of the lower AO, and the energy of the antibonding MO is only slightly higher than that of the higher AO. As the overlap increases, these differences become greater, and the difference between the MO energies becomes greater. The change in the energy change of the bonding MO is greater than that of the antibonding MO.

P24.3) Calculate the value for the coefficients of the AOs in Example Problem 24.1 for $S_{12} = 0.6$. How are they different from the values calculated in that problem for $S_{12} = 0.3$? Can you offer an explanation for the changes?

We first obtain the result $H_{12} = -1.75 S_{12} \sqrt{H_{11} H_{22}} = -16.7 \text{ eV}$

Solving for the energies of ε_1 and ε_2 (bonding and antibonding MOs, respectively) gives the values $\varepsilon_1 = -20.9 \text{ eV}$, and $\varepsilon_2 = +1.94 \text{ eV}$.

We calculate $\frac{c_{12}}{c_{22}}$ by substituting the values for ε_1 and ε_2 in the first of the

Equations (24.9). Both equations give the same result.

$$c_{12}(H_{11} - \varepsilon) + c_{22}(H_{12} - \varepsilon S_{12}) = 0.$$

$$\text{For } \varepsilon_2 = 1.94 \text{ eV}, c_{12}(-13.6 - 1.94) + c_{22}(-16.7 - 0.6 \times 1.94) = 0$$

$$\frac{c_{12}}{c_{22}} = -1.15$$

Using this result in the normalization equation $c_{12}^2 + c_{22}^2 + 2c_{12}c_{22}S_{12} = 1$.

$$(-1.15c_{22})^2 + c_{22}^2 + 2(-1.15c_{22}) \times 0.6 = 1$$

$$1.3225c_{22}^2 + c_{22}^2 - 1.38c_{22} = 0; c_{22} = -1.03$$

$$c_{12} = 1.18, \text{ and } \sigma_2 = 1.18\phi_{H1s} - 1.03\phi_{F2p_z}$$

$$c_{12}(H_{11} - \varepsilon) + c_{22}(H_{12} - \varepsilon S_{12}) = 0.$$

$$\text{For } \varepsilon_2 = -20.9 \text{ eV}, c_{11}(-13.6 + 20.9) + c_{21}(-16.7 + 0.6 \times 20.9) = 0$$

$$\frac{c_{11}}{c_{21}} = 0.57$$

Using this result in the normalization equation $c_{11}^2 + c_{21}^2 + 2c_{11}c_{21}S_{12} = 1$.

$$(0.57c_{21})^2 + c_{21}^2 + 2(0.57c_{21}) \times 0.6 = 1$$

$$0.3249c_{21}^2 + c_{21}^2 + 0.684c_{21}^2 = 0; c_{21} = 0.71$$

$$c_{11} = 0.40, \text{ and } \sigma_2 = 0.40\phi_{H1s} + 0.71\phi_{F2p_z}$$

The increase in the overlap results in $c_{11} = 0.40$ and $c_{21} = 0.71$ for $\varepsilon_1 = -20.9$ eV and in $c_{22} = -1.03$ and $c_{12} = 1.18$ for $\varepsilon_2 = +1.94$ eV. As for $S_{12} = 0.3$, the coefficient on the lower lying AO is greater for the bonding orbital and less for the antibonding orbital. Also as before, the signs of the coefficients are the same for the bonding orbital and opposite for the antibonding orbital. However, the magnitude of the coefficients is more nearly equal, due to the greater interaction that arises from a greater overlap, because H_{12} increases linearly with S_{12} . In the bonding MO, the electron is shared more equally by the two atoms for the greater overlap.

P24.4) The expressions $(c_{11})^2 + c_{11}c_{21}S_{12}$ and $(c_{12})^2 + c_{11}c_{21}S_{12}$ for the probability of finding an electron on the H and F atoms in HF, respectively, were derived in Section 24.3. Use your results from Problem P24.2 and these expressions to calculate the probability of finding an electron in the bonding orbital on the F atom for $S_{12} = 0.1, 0.2$, and 0.6 . Explain the trend shown by these results.

To solve this problem, we must first solve for the coefficients c_{21} and c_{11} .

Chapter 24/Chemical Bonding in Diatomic Molecules

$$c_{12}(H_{11} - \varepsilon) + c_{22}(H_{12} - \varepsilon S_{12}) = 0 \text{ and } S_{12} = 0.1$$

$$\text{For } \varepsilon_2 = -18.8 \text{ eV}, c_{11}(-13.6 + 18.8) + c_{21}(-2.78 + 0.1 \times 18.8) = 0$$

$$\frac{c_{11}}{c_{21}} = 0.173$$

Using this result in the normalization equation $c_{11}^2 + c_{21}^2 + 2c_{11}c_{21}S_{12} = 1$

$$(0.173c_{21})^2 + c_{21}^2 + 2(0.173c_{21}^2) \times 0.1 = 1$$

$$0.02996c_{21}^2 + c_{21}^2 + 0.03462c_{21}^2 = 1$$

$$c_{21} = 0.97 \text{ and } c_{11} = 0.17$$

The total probability of finding the electron on the F atom is

$$c_{21}^2 + c_{11}c_{21}S_{12} = (0.97)^2 + 0.17 \times 0.97 \times 0.1 = 0.97.$$

$$c_{12}(H_{11} - \varepsilon) + c_{22}(H_{12} - \varepsilon S_{12}) = 0 \text{ and } S_{12} = 0.2$$

$$\text{For } \varepsilon_2 = -119.1 \text{ eV}, c_{11}(-13.6 + 19.1) + c_{21}(-5.57 + 0.1 \times 19.1) = 0$$

$$\frac{c_{11}}{c_{21}} = 0.32$$

Using this result in the normalization equation $c_{11}^2 + c_{21}^2 + 2c_{11}c_{21}S_{12} = 1$

$$(0.32c_{21})^2 + c_{21}^2 + 2(0.32c_{21}^2) \times 0.2 = 1$$

$$0.101c_{21}^2 + c_{21}^2 + 0.127c_{21}^2 = 1$$

$$c_{21} = 0.90 \text{ and } c_{11} = 0.29$$

The total probability of finding the electron on the F atom is

$$c_{21}^2 + c_{11}c_{21}S_{12} = (0.90)^2 + 0.29 \times 0.90 \times 0.2 = 0.86.$$

$$c_{12}(H_{11} - \varepsilon) + c_{22}(H_{12} - \varepsilon S_{12}) = 0 \text{ and } S_{12} = 0.6$$

$$\text{For } \varepsilon_2 = -20.9 \text{ eV}, c_{11}(-13.6 + 20.9) + c_{21}(-16.7 + 0.6 \times 20.9) = 0$$

$$\frac{c_{11}}{c_{21}} = 0.563$$

Using this result in the normalization equation $c_{11}^2 + c_{21}^2 + 2c_{11}c_{21}S_{12} = 1$

$$(0.563c_{21})^2 + c_{21}^2 + 2(0.563c_{21}^2) \times 0.6 = 1$$

$$0.317c_{21}^2 + c_{21}^2 + 0.676c_{21}^2 = 1$$

$$c_{21} = 0.71 \text{ and } c_{11} = 0.40$$

The total probability of finding the electron on the F atom is

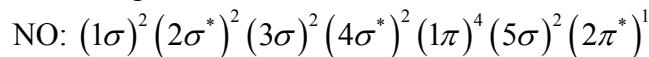
$$c_{21}^2 + c_{11}c_{21}S_{12} = (0.71)^2 + 0.40 \times 0.71 \times 0.6 = 0.67.$$

Summarizing the results, the probability of finding the electron on the F atom is 0.97, 0.86, and 0.67 for overlap values of 0.1, 0.2, and 0.6, respectively. When the overlap is

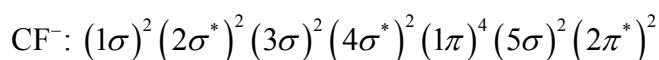
very small, the electron is found on the F atom with a probability approaching one. As the overlap increases, the electron becomes more delocalized over the molecule. Even though the probability for finding the electron on F is always higher than 0.5 because the F AO energy lies lower than the H AO energy, it decreases from one as S increases.

P24.5) The bond dissociation energies of the species NO, CF⁻ and CF⁺ follow the trend CF⁺ > NO > CF⁻. Explain this trend using MO theory.

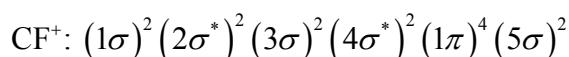
The configurations for the molecules are



$$\text{Bond Order} = \frac{10 - 5}{2} = 2.5$$



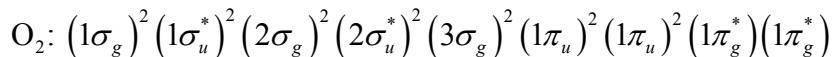
$$\text{Bond Order} = \frac{10 - 6}{2} = 2$$



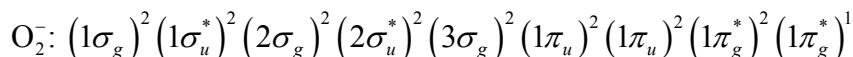
$$\text{Bond Order} = \frac{10 - 4}{2} = 3$$

We see that the calculated bond orders account for the relative bond strengths.

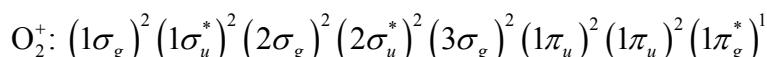
P24.6) What is the electron configuration corresponding to O₂, O₂⁻ and O₂⁺? What do you expect the relative order of bond strength to be for these species? What do you expect for the relative order of bond strength of these species? Which, if any, have unpaired electrons?



$$\text{Bond Order} = \frac{10 - 6}{2} = 2$$



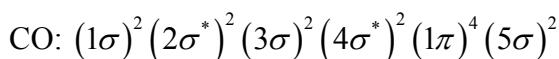
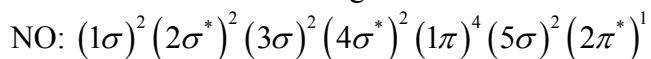
$$\text{Bond Order} = \frac{10 - 7}{2} = 1.5$$



$$\text{Bond Order} = \frac{10 - 5}{2} = 2.5$$

Because the bond strengths increase with increasing bond order, the relative order of bond strength is and O₂⁺ > O₂ > O₂⁻. O₂ has two unpaired electrons, and the positively and negatively charged species each have one.

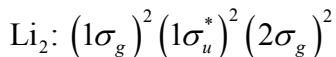
P24.7) The ionization energy of CO is greater than that of NO. Explain this difference based on the electron configuration of these two molecules.



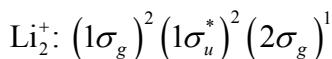
To first order, we assume that the MO energies are the same in each molecule. This is an approximation. Next, we look at the occupied MOs. In CO, the electron is removed from an HOMO that is a bonding orbital. This MO lies lower in energy than the antibonding HOMO in NO from which the electron is removed. Therefore, the ionization energy of CO is greater than that of NO.

P24.8) Calculate the bond order in each of the following species. Which of the species in parts (a–d) do you expect to have the smaller bond length?

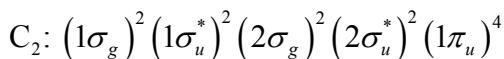
- a) Li_2 or Li_2^+
- b) C_2 or C_2^+
- c) O_2 or O_2^+
- d) F_2 or F_2^-



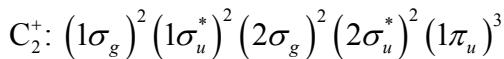
$$\text{Bond Order} = \frac{4-2}{2} = 1$$



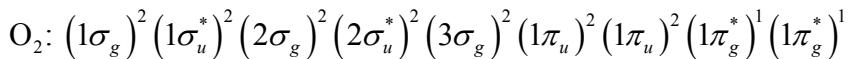
$$\text{Bond Order} = \frac{3-2}{2} = 0.5$$



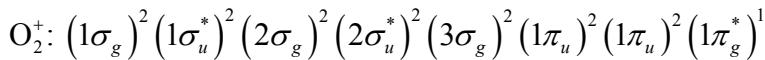
$$\text{Bond Order} = \frac{8-4}{2} = 2$$



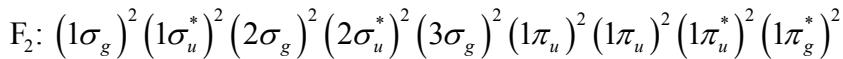
$$\text{Bond Order} = \frac{7-4}{2} = 1.5$$



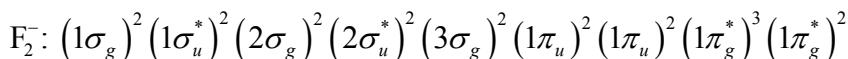
$$\text{Bond Order} = \frac{10-6}{2} = 2$$



$$\text{Bond Order} = \frac{10-5}{2} = 2.5$$



$$\text{Bond Order} = \frac{10-8}{2} = 1$$

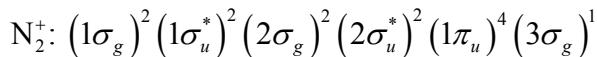


$$\text{Bond Order} = \frac{10-9}{2} = 0.5$$

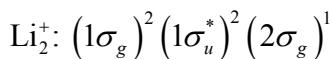
Because the bond length is shorter for a greater bond order, the answers are Li_2 , C_2 , O_2^+ , F_2 .

P24.9) Predict the bond order in the following species:

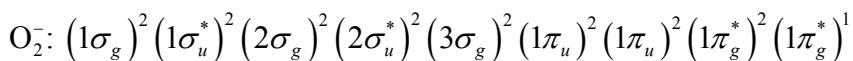
- a) N_2^+ b) Li_2^+ c) O_2^- d) H_2^- e) C_2^+



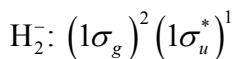
$$\text{Bond Order} = \frac{9-4}{2} = 2.5$$



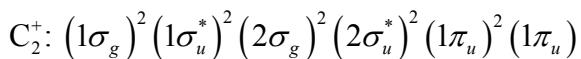
$$\text{Bond Order} = \frac{3-2}{2} = 0.5$$



$$\text{Bond Order} = \frac{10-7}{2} = 1.5$$



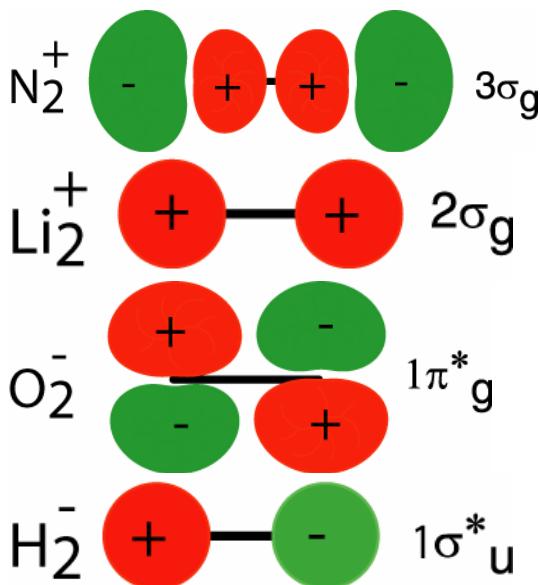
$$\text{Bond Order} = \frac{2-1}{2} = 0.5$$

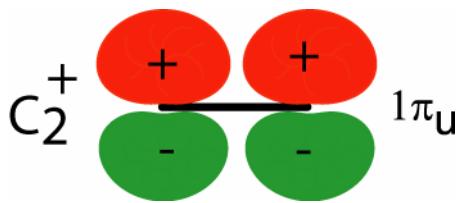


$$\text{Bond Order} = \frac{7-4}{2} = 1.5$$

P24.10) Make a sketch of the highest occupied molecular orbital (HOMO) for the following species:

- a) N_2^+ b) Li_2^+ c) O_2^- d) H_2^- e) C_2^+





P24.11) Calculate the bond order in each of the following species. Predict which of the two species in the following pairs has the higher vibrational frequency:

- a) Li_2 or Li_2^+ b) C_2 or C_2^+ c) O_2 or O_2^+ d) F_2 or F_2^-

$$Li_2: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2$$

$$\text{Bond Order} = \frac{4-2}{2} = 1$$

$$Li_2^+: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^1$$

$$\text{Bond Order} = \frac{3-2}{2} = 0.5$$

$$C_2: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (1\pi_u)^4$$

$$\text{Bond Order} = \frac{8-4}{2} = 2$$

$$C_2^+: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (1\pi_u)^3$$

$$\text{Bond Order} = \frac{7-4}{2} = 1.5$$

$$O_2: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u)^2 (1\pi_g^*)^1 (1\pi_g^*)^1$$

$$\text{Bond Order} = \frac{10-6}{2} = 2$$

$$O_2^+: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u)^2 (1\pi_g^*)^1$$

$$\text{Bond Order} = \frac{10-5}{2} = 2.5$$

$$F_2: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u)^2 (1\pi_g^*)^2 (1\pi_g^*)^2$$

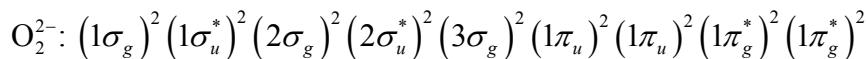
$$\text{Bond Order} = \frac{10-8}{2} = 1$$

$$F_2^-: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u)^2 (1\pi_g^*)^3 (1\pi_g^*)^2$$

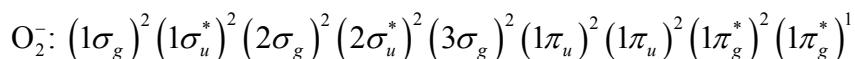
$$\text{Bond Order} = \frac{10-9}{2} = 0.5$$

The species with the higher bond order will have the higher vibrational frequency, so the answers are Li₂, C₂, O₂⁺, F₂.

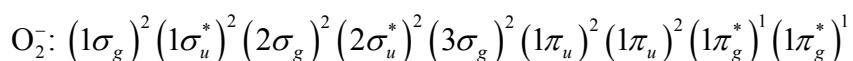
P24.12) Arrange the following in terms of decreasing bond energy and bond length:
 O₂⁺, O₂, O₂⁻, and O₂²⁻.



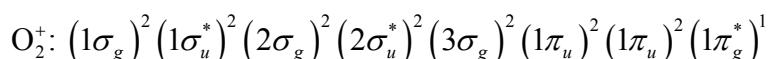
$$\text{Bond Order} = \frac{10-8}{2} = 1$$



$$\text{Bond Order} = \frac{10-7}{2} = 1.5$$



$$\text{Bond Order} = \frac{10-6}{2} = 2$$

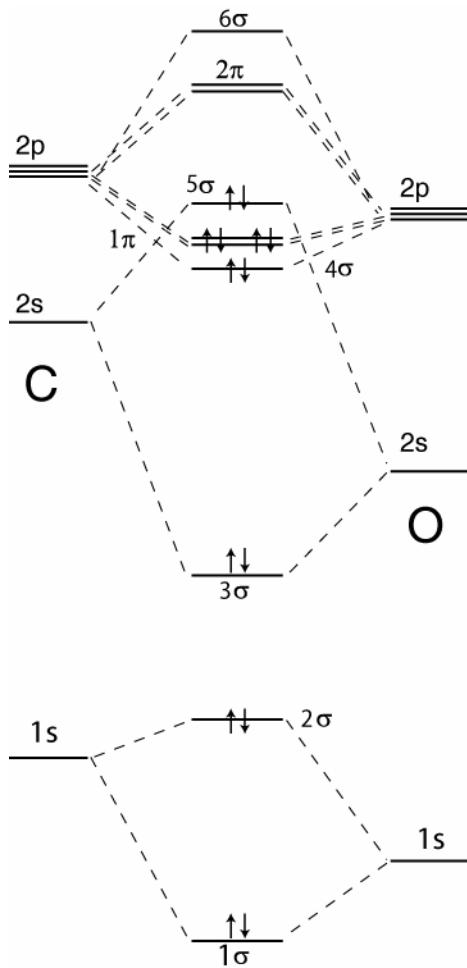


$$\text{Bond Order} = \frac{10-5}{2} = 2.5$$

Bond energy: O₂⁺ > O₂ > O₂⁻ > O₂²⁻

Bond length: O₂²⁻ > O₂⁻ > O₂ > O₂⁺

P24.13) Sketch out a molecular orbital energy diagram for CO and place the electrons in the levels appropriate for the ground state. The AO ionization energies are O2s: 32.3 eV; O2p: 15.8 eV; C2s; 19.4 eV; and C2p: 10.9 eV. The MO energies follow the sequence (from lowest to highest) 1σ, 2σ, 3σ, 4σ, 1π, 5σ, 2π, 6σ. Assume that the 1s orbital need not be considered and define the 1σ orbital as originating primarily from the 2s AOs on C and O. Connect each MO level with the level of the major contributing AO on each atom.



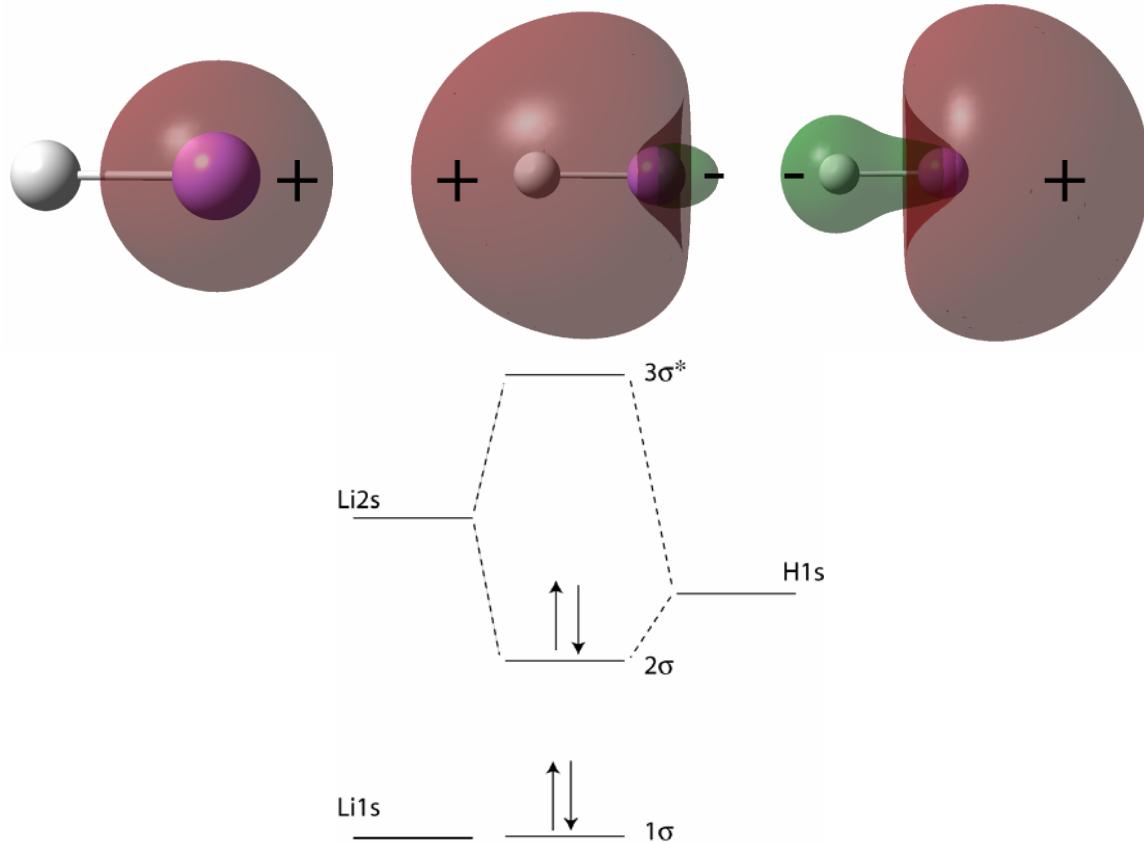
P24.14) Calculate the dipole moment of HF for the bonding described by the two MOs of Equation (24.13). Use the method outlined in Section 24.3 and the results of Example Problem 24.1 to calculate the charge on each atom. The bond length in HF is 91.7 pm. The experimentally determined dipole moment of ground-state HF is 1.91 Debye, where 1 Debye = 3.33×10^{-30} C m. Compare your result with this value. Does the simple theory give a reliable prediction of the dipole moment?

As discussed in Section 24.3, the probabilities for finding the electron on the H and F atoms are $(c_{11})^2 + c_{11}c_{21}S_{12} = 0.201$ and $(c_{21})^2 + c_{11}c_{21}S_{12} = 0.791$ for finding the electron on the H and F atoms respectively. The magnitude of the dipole moment for this diatomic molecule is given by $\mu = e(z_2 - z_1)r$, where z_i is the charge on each atom, and r is the bond length.

$$\begin{aligned}\mu &= 1.609 \times 10^{-19} \text{ C} \times 91.7 \times 10^{-12} \text{ m} \times |(0.791 - 0.201)| \\ &= 8.67 \times 10^{-30} \text{ C m} = 2.60 \text{ D}\end{aligned}$$

The error, although considerable, indicates that this very simple model is reasonable.

P24.15) Images of molecular orbitals for LiH calculated using the minimal basis set are shown here. In these images, the smaller atom is H. The H 1s AO has a lower energy than the Li 2s AO. The energy of the MOs is (left to right) -63.9 eV , -7.92 eV , and $+2.14\text{ eV}$. Make a molecular orbital diagram for this molecule, associate the MOs with the images, and designate the MOs in the images below as filled or empty. Which MO is the HOMO? Which MO is the LUMO? Do you expect the dipole moment in this molecule to have the negative end on H or Li?



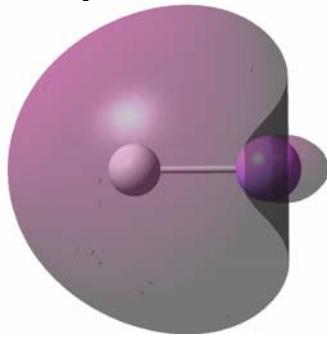
The left image corresponds to the 1σ MO, because the MO is localized on the Li atom. From the MO diagram, the 2σ MO should have a larger coefficient for the $\text{H}1\text{s}$ AO than for the $\text{Li}2\text{s}$ AO, following the rules outlined in Section 24.2. Therefore, the middle image is the 2σ MO. Following the same reasoning, the $3\sigma^*$ MO should have a larger coefficient for the $\text{Li}2\text{s}$ AO. Therefore, the right image is the $3\sigma^*$ MO. The 1σ and 2σ MOs are filled, and the $3\sigma^*$ is empty.

Because the coefficient for the $\text{H}1\text{s}$ AO is larger than that for the $\text{Li}2\text{s}$ AO in the 2σ MO, the bonding electrons have a higher probability of being on the H than on the Li. Therefore, the negative end of the dipole is on the H atom.

P24.16) Explain the difference in the appearance of the MOs in Problem P24.15 with those for HF. Based on the MO energies, do you expect LiH^+ to be stable? Do you expect LiH^- to be stable?

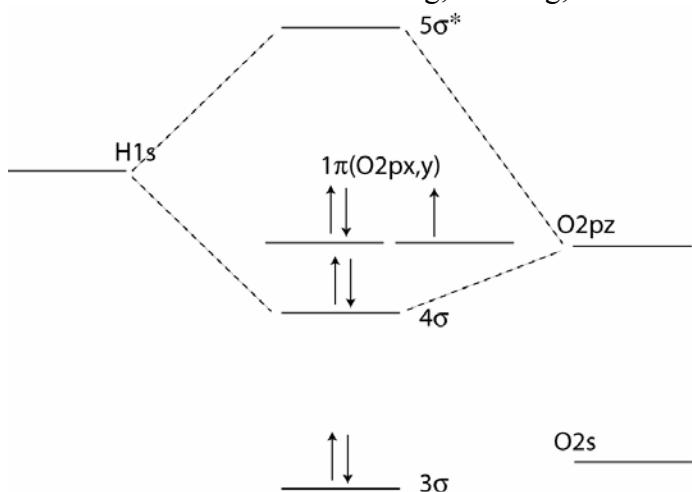
The MOs on LiH are more delocalized than on HF, so that this molecule has much less ionic character than HF. Removing one electron from LiH will not cause the molecule to dissociate, because the MO energy is below that of the AOs involved in the bonding. However, adding an electron to form LiH^- places the electron in an antibonding MO that lies above the AOs. It is likely that this molecule is not stable. However, because the total energy of a molecule is not the sum of the orbital energies, the stability of the molecule can not be determined from the MO diagram.

P24.17) A surface displaying a contour of the total charge density in LiH is shown below. What is the relationship between this surface and the MOs displayed in Problem P24.15? Why does this surface closely resemble one of the MOs?



The surface of electron density will be determined by all filled MOs, but the unfilled MOs will not contribute. Therefore, the $3\sigma^*$ MO has no influence in determining the electron density surface. Higher energy MOs are further out from the molecular skeleton than lower lying MOs. Therefore, they have more influence in determining the electron density contour. Therefore, the contour looks like the 2σ rather than the 1σ MO.

P24.18) Sketch the molecular orbital energy diagram for the radical OH based on what you know about the corresponding diagram for HF. How do the diagrams differ? Characterize the HOMO and LUMO as antibonding, bonding, or nonbonding.



The diagrams differ in the relative energies of the AOs involved and in that there are nonbonding valence electrons on the OH radical, whereas there are none on HF. The

HOMO is the 1π , which is a nonbonding MO. The LUMO is the $5\sigma^*$, which is an antibonding MO.

P24.19) A Hartree-Fock calculation using the minimal basis set of the $1s$, $2s$, $2p_x$, $2p_y$, and $2p_z$ AOs on each of N and O generated the energy eigenvalues and AO coefficients listed in the following table.

a) Designate the MOs in the table below as σ or π symmetry and as bonding or antibonding. Assign the MOs to the following images, in which the O atom is red. The molecular axis is the z axis. In doing so, keep the following criteria in mind:

MO	ϵ (eV)	c_{N1s}	c_{N2s}	c_{N2pz}	c_{N2px}	c_{N2py}	c_{O1s}	c_{O2s}	c_{O2pz}	c_{O2px}	c_{O2py}
3	-41.1	-0.13	+0.39	+0.18	0	0	-0.20	+0.70	+0.18	0	0
4	-24.2	-0.20	0.81	-0.06	0	0	0.16	-0.71	-0.30	0	0
5	-18.5	0	0	0	0	0.70	0	0	0	0	0.59
6	-15.2	+0.09	-0.46	+0.60	0	0	+0.05	-0.25	-0.60	0	0
7	-15.0	0	0	0	0.49	0	0	0	0	0.78	0
8	-9.25	0	0	0	0	0.83	0	0	0	0	-0.74

- If AOs of the same type on the two atoms have the same sign, they are in phase; if they have the opposite sign, they are out of phase.
- The energy increases with the number of nodes.
- If the coefficients of the s and p_z AOs are zero, the MO has π symmetry.
- If the coefficients of the p_x and p_y AOs are zero, the MO has σ symmetry.

b) Explain why MOs 6 and 7 do not have the same energy. Why is the energy of MO 6 lower than that of MO 7?

Therefore, considering the coefficients of the s , p_x , p_y , and p_z AOs, MOs 3, 4, and 6 have σ symmetry, and MOs 5, 7, and 8 have π symmetry. Considering the relative signs of the AOs of the same type on the two atoms, 3, 5, and 7 are bonding, whereas 4 and 8 are antibonding. MO 6 is bonding because the AOs that contribute most to the MO have the same sign on N and O.

Of the σ MOs, the energy increases with the number of nodes. Therefore, MO 3 has the lowest energy and corresponds to image f. MOs 4 and 6 correspond to images b and a, respectively. Of the π MOs, the energy also increases with the number of nodes. MOs 5 and 7 correspond to images c and e. Note that $c_{O2px} > c_{N2px}$ for MO 7, whereas $c_{N2py} > c_{O2py}$ for MO 5. Therefore, the size of the π lobe around the O atom should be larger than that on the N atom for MO 7, and less on MO 5. We conclude that image c corresponds to MO 5, and image e corresponds to MO 7. The antibonding π MO 8 corresponds to image d.

Chapter 25: Molecular Structure and Energy Levels for Polyatomic Molecules

Questions on Concepts

Q25.1) On the basis of what you know about the indistinguishability of electrons and the difference between the wave functions for bonding electrons and lone pairs, discuss the validity and usefulness of the Lewis structure for the fluorine molecule, $\ddot{\text{F}}-\ddot{\text{F}}:$

The Lewis structure is based on a localized assumption, specifying that electrons are restricted to specific orbitals, involving bonds and lone pairs. We know that this description is too specific. Electrons can tunnel from one localized orbital to another, and electron indistinguishability keeps us from knowing where a given electron actually is. Therefore, it is not possible to say that a given electron is a bonding electron as opposed to being localized in a lone pair.

Q25.2) The hybridization model assumes that atomic orbitals are recombined to prepare directed orbitals that have the bond angles appropriate for a given molecule. What aspects of the model can be tested by experiments, and what aspects are conjectures that are not amenable to experimental verification?

Bond lengths, bond angles, the distribution of the electron density in a molecule, the dipole moment associated with a bond, and the number of unpaired electrons are accessible through experiments. Bond angles, relative bond lengths, and the dependence of the electronegativity on the degree of $s-p$ hybridization can be predicted by the hybridization model. To the extent that agreement exists, it can be viewed as a confirmation of the model. However, the concept that individual atomic orbitals are combined to form new directed orbitals is useful as a model, but is not something that can be verified by an experiment.

Q25.3) What experimental evidence can you cite in support of the hypothesis that the electronegativity of a hybridized atom increases with increasing s character?

Evidence for this effect can be seen in the observation that the positive end of the dipole moment in $\text{N}\equiv\text{C}-\text{Cl}$ is on the Cl atom. We conclude that the carbon atom in the cyanide group is more electronegative than a chlorine atom. One can also consider the acidity of ethane, ethene, and acetylene. As the s -character of the hybridization increases (ethane, ethene, acetylene), the pK_a decreases (>50 for ethane, ~ 44 for ethene, and ~ 25 for acetylene). Since pK_a is inversely related to electronegativity, it is clear that as the s -character increases, the electronegativity also increases.

Q25.4) In using the sum of the occupied MO energies to predict the bond angle in H_2A molecules, the total energy of the molecule is assumed to be proportional to the sum of

the occupied MO energies. This assumption can be justified. Do you expect this sum to be greater than or smaller than the total energy? Justify your answer.

The calculated molecular orbitals are obtained through use of Hartree-Fock theory and a variational method involving calculations with incomplete basis sets. As discussed in Chapter 21, summing the orbital energies counts the repulsion between electrons twice. Because the orbital energies are negative and the repulsive contribution to the energy is positive, the sum of the orbital energies will be greater than the true energy. This is true even for a complete basis set. Since the energy obtained through a variational method or by using incomplete basis sets is always larger than the true ground state energy, the effect is even more pronounced in practical calculations.

Q25.5) In explaining molecular structure, the MO model uses the change in MO energy with bond angle. Explain why the decrease in energy of the $1a_1$ and $2a_1$ MOs as 2θ decreases more than offsets the increase in energy for the $1b_2$ MO for water.

The MO energies change because of the overlap of the AOs. For the $1b_2$ MO, the overlap between the $O2p_y$ and the $H1s$ AOs has its maximum value at 180° . Therefore, the $1b_2$ MO energy increases as the molecule is bent. The opposite is true for the $2a_1$ MO, where the overlap is zero for 180° and increases as the molecule is bent. The decrease in the $1a_1$ MO as the molecule is bent is a secondary effect, resulting from an increase in the H–H overlap. The change in energy of the molecule with bond angle is determined by the sum of these three factors. Because the lowering of the $1a_1$ and $2a_1$ energies is greater than the increase in the $1b_2$ MO energy, the H_2O molecule is bent rather than linear.

Q25.6) Why are localized and delocalized models equally valid in describing bonding in closed-shell molecules? Why can't experiments distinguish between these models?

Molecular quantum mechanical calculations rely upon basis sets to be made more tractable. The localized model uses hybridized orbitals as the basis set, and the delocalized model uses the MOs as a basis set. The molecular wave function for a closed shell molecule is equally well described by the hybridized linear combination of AOs and the MO linear combination of AOs. Because the molecular wave functions are the same for the two models, no experiment can decide between them.

Q25.7) A cyclic polyene is known to be nonplanar. Are the MO energy levels of this molecule well described by the Hückel model? Justify your answer.

The Hückel model assumes an optimal coupling of all sp^2 hybridized carbon atoms so that the π electrons are delocalized throughout the molecule. This is the case if all carbon atoms lie in the same plane. The conjugation is decreased significantly if the molecule is nonplanar. Therefore, the MO energy levels of a nonplanar molecule are not well described by the Hückel model.

Q25.8) What is the amplitude of the wave functions describing the π network in the conjugated molecules shown in Figures 25.15 to 25.17 in the plane of the molecule?

The Hückel model is valid for a planar conjugated molecule. The p orbital that gives rise to the π network has a node in the plane of the molecule. Therefore, the amplitude of the wave functions describing the π network in the conjugated is zero in the plane of the molecules.

Q25.9) Explain why all possible wave functions between the fully bonding and the fully antibonding are possible for the bands shown in Figure 25.21.

A linear molecule containing N atoms will form a pseudo-molecule composed of N molecular orbitals, each of which is a linear combination of N atomic orbitals. To ensure that all MOs are orthogonal, each MO combination must include an additional sign change (node) relative to the MO just below it in energy. This generates N possible wave functions between fully bonding and fully antibonding.

Q25.10) For what condition is it difficult to say whether a material is a semiconductor or an insulator?

The conductivity of a material is dependent on the population of electrons in the conduction band. As this population is dependent itself upon the temperature, the conductivity of the material is dependent upon temperature. Many materials may be insulating at low temperatures, but become semi-conducting at higher temperatures. Furthermore, even at low temperatures, sufficient electron populations exist in the conduction bands to permit a very small conductivity. Therefore, it is not always possible to describe a material strictly as either a semiconductor or an insulator.

Problems

P25.1) Use the VSEPR method to predict the structures of the following:

- a) PF₃ b) CO₂ c) BrF₅ d) SO₃²⁻

- a) PF₃ has 3 ligands and a lone pair. VSEPR predicts that the structure is pyramidal.
- b) CO₂ has 2 double-bonded ligands and no lone pairs. VSEPR predicts that the structure is linear.
- c) BrF₅ has 5 ligands and a lone pair. VSEPR predicts that the structure is square pyramidal.
- d) SO₃²⁻ has 3 ligands and a lone pair. VSEPR predicts that the structure is pyramidal.

P25.2) Use the VSEPR method to predict the structures of the following:

- a) PCl_5 b) SO_2 c) XeF_2 d) XeF_5

a) PCl_5 has 5 ligands and a lone pair. VSEPR predicts that the structure is a distorted trigonal bipyramidal.

b) SO_2 has 2 ligands and a lone pair. VSEPR predicts that the structure is bent.

c) XeF_2 has 2 ligands and 3 lone pairs. VSEPR predicts that the structure is a triangular bipyramidal with all three atoms on the axis, making it a linear molecule.

d) XeF_5 has 5 ligands and 2 lone pairs. VSEPR predicts that the structure is a pentagonal bipyramidal.

P25.3) Show that the water hybrid bonding orbitals given by

$$\psi_a = 0.55 \phi_{2p_z} + 0.71 \phi_{2p_y} - 0.45 \phi_{2s} \text{ and } \psi_b = 0.55 \phi_{2p_z} - 0.71 \phi_{2p_y} - 0.45 \phi_{2s}$$

are orthogonal.

$$\psi_a = 0.55 \phi_{2p_z} + 0.71 \phi_{2p_y} - 0.45 \phi_{2s}$$

$$\psi_b = 0.55 \phi_{2p_z} - 0.71 \phi_{2p_y} - 0.45 \phi_{2s}$$

$$\begin{aligned} \int \psi_a^* \psi_b d\tau &= \int \left[0.55 \phi_{2p_z} + 0.71 \phi_{2p_y} - 0.45 \phi_{2s} \right]^* \left[0.55 \phi_{2p_z} - 0.71 \phi_{2p_y} - 0.45 \phi_{2s} \right] d\tau \\ &= (0.55)^2 \int (\phi_{2p_z})^2 d\tau - (0.55)(0.71) \int \phi_{2p_z} \phi_{2p_y} d\tau - (0.55)(0.45) \int \phi_{2p_z} \phi_{2s} d\tau \\ &\quad + (0.71)(0.55) \int \phi_{2p_y} \phi_{2p_z} d\tau - (0.71)^2 \int (\phi_{2p_y})^2 d\tau - (0.71)(0.55) \int \phi_{2p_y} \phi_{2s} d\tau \\ &\quad - (0.45)(0.55) \int \phi_{2s} \phi_{2p_z} d\tau + (0.45)(0.71) \int \phi_{2s} \phi_{2p_y} d\tau + (0.45)^2 \int (\phi_{2s})^2 d\tau \end{aligned}$$

All integrals in which the atomic orbitals are different are zero because the atomic orbitals are orthogonal. All integrals in which the atomic orbitals are identical equal one because the atomic orbitals are normalized.

$$\begin{aligned} \int \psi_a^* \psi_b d\tau &= (0.55)^2 - 0 - 0 + 0 - (0.71)^2 - 0 - 0 + 0 + (0.45)^2 \\ &= (0.55)^2 - (0.71)^2 + (0.45)^2 \\ &= 0.0009 \end{aligned}$$

To within the round-off error that occurs because the coefficients of the atomic orbitals are expressed only to two significant figures, $\int \psi_a^* \psi_b d\tau = 0$ showing that ψ_a and ψ_b are orthogonal.

P25.4) Calculate the *s* and *p* character of the water lone pair hybrid orbitals

$$\psi_c = -0.45\phi_{2p_z} - 0.55\phi_{2s} + 0.71\phi_{2p_x} \text{ and } \psi_d = -0.45\phi_{2p_z} - 0.55\phi_{2s} - 0.71\phi_{2p_x}.$$

Because the orbitals are normalized, the *s* character is given by the square of the coefficient of ϕ_{2s} . It is the same for both the hybrid orbitals and is equal to

$(0.55)^2 \approx 0.30$. The *p* character is given by the sum of the squares of the coefficients of ϕ_{2p_z} and ϕ_{2p_y} . It is the same for both hybrid orbitals and is equal to

$$(0.45)^2 + (0.55)^2 \approx 0.70.$$

P25.5) Use the formula $\cos 2\theta = -\alpha^2$ and the method in Section 25.2 to derive the

$$\text{formula } \psi_a = \frac{1}{\sqrt{2}}(-\phi_{2s} + \phi_{2p_z}) \text{ and } \psi_b = \frac{1}{\sqrt{2}}(-\phi_{2s} - \phi_{2p_z}) \text{ for two } sp \text{ hybrid orbitals}$$

directed 180° apart. Show that these hybrid orbitals are orthogonal.

The two orbitals take the form

$$\psi_a = c_1\phi_{2s} + c_2\phi_{2p_z}$$

$$\psi_b = c_3\phi_{2s} + c_4\phi_{2p_z}$$

Due to the spherical symmetry of ϕ_{2s} , $c_1 = c_3$. Conservation of probability tells us that $c_1^2 + c_3^2 = 1$ (e.g., all of the 2s orbital must be on the linear combinations). Thus:

$$c_1^2 + c_3^2 = 1$$

$$2c_1^2 = 1$$

$$c_1 = \pm \frac{1}{\sqrt{2}} = c_3$$

Due to the node in the 2s orbital, we choose $c_1 = c_3 = -\frac{1}{\sqrt{2}}$.

This leads to the result $\psi_a = -\frac{1}{\sqrt{2}}\phi_{2s} + c_2\phi_{2p_z}$ and $\psi_b = -\frac{1}{\sqrt{2}}\phi_{2s} + c_4\phi_{2p_z}$

The angle between the two orbitals must be 180°, requiring that $c_2 = -c_4$. Again, conservation of probability requires that $c_2^2 + c_4^2 = 1$. Thus

$$c_2^2 + c_4^2 = 1$$

$$2c_2^2 = 1$$

$$c_2 = \pm \frac{1}{\sqrt{2}}$$

We choose $c_2 = \frac{1}{\sqrt{2}}$, $c_4 = -\frac{1}{\sqrt{2}}$ to make the positive lobe of ϕ_{2p_z} point along the positive z direction in ψ_a . This choice is arbitrary, and the signs of c_2 and c_4 could equally well be reversed. With this choice

$$\psi_a = -\frac{1}{\sqrt{2}}(\phi_{2s} - \phi_{2p_z})$$

$$\psi_b = -\frac{1}{\sqrt{2}}(\phi_{2s} + \phi_{2p_z})$$

To show that the hybrid orbitals are orthogonal, we must show that $\int \psi_a^* \psi_b d\tau = 0$

$$\begin{aligned} \int \psi_a^* \psi_b d\tau &= \frac{1}{2} \int (\phi_{2s} - \phi_{2p_z})(\phi_{2s} + \phi_{2p_z}) d\tau \\ &= \frac{1}{2} \left[\int (\phi_{2s})^2 d\tau + \int \phi_{2s} \phi_{2p_z} d\tau - \int \phi_{2s} \phi_{2p_z} d\tau - \int (\phi_{2p_z})^2 d\tau \right] \\ &= \frac{1}{2} \left[\int (\phi_{2s})^2 d\tau - \int (\phi_{2p_z})^2 d\tau \right] \\ &= \frac{1}{2}[1 - 1] = 0 \end{aligned}$$

Therefore, the hybrid orbitals are orthogonal.

P25.6) Show that two of the set of four equivalent orbitals appropriate for sp^3 hybridization, $\psi_a = \frac{1}{2}(-\phi_{2s} + \phi_{2p_x} + \phi_{2p_y} + \phi_{2p_z})$ and $\psi_b = \frac{1}{2}(-\phi_{2s} - \phi_{2p_x} - \phi_{2p_y} + \phi_{2p_z})$ are orthogonal.

To show that $\psi_a = \frac{1}{2}(-\phi_{2s} + \phi_{2p_x} + \phi_{2p_y} + \phi_{2p_z})$ and $\psi_b = \frac{1}{2}(-\phi_{2s} - \phi_{2p_x} - \phi_{2p_y} + \phi_{2p_z})$ are orthogonal, we must evaluate

$$\begin{aligned} \int \psi_a^* \psi_b d\tau &= \frac{1}{4} \left\{ \int (\phi_{2s})^2 d\tau + \int \phi_{2s} \phi_{2p_x} d\tau + \int \phi_{2s} \phi_{2p_y} d\tau - \int \phi_{2s} \phi_{2p_z} d\tau \right. \\ &\quad - \int \phi_{2p_x} \phi_{2s} d\tau - \int (\phi_{2p_x})^2 d\tau - \int \phi_{2p_x} \phi_{2p_y} d\tau + \int \phi_{2p_y} \phi_{2p_z} d\tau \\ &\quad - \int \phi_{2p_y} \phi_{2s} d\tau - \int \phi_{2p_y} \phi_{2p_x} d\tau - \int (\phi_{2p_y})^2 d\tau + \int \phi_{2p_y} \phi_{2p_z} d\tau \\ &\quad \left. - \int \phi_{2p_z} \phi_{2s} d\tau - \int \phi_{2p_z} \phi_{2p_x} d\tau - \int \phi_{2p_z} \phi_{2p_y} d\tau + \int (\phi_{2p_z})^2 d\tau \right\} \end{aligned}$$

Because the atomic orbitals are orthonormal, each integral containing two different atomic orbitals has the value zero, and the value one if the two atomic orbitals are identical.

$$\int \psi_a^* \psi_b d\tau = \frac{1}{4}[1 - 1 - 1 + 1] = 0$$

P25.7) Use the framework described in Section 25.3 to construct normalized hybrid bonding orbitals on the central oxygen in O₃ that are derived from 2s and 2p atomic orbitals. The bond angle in ozone is 116.8°.

Assume a single resonance structure in which the O–O bonds are equivalent. The first approximation is sp^2 hybridization. A possible configuration can be written as

$1s_O^2 (\psi_{O-O})^3 (\psi_{O-O})^3 (\psi_{ep})^2$, where the resonance requires a net 6 electrons in the $2\psi_{O-O}$ orbitals and 2 electrons in the ψ_{ep} lone pair.

Geometrically, it can be seen that the bonding orbitals are equivalent to those in the H₂O example, taking the form

$$\psi_a = N \left[\cos \theta \phi_{2p_z} + \sin \theta \phi_{2p_y} - \alpha \phi_{2s} \right]$$

$$\psi_b = N \left[\cos \theta \phi_{2p_z} - \sin \theta \phi_{2p_y} - \alpha \phi_{2s} \right]$$

where

$$\cos \theta = \cos \left(\frac{116.8^\circ}{2} \right) = 0.5240$$

$$\sin \theta = \sin \left(\frac{116.8^\circ}{2} \right) = 0.8517$$

$$\alpha = \sqrt{-\cos(116.8^\circ)} = 0.6715$$

We find that $\psi_a = N \left[0.5240 \phi_{2p_z} + 0.8517 \phi_{2p_y} - 0.6715 \phi_{2s} \right]$ and, invoking normalization:

$$\psi_a^* \psi_a d\tau = 1 = N^2 \left[0.5240^2 + 0.8517^2 + 0.6715^2 \right]$$

$$1 = N^2 \times 1.4509$$

giving

$$N = 0.8302$$

The final normalized hybrid orbitals are

$$\psi_a = 0.8302 \left[0.5240 \phi_{2p_z} + 0.8517 \phi_{2p_y} - 0.6715 \phi_{2s} \right] =$$

$$\psi_a = 0.4350 \phi_{2p_z} + 0.7071 \phi_{2p_y} - 0.5575 \phi_{2s}$$

and

$$\psi_b = 0.4350 \phi_{2p_z} - 0.7071 \phi_{2p_y} - 0.5575 \phi_{2s}$$

P25.8) Use the framework described in Section 25.3 to derive the normalized hybrid lone pair orbital on the central oxygen in O₃ derived from 2s and 2p atomic orbitals. The bond angle in ozone is 116.8°.

Ozone has only one lone pair (instead of 2 like H₂O). The lone pair lies along the *z* axis and therefore is a combination of the 2s and 2*p_z* orbitals. Therefore

$$\psi_{lp} = d_1\phi_{2p_z} + d_2\phi_{2s}$$

Normalization requires that $d_1^2 + d_2^2 = 1$. Secondly, conservation of probability requires that the sum of the squares of the coefficients of ψ_{2p_z} in the 3 hybrids must equal one.

Thus

$$1 = d_1^2 + 0.4350^2 + 0.4350^2$$

or

$$d_1 = \sqrt{1 - 2 \times 0.4350^2}$$

$$d_1 = \pm 0.7884$$

and

$$1 = d_2^2 + 0.5575^2 + 0.5575^2$$

or

$$d_2 = \sqrt{1 - 2 \times 0.5575^2}$$

$$d_2 = \pm 0.6151$$

Because of the node in the 2s orbital, we choose $d_2 = -0.6151$, which gives the amplitude of the orbital a positive sign in the region of interest. We choose $d_1 = -0.7884$ because this makes ψ_{ep} orthogonal to ψ_a and ψ_b as shown here.

$$\psi_{ep} = -0.7884\phi_{2p_z} - 0.615\phi_{2s}$$

$$\begin{aligned} \int \psi_{ep}^* \psi_a d\tau &= \int (-0.7884\phi_{2p_z} - 0.615\phi_{2s})(0.4350\phi_{2p_z} - 0.7071\phi_{2p_y} - 0.5575\phi_{2s}) d\tau \\ &= -(0.7884)(0.4350) \int (\phi_{2p_z})^2 d\tau + (0.6151)(0.5575) \int \phi_{2s}^2 d\tau \\ &= -(0.7884)(0.4350) + (0.6151)(0.5575) \\ &= 0.00004 \approx 0 \end{aligned}$$

With this choice of coefficients, ψ_{ep} is normalized as shown below

$$\begin{aligned} \int \psi_{ep}^* \psi_{ep} d\tau &= \int (-0.7884\phi_{2p_z} - 0.6151\phi_{2s})^2 d\tau \\ &= (0.7884)^2 \int (\phi_{2p_z})^2 d\tau + 2 \times (0.7884)(0.6151) \int \phi_{2p_z}\phi_{2s} d\tau \\ &\quad + (0.6151)^2 \int (\phi_{2s})^2 d\tau \\ &= (0.7884)^2 + (0.6151)^2 \\ &= 0.984 \approx 1 \end{aligned}$$

P25.9) Use the method described in Example Problem 25.3 to show that the *sp*-hybrid orbitals $\psi_a = \frac{1}{\sqrt{2}}(-\phi_{2s} + \phi_{2p_z})$ and $\psi_b = \frac{1}{\sqrt{2}}(-\phi_{2s} - \phi_{2p_z})$ are oriented 180° apart.

$$\begin{aligned}\frac{d\phi_{2p_z}}{dt} &= \frac{d}{dt} \left(\frac{1}{\sqrt{32\pi}} \left(\frac{\zeta}{a_0} \right)^{3/2} \left(\frac{r}{a_0} \right) e^{-\zeta r/a_0} \cos \theta \right) \\ \frac{d\psi_a}{dG} &= \frac{1}{\sqrt{2}} \frac{d}{dt} \left[-\frac{1}{\sqrt{32\pi}} \left(\frac{\zeta}{a_0} \right)^{3/2} \left(2 - \frac{r}{a_0} \right) e^{-r/a_0} + \frac{1}{\sqrt{32\pi}} \left(\frac{\zeta}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-\zeta r/a_0} \cos \theta \right] \\ &= -\frac{1}{\sqrt{32\pi}} \left(\frac{\zeta}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-\zeta r/a_0} \sin \theta = 0\end{aligned}$$

This equation is satisfied for $\theta = 0$ and $\theta = 180^\circ$. The second derivative is used to establish which of these corresponds to a maximum.

$$\begin{aligned}\frac{d^2\psi_a}{dt^2} &= -\frac{1}{\sqrt{32\pi}} \left(\frac{\zeta}{a_0} \right)^{3/2} \left(\frac{r}{a_0} \right) e^{-\zeta r/a_0} \cos \theta \\ &= -\frac{1}{\sqrt{32\pi}} \left(\frac{\zeta}{a_0} \right)^{3/2} \left(\frac{r}{a_0} \right) e^{-\zeta r/a_0} \text{ at } \theta = 0 \\ &= \frac{1}{\sqrt{32\pi}} \left(\frac{\zeta}{a_0} \right)^{3/2} \left(\frac{r}{a_0} \right) e^{-\zeta r/a_0} \text{ at } \theta = 180^\circ\end{aligned}$$

At a maximum, $\frac{d^2\psi_a}{d\theta^2} < 0$ and at a minimum, $\frac{d^2\psi_a}{d\theta^2} > 0$. Therefore, the maximum is at 0°, and a minimum at 180°. Applying the same procedure to ψ_b shows that the maximum is at 0°. Therefore, ψ_a and ψ_b point in opposite directions separated by 180°.

P25.10) Predict whether LiH₂⁺ and NH₂⁻ should be linear or bent based on the Walsh correlation diagram in Figure 25.10. Explain your answers.

The LiH₂⁺ molecule has two valence electrons. These fill only the 1a₁ MO. The correlation diagram shows that the energy of this MO is lowered if the molecule is bent. The molecule has eight valence electrons, as does H₂O, and is bent for the same reason.

P25.11) Predict which of the bent molecules, BH₂ or NH₂, should have the larger bond angle on the basis of the Walsh correlation diagram in Figure 25.10. Explain your answer.

Molecule:	BH ₂	NH ₂
Valence e ⁻ :	5	7
HOMO:	2a ₁	1b ₁

Both molecules are equivalent through the $(2a_1)^1$ orbital. However, by adding the second electron to the $2a_1$ orbital and the electron to the $1b_1$ orbital, the NH_2 molecule is shifted more to the bent form to lower the energy. Thus, the BH_2 molecule has the larger bond angle.

P25.12) Predict whether the ground state or the first excited state of CH_2 should have the larger bond angle on the basis of the Walsh correlation diagram in Figure 25.11. Explain your answer.

CH_2 has 6 valence electrons. In the ground state, the HOMO is the $2a_1$ MO and in the excited state, the HOMO is the $1b_1$ MO. The promotion of the electron from the doubly occupied $2a_1$ MO to the non-bonding $1b_1$ will increase the energy and shift the geometry to a more linear orientation. Thus the first excited state of CH_2 will have a larger bond angle.

P25.13) Show that the determinantal property $\begin{vmatrix} a & c \\ b & d \end{vmatrix} = \begin{vmatrix} a & \gamma a + c \\ b & \gamma b + d \end{vmatrix}$ used in the discussion of localized and delocalized orbitals in Section 25.6 is correct.

We first assume that $\begin{vmatrix} a & c \\ b & d \end{vmatrix} = \begin{vmatrix} a & \gamma a + c \\ b & \gamma b + d \end{vmatrix}$ for some constant γ .

If this is true, the values of the determinants must be equal.

$$ad - bc = a(\gamma b + d) - (\gamma a + c)b$$

$$ad - bc = \gamma ab + ad - \gamma ab + cb$$

$$ad - bc = ad - cb$$

The equality shows that the assumption is true.

P25.14) Are the localized bonding orbitals in Equation (25.14) defined by

$$\sigma' = 2c_1\phi_{H1sA} + \left(c_2\phi_{Be2s} - \frac{c_1c_4}{c_3}\phi_{Be2pz} \right) \text{ and } \sigma'' = 2c_1\phi_{H1sB} + \left(c_2\phi_{Be2s} + \frac{c_1c_4}{c_3}\phi_{Be2pz} \right)$$

orthogonal? Answer this question by evaluating the integral $\int (\sigma')^* \sigma'' d\tau$.

$$\begin{aligned}
 \int (\sigma')^* \sigma'' d\tau &= \int \left[2c_1 \phi_{H1sA} + c_2 \phi_{Be2s} - \frac{c_1 c_4}{c_3} \phi_{Be2p_z} \right] \\
 &\quad \times \left[2c_1 \phi_{H1sB} + \left(c_2 \phi_{Be2s} + \frac{c_1 c_4}{c_3} \right) \phi_{Be2p_z} \right] d\tau \\
 &= 4c_1^2 \int \phi_{H1sA} \phi_{H1sB} d\tau + 2c_1 c_2 \int \phi_{H1sA} \phi_{Be2s} d\tau + 2c_1 c_2 \int \phi_{H1sB} \phi_{Be2s} d\tau \\
 &\quad + c_2^2 \int (\phi_{Be2s})^2 d\tau - \frac{2c_1^2 c_4}{c_3} \int \phi_{H1sA} \phi_{Be2p_z} d\tau + \frac{2c_1^2 c_4}{c_3} \int \phi_{H1sB} \phi_{Be2p_z} d\tau \\
 &\quad - \left(\frac{c_1 c_4}{c_3} \right)^2 \int (\phi_{Be2p_z})^2 d\tau
 \end{aligned}$$

Because of the symmetry of the molecule,

$$\int \phi_{H1sA} \phi_{Be2s} = \int \phi_{H1sB} \phi_{Be2s} \text{ and}$$

$$\int \phi_{H1sA} \phi_{Be2p_z} = \int \phi_{H1sB} \phi_{Be2p_z}$$

Because of the orthogonality of the atomic orbitals on Be, $\int \phi_{Be2s} \phi_{Be2p_z} = 0$.

Because the atomic orbitals are normalized

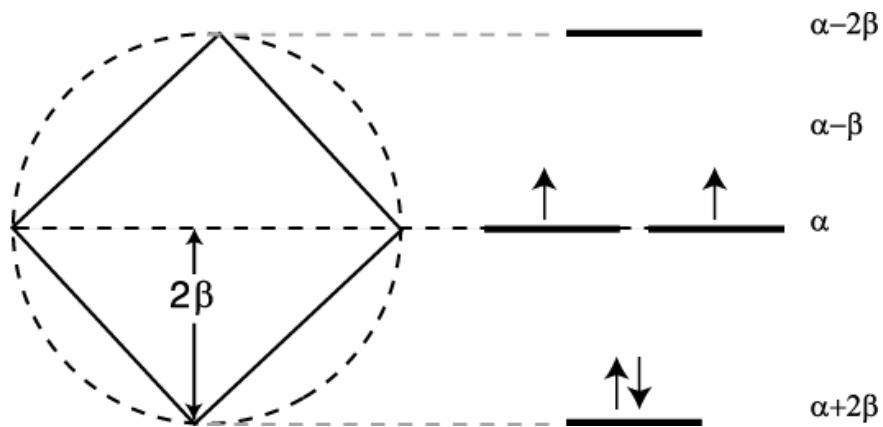
$$\int (\phi_{H1s})^2 d\tau = \int (\phi_{Be2s})^2 d\tau = \int (\phi_{Be2p_z})^2 d\tau = 1$$

Using these results,

$$\int (\sigma')^* (\sigma'') d\tau = c_2^2 + 4c_1 c_2 \int \phi_{H1sA} \phi_{Be2s} d\tau + c_1^2 \left(4 \int \phi_{H1sA} \phi_{H1sB} d\tau - \left(\frac{c_4}{c_3} \right)^2 \right)$$

Because this expression is not equal to zero, the localized bonding orbitals σ' and σ'' are not orthogonal.

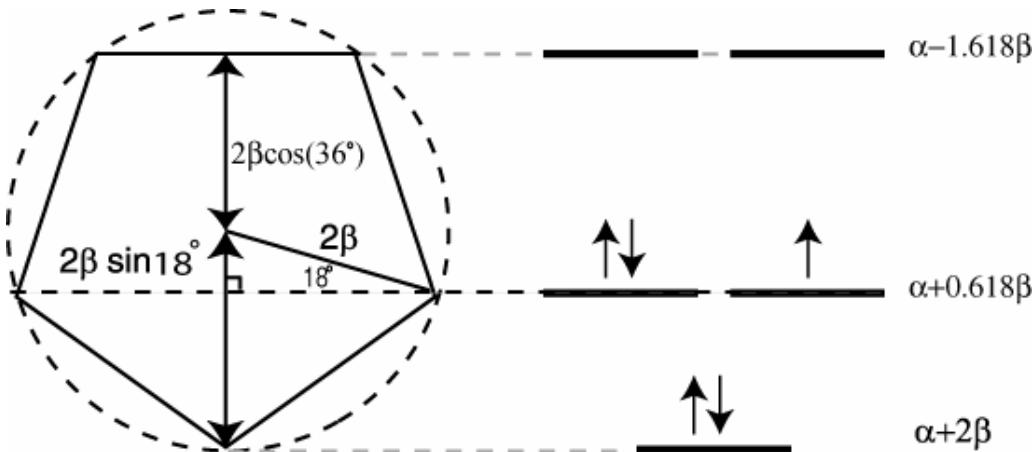
P25.15) Use the geometrical construction shown in Example Problem 25.10 to derive the π electron MO levels for cyclobutadiene. What is the total π energy of the molecule? How many unpaired electrons will the molecule have?



There are 2 unpaired electrons.

$$\text{The total } \pi \text{ energy is } E_{\pi} = 2(\alpha + 2\beta) + 2(\alpha) = 4\alpha + 4\beta$$

P25.16) Use the geometrical construction shown in Example Problem 25.10 to derive the π electron MO levels for the cyclopentadienyl radical. What is the total π energy of the molecule? How many unpaired electrons will the molecule have?



$$2\beta \sin(18^\circ) = 0.618$$

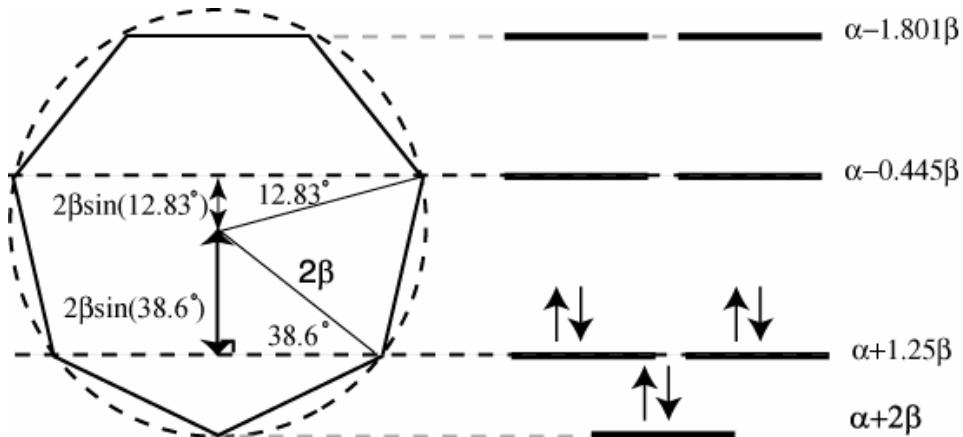
$$2\beta \cos(36^\circ) = 1.618$$

There is one unpaired electron. The π energy is

$$E_{\pi} = 2[\alpha + 2\beta] + 3(\alpha + 0.618\beta)$$

$$E_{\pi} = 5\alpha + 5.85\beta$$

P25.17) Use the geometrical construction shown in Example Problem 25.10 to derive the energy levels of the cycloheptatrienyl cation. What is the total π energy of the molecule? How many unpaired electrons will the molecule have? Would you expect this species, the neutral species, or the anion to be aromatic? Justify your answer.



There are zero unpaired electrons. The π energy is

$$E_{\pi} = 2[\alpha + 2\beta + 2(\alpha + 1.25\beta)]$$

$$E_{\pi} = 6\alpha + 9\beta$$

Using the Hückel rule, $4 \times 1 + 2 = 6e^-$. The cation is the form that is aromatic.

P25.18) The allyl cation $\text{CH}_2=\text{CH}-\text{CH}$ has a delocalized π network that can be described by the Hückel method. Derive the MO energy levels of this species and place the electrons in the levels appropriate for the ground state. Using the butadiene MOs as an example, sketch what you would expect the MOs to look like. Classify the MOs as bonding, antibonding, or nonbonding.



The secular determinant has the form:

$$\begin{vmatrix} \alpha - \varepsilon & \beta & 0 \\ \beta & \alpha - \varepsilon & \beta \\ 0 & \beta & \alpha - \varepsilon \end{vmatrix} = \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

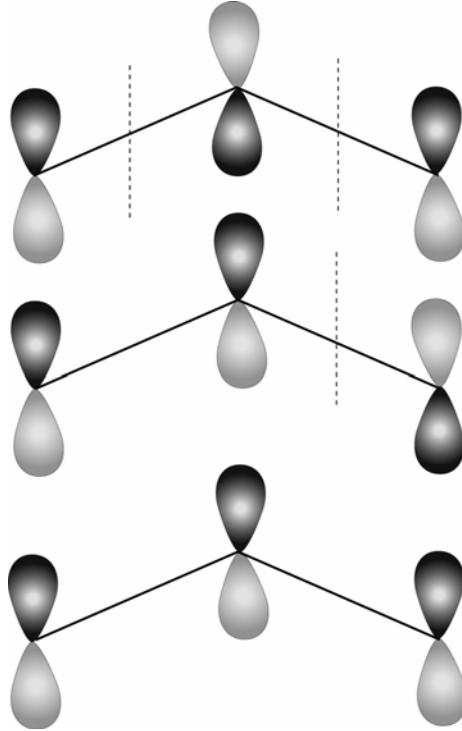
where $x = \frac{\alpha - \varepsilon}{\beta}$. Thus, the secular equation is

$$\begin{aligned} 0 &= x(x^2 - 1) - 1(x - 0) + 0(1 - 0) \\ &= x(x^2 - 1) - x \\ 0 &= x(x^2 - 2) \end{aligned}$$

The solutions to this equation are $x = (0, \pm\sqrt{2})$. Substituting $x = \frac{\alpha - \varepsilon}{\beta}$ gives the energy levels $\varepsilon = (\alpha, \alpha \pm \sqrt{2}\beta)$.

The nodal structure of the MOs is shown below. The lowest energy MO ($\varepsilon = \alpha + \sqrt{2}\beta$) has no nodes, the next highest MO ($\varepsilon = \alpha$) has one node, and the highest occupied MO

$(\varepsilon = \alpha - \sqrt{2}\beta)$ has two nodes. The orbitals are not to scale, because the coefficients of the $2p_z$ orbital on different C atoms is not the same.



P25.19) Determine the AO coefficients for the lowest energy Hückel π MO for butadiene.

The energy is given by $\varepsilon = \alpha + 1.62\beta$ and $\psi_\pi = c_1\psi_{2p_z}^a + c_2\psi_{2p_z}^b + c_3\psi_{2p_z}^c + \psi_{2p_z}^d$

Thus, the secular equations are

- 1): $c_1(H_{aa} - \varepsilon S_{aa}) + c_2(H_{ab} - \varepsilon S_{ab}) + c_3(H_{ac} - \varepsilon S_{ac}) + c_4(H_{ad} - \varepsilon S_{ad}) = 0$
- 2): $c_1(H_{ba} - \varepsilon S_{ba}) + c_2(H_{bb} - \varepsilon S_{bb}) + c_3(H_{bc} - \varepsilon S_{bc}) + c_4(H_{bd} - \varepsilon S_{bd}) = 0$
- 3): $c_1(H_{ca} - \varepsilon S_{ca}) + c_2(H_{cb} - \varepsilon S_{cb}) + c_3(H_{cc} - \varepsilon S_{cc}) + c_4(H_{cd} - \varepsilon S_{cd}) = 0$
- 4): $c_1(H_{da} - \varepsilon S_{da}) + c_2(H_{db} - \varepsilon S_{db}) + c_3(H_{dc} - \varepsilon S_{dc}) + c_4(H_{dd} - \varepsilon S_{dd}) = 0$

The overlap is given by $S_{jk} = \delta_{jk}$, and we assign values to the H_{jk} as follows:

$$H_{jk} = \begin{cases} \alpha & \text{if } j = k \\ \beta & \text{if } j \text{ and } k \text{ differ by 1, and} \\ 0 & \text{otherwise} \end{cases}$$

Substituting in the four secular equations gives the following relations:

- 1) $c_1[\alpha - (\alpha + 1.62\beta)] + c_2[\beta] = 0$

We conclude that $c_2 = 1.62 c_1$

$$2) c_1\beta + c_2 [\alpha - (\alpha + 1.62\beta)] + c_3\beta = 0$$

We conclude that $c_1 + c_3 = 1.62 c_2$ or $c_3 = (1.62^2 - 1)c_1$

$$3) c_2\beta + c_3 [\alpha - (\alpha + 1.62\beta)] + c_4\beta = 0$$

We conclude that $c_2 + c_4 = 1.62 c_3$ or $c_4 = \frac{(1.62^2 - 1)}{1.62} c_1$

The 4th equation needed to solve this system is the normalization condition, defined by

$$\begin{aligned} 1 &= \int (\psi_\pi)^* \psi_\pi d\tau = \int (c_1 \psi_{2p_z}^a + c_2 \psi_{2p_z}^b + c_3 \psi_{2p_z}^c + c_4 \psi_{2p_z}^d)^2 d\tau \\ &= c_1^2 \int (\psi_{2p_z}^a)^2 d\tau + c_2^2 \int (\psi_{2p_z}^b)^2 d\tau + c_3^2 \int (\psi_{2p_z}^c)^2 d\tau + c_4^2 \int (\psi_{2p_z}^d)^2 d\tau \\ &\quad + 2c_1c_2 \int \psi_{2p_z}^a \psi_{2p_z}^b d\tau + 2c_1c_3 \int \psi_{2p_z}^a \psi_{2p_z}^c d\tau + 2c_1c_4 \int \psi_{2p_z}^a \psi_{2p_z}^d d\tau \\ &\quad + 2c_2c_3 \int \psi_{2p_z}^b \psi_{2p_z}^c d\tau + 2c_2c_4 \int \psi_{2p_z}^b \psi_{2p_z}^d d\tau \\ &= c_1^2 + c_2^2 + c_3^2 + c_4^2 + 2c_1c_2 S_{ab} + 2c_1c_3 S_{ac} + 2c_1c_4 S_{ad} + 2c_2c_3 S_{bc} + 2c_2c_4 S_{bd} \\ &= c_1^2 + c_2^2 + c_3^2 + c_4^2 \end{aligned}$$

Substituting 1-3 into the normalization equation yields

$$c_1^2 + 1.62^2 c_1^2 + (1.62^2 - 1)^2 c_1^2 + \left[\frac{(1.62^2 - 1)}{1.62} \right]^2 c_1^2 = 1$$

or

$$c_1^2 = \frac{1}{1 + 1.62^2 + (1.62^2 - 1)^2 + \left[\frac{1.62^2 - 1}{1.62} \right]^2}$$

and

$$c_1 = 0.3715$$

$$c_2 = 1.62 \cdot 0.3715 = 0.602$$

$$c_3 = (1.62^2 - 1) 0.3715 = 0.602$$

$$c_4 = \left(1.62 - \frac{1}{1.62} \right) 0.3715 = 0.3715$$

$$\psi_\pi = 0.3715 \psi_{2p_z}^a + 0.602 \psi_{2p_z}^b + 0.602 \psi_{2p_z}^c + 0.3715 \psi_{2p_z}^d$$

P25.20) Using the Boltzmann distribution to answer parts (a) and (b):

- Calculate the ratio of electrons at the bottom of the conduction band to those at the top of the valence band for pure Si at 300 K. The Si band gap is 1.1 eV.
- Calculate the ratio of electrons at the bottom of the conduction band to those at the top of the dopant band for P-doped Si at 300 K. The top of the dopant band lies 0.04 eV below the bottom of the Si conduction band.

Chapter 25/Molecular Structure and Energy Levels for Polyatomic Molecules

Assume for these calculations that the ratio of the degeneracies is unity. What can you conclude about the room temperature conductivity of these two materials on the basis of your calculations?

Assuming that $\frac{g_2}{g_1} = 1$, then

$$\frac{n_2}{n_1} = e^{-\Delta E / kT}$$

$$\text{a) } \frac{n_2}{n_1} = \exp \left[-\frac{1.1 \text{ eV}}{1.381 \times 10^{-23} \text{ JK}^{-1} \times 300 \text{ K}} \times \frac{1 \text{ J}}{6.242 \times 10^{18} \text{ eV}} \right]$$

$$= \exp[-42.54]$$

$$\frac{n_2}{n_1} = 3.35 \times 10^{-18}$$

Pure Si at 300 K is an insulator.

$$\text{b) } \frac{n_2}{n_1} = \exp \left[-\frac{0.04 \text{ eV}}{1.381 \times 10^{-23} \text{ JK}^{-1} \times 300 \text{ K}} \times \frac{1 \text{ J}}{6.242 \times 10^{18} \text{ eV}} \right]$$

$$= \exp[-1.547]$$

$$= 0.213$$

Doped Si at 300 K is a semiconductor.

Chapter 26: Electronic Spectroscopy

Q26.1) Calculate the bond order for O₂ in the $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$, $A^3\Sigma_u^+$, and the $B^3\Sigma_u^-$ states. Arrange these states in order of increasing bond length on the basis of bond order. Do your results agree with the potential energy curves shown in Figure 26.1?

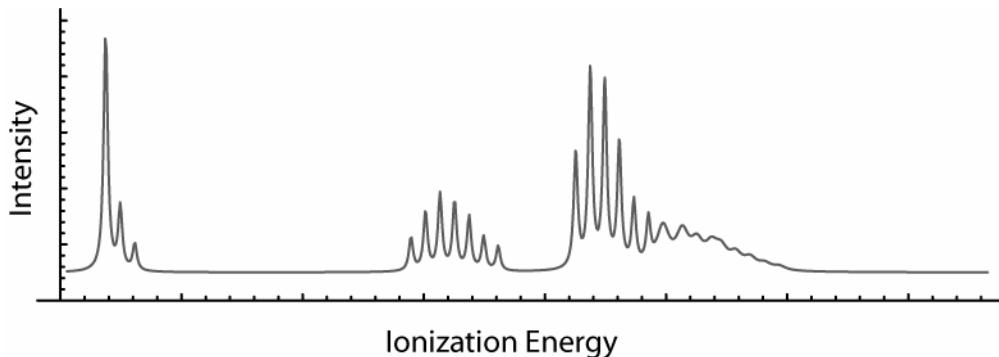
The $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$ states all belong to the ground-state configuration $(1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u^*)^2 (1\pi_g^*)^1 (1\pi_g^*)^1$, but are associated with different M_L and M_S values as was shown in Example Problem 26.2. The bond order for these states is 2. The $A^3\Sigma_u^+$ and $B^3\Sigma_u^-$ states are associated with the $(1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^1 (1\pi_u^*)^2 (1\pi_g^*)^1 (1\pi_g^*)^2$ configuration. The bond order for these states is 1.

These results agree with the potential energy curves shown in Figure 26.1, because the bond length of O₂ in the $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$ states are equal and shorter than those in the $A^3\Sigma_u^+$ and $B^3\Sigma_u^-$ states.

Q26.2) The relative intensities of vibrational peaks in an electronic spectrum are determined by the Franck-Condon factors. How would the potential curve for the excited state in Figure 26.2 need to be shifted along the distance axis for the $n = 0 \rightarrow n' = 0$ transition to have the highest intensity? The term n refers to the vibrational quantum number in the ground state, and n' refers to the vibrational quantum number in the excited state.

It would need to be shifted to the left, corresponding to a shorter bond length. The $n = 0 \rightarrow n' = 0$ transition will have the highest intensity if the bond length in the ground and excited states is the same.

Q26.3) Suppose you obtain the UV photoelectron spectrum shown here for a gas-phase molecule. Each of the groups corresponds to a cation produced by ejecting an electron from a different MO. What can you conclude about the bond length of the cations in the three states formed relative to the ground-state neutral molecule? Use the relative intensities of the individual vibrational peaks in each group to answer this question.



Because the most intense peak in the first group corresponds to $n = 0$, we conclude that the bond length in the cation is very similar to that in the ground state. The most intense peak in the second and third groups correspond to $n = 3$, and $n = 4$ respectively. We conclude that the bond length in the cations corresponding to both groups of peaks is longer than that in the ground state. The cation corresponding to the second group of peaks has the longest bond.

Q26.4) The ground state of O_2^+ is $X^2\Pi_g$ and the next few excited states, in order of increasing energy, are $a^4\Pi_u$, $A^2\Pi_u$, $b^4\Sigma_g^-$, ${}^2\Delta_g$, ${}^2\Sigma_g^-$, and $c^4\Sigma_u^-$. On the basis of selection rules, which of the excited states can be accessed from the ground state by absorption of UV light?

The selection rules for homonuclear diatomics are $\Delta\Lambda = 0, \pm 1$ and $\Delta S = 0$, and furthermore, $u \leftrightarrow g$ transitions are allowed, but $u \leftrightarrow u$ and $g \leftrightarrow g$ transitions are forbidden. The transitions $\Sigma^- \leftrightarrow \Sigma^-$ and $\Sigma^+ \leftrightarrow \Sigma^+$ are allowed, but $\Sigma^+ \leftrightarrow \Sigma^-$ transitions are forbidden. The transitions can be summarized as follows:

Excited state	$\Delta\Lambda$	ΔS	$g \rightarrow g$ or $u \rightarrow u$	Allowed?
$a^4\Pi_u$	0	1	no	no
$A^2\Pi_u$	0	0	no	yes
$b^4\Sigma_g^-$	-1	1	yes	no
${}^2\Delta_g$	1	0	yes	no
${}^2\Sigma_g^-$	-1	0	yes	no
$c^4\Sigma_u^-$	-1	1	no	no

Only the $X^2\Pi_g \rightarrow A^2\Pi_u$ transition is allowed.

Q26.5) Photoionization of a diatomic molecule produces a singly charged cation. An electronic spectrum will show vibrational transitions as discussed in Section 26.4. For the

molecules listed here, calculate the bond order of the neutral molecule and the lowest energy cation:

a) H₂

neutral molecule: $(1\sigma_g)^2$ bond order 1

cation: $(1\sigma_g)^1$ bond order 1/2

b) O₂

neutral molecule: $(1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u^*)^2 (1\pi_g^*)^1 (1\pi_g)^1$

bond order 2

cation: $(1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u^*)^2 (1\pi_g^*)^1$

bond order 1.5

c) F₂

neutral molecule: $(1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u^*)^2 (1\pi_g^*)^2 (1\pi_g^*)^2$

bond order 1

cation: $(1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u^*)^2 (1\pi_g^*)^2 (1\pi_g^*)^1$

bond order 1.5

d) NO

neutral molecule: $(1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u^*)^2 (1\pi_g^*)^1$

bond order 2.5

cation: $(1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u^*)^2$

bond order 3

For which of the molecules do you expect the $n = 0 \rightarrow n' = 1$ vibrational peak to have a higher intensity than the $n = 0 \rightarrow n' = 0$ vibrational peak? The term n refers to the vibrational quantum number in the ground state, and n' refers to the vibrational quantum number in the excited state.

The $n = 0 \rightarrow n' = 1$ vibrational peak will have a higher intensity than the $n = 0 \rightarrow n' = 0$ vibrational peak if the bond length is different in the neutral molecule and cation. This is the case for all three molecules.

Q26.6) Explain why the fluorescence and absorption groups of peaks in Figure 26.10 are shifted and show mirror symmetry for idealized symmetrical ground-state and excited-state potentials.

The absorption event is initiated from the $n = 0$ vibrational level of the ground state. The relative order of peak intensities for different vibrational quantum

numbers of the excited state is governed by the Franck-Condon principle. Assume, as is often the case, that the excited state has a longer bond. In that case the maximum intensity is observed for $n' > 0$, where the prime refers to the excited state. The molecule will quickly lose energy, and be in the $n' = 0$ vibrational level. Because fluorescence to the ground state occurs from this level, the whole fluorescence spectrum is shifted to lower frequencies relative to the absorption spectrum. The reason for the mirror symmetry can best be understood by looking at Figure 26.10. For a symmetric potential, the progression from the maximum to the minimum overlap leads to a decrease in the frequency of the absorption transition, but to an increase in the frequency of the fluorescence transition.

Q26.7) What would the intensity versus frequency plot in Figure 26.10 look like if fluorescence were fast with respect to internal conversion?

See the discussion for the previous answer. If fluorescence were fast with respect to internal conversion, there would not be relaxation to the $n' = 0$ vibrational level, and the fluorescence and absorption spectra would be identical.

Q26.8) The rate of fluorescence is higher than that for phosphorescence. Can you explain this fact?

In fluorescence, $\Delta S = 0$, so the transition is allowed. In phosphorescence, $\Delta S \neq 0$, so the transition is forbidden. This leads to a very low rate for phosphorescence.

Q26.9) In a simple model used to analyze UV photoelectron spectra, the orbital energies of the neutral molecule and the cation formed by ejection of an electron are assumed to be the same. In fact, some relaxation occurs to compensate for the reduction in the number of electrons by one. Would you expect the orbital energies to increase or decrease in the relaxation? Explain your answer.

Because the number of electrons in the species is reduced by one, the effective nuclear charge decreases. Consequently, the affected orbital energies are lowered.

Q26.10) Explain why the spectator species M in Equation (26.5) is needed to make the reaction proceed.

It is needed to satisfy the requirement that energy is conserved in the process. Without the spectator, the reaction complex has no possibility to lose energy and reach the ground state.

Q26.11) Because internal conversion is in general very fast, the absorption and fluorescence spectra are shifted in frequency as shown in Figure 26.10. This shift is

crucial in making fluorescence spectroscopy capable of detecting very small concentrations. Can you explain why?

In the experiment, the sample is constantly being illuminated with light to effect the transition of interest. If fluorescence occurred at exactly the same frequency as absorption, the signal would not be detectable because it is indistinguishable for the light used to excite the molecule. Because the fluorescence spectrum is shifted to lower frequencies, a filter can be used in front of the detector that will block light at the absorption frequency. Consequently, the signal has a very low background.

Q26.12) How many distinguishable states belong to the following terms:

- a) $^1\Sigma_g^+$ The number of state is $2S + 1$ multiplied by the allowed values of M_L . This is 1 for a S term, and 2 for P and D terms. Therefore, there is only one state consistent with the $^1\Sigma_g^+$ term.
- b) $^3\Sigma_g^-$ Following the analysis for part (a), there are three states consistent with the term $^3\Sigma_g^-$.
- c) $^2\Pi$ Following the analysis for part (a), there are four states consistent with the term $^2\Pi$.
- d) $^2\Delta$ Following the analysis for part (a), there are four states consistent with the term $^2\Delta$.

Q26.13) Predict the number of unpaired electrons and the ground-state term for the following:

a) NO

CH has 7 electrons and the configuration $(1\sigma)^2 (2\sigma)^2 (3\sigma)^2 (1\pi)^1$. It will have one unpaired electron. Because only the unpaired electron with $M_L = \pm 1$ is relevant, the ground state is a $^2\Pi$ term.

b) CO

NH has 8 electrons and the configuration $(1\sigma)^2 (2\sigma)^2 (3\sigma)^2 (1\pi)^1 (1\pi)^1$. Using the same analysis as in Example Problem 26.2, the ground state is $^3\Sigma$.

Q26.14) Predict the number of unpaired electrons and the ground-state term for the following:

a) BO

Chapter 26/Electronic Spectroscopy

OH has 9 electrons and the configuration $(1\sigma)^2 (2\sigma)^2 (3\sigma)^2 (1\pi)^2 (1\pi)^1$. It has one unpaired electron. Because only the unpaired electron with $M_L = \pm 1$ is relevant, the ground state is a $^2\Pi$ term.

b) LiO

HF has 10 electrons and the configuration $(1\sigma)^2 (2\sigma)^2 (3\sigma)^2 (1\pi)^2 (1\pi)^2$. It has no unpaired electron. Therefore, the ground state is a $^1\Sigma$ term.

Chapter 27: Computational Chemistry

As indicated in the introduction to Chapter 27, “Computational Chemistry,” the associated problems require the use of Spartan or another electronic structure program. This being the case, written solutions, as provided here, tell only one part of the story. Equally important are the text and graphical outputs from the actual calculations. Therefore, Spartan files for all problems are provided on the Instructor Resource CD-ROM for your reference. These Spartan files are subdivided into directories bearing the name of the problem—for example, “27.7.” Each directory contains one or more Spartan files with one or more molecules—for example, the Spartan file “acetonitrile, methyl isocyanide.spartan” contains results for both acetonitrile and methyl isocyanide. The files, which are identified at the beginning of the written solution of each problem, should be examined in conjunction with the written solutions.

Problems

P27.1) The assumption that the reaction coordinate in going from *gauche* to *anti n*-butane is a simple torsion is an oversimplification, because other geometrical changes no doubt also occur during rotation around the carbon–carbon bond, for example, changes in bond lengths and angles. Examine the energy profile for *n*-butane (“*n*-butane”) along the change in distance of the central CC bond and CCC bond angle as a function of the torsion angle. Are the bond length and bond angle nearly identical or significantly different ($>0.02 \text{ \AA}$ and $>2^\circ$) for the two equilibrium forms of *n*-butane? Are the two parameters nearly identical or significantly different between the *anti* form and either or both of the transition states? Explain your results.

(*n*-butane) The change in the central carbon–carbon bond in *n*-butane closely parallels the change in energy according to HF/3-21G calculations. The shortest bond (1.54 Å) is for the lowest energy *anti* structure and the longest bond (1.57 Å) is for the highest-energy *syn* rotational transition state. Bond angle variations also parallel energy insofar as the bond angle in the high-energy *syn* structure (116°) where the terminal methyl groups are proximate is much larger than bond angles in structures where the methyl groups are further apart. Steric crowding seems to be responsible.

P27.2) Ammonia provides a particularly simple example of the dependence of vibrational frequencies on the atomic masses and of the use of vibrational frequencies to distinguish between a stable molecule and a transition state. First examine the vibrational spectrum of pyramidal ammonia (“ammonia”).

- How many vibrational frequencies are there? How does this number relate to the number of atoms? Are all frequencies real numbers or are one or more imaginary numbers? Describe the motion associated with each frequency and characterize each as being primarily bond stretching, angle bending, or a combination of the two. Is bond stretching or angle bending easier? Do the stretching motions each involve a single NH bond or do they involve combinations of two or three bonds?

(*ammonia*) There are six vibrational frequencies. This corresponds to three times the number of atoms (four) minus three translational and three rotational degrees of freedom. All the frequencies are real numbers

<i>frequency (cm⁻¹)</i>	<i>description</i>
1209	NH ₃ puckering mode
1850	HNH angle bend
1850	HNH angle bend
3686	NH symmetric stretch
3819	NH asymmetric stretch
3819	NH asymmetric stretch

Bond stretching is harder (higher energy) than angle bonding. The symmetric stretch and one of the two (degenerate) asymmetric stretches involve all three NH bonds. The other asymmetric stretch involves two NH bonds.

b) Next, consider changes to the vibrational frequencies of ammonia as a result of substituting deuteriums for hydrogens (“perdeuteroammonia”). Are the frequencies in ND₃ larger, smaller, or unchanged from those in NH₃? Are any changes greater for motions that are primarily bond stretching or motions that are primarily angle bending?

<i>(perdeuteroammonia)</i>	
<i>frequency change (cm⁻¹)</i>	<i>% reduction</i>
1209→919	32%
1850→1343	38%
1850→1343	38%
3686→2633	40%
3819→2812	36%
3819→2812	36%

Frequencies for ND₃ are uniformly smaller than those for NH₃. The % reduction is similar for both stretching and bending motions.

c) Finally, examine the vibrational spectrum of an ammonia molecule that has been constrained to a planar geometry (“planar ammonia”). Are all the frequencies real numbers? If not, describe the motions associated with any imaginary frequencies and relate them to the corresponding motion(s) in the pyramidal equilibrium form.

(*planar ammonia*) One of the six frequencies is an imaginary number. This corresponds to an out-of-plane puckering motion and relates to the puckering motion of ammonia (at 1209 cm⁻¹).

P27.3) The presence of the carbonyl group in a molecule is easily confirmed by an intense line in the infrared spectrum around 1700 cm⁻¹ that corresponds to a C=O stretching vibration. Locate this line in the calculated infrared spectrum of acetone

("acetone") and note its position in the overall spectrum (relative to the positions of the other lines) and the intensity of the absorption.

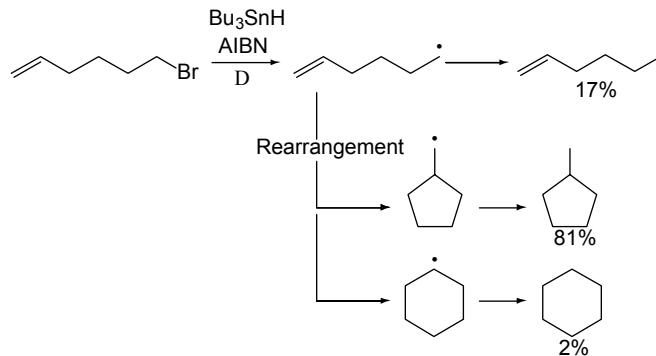
a) Speculate why infrared spectroscopy is a reliable diagnostic for carbonyl functionality.

(acetone) According to HF/3-21G calculations the vibration corresponding to the CO stretch occurs at 1940 cm^{-1} . This line is very intense and quite far removed from the other lines in the infrared spectrum. This makes it "easy to find" and is why infrared spectroscopy is a useful diagnostic for carbonyl functionality.

b) Examine the lowest frequency mode for acetone and then the highest frequency mode. Describe each and relate to the relative ease of difficulty of the associated motion.

The lowest frequency mode (91 cm^{-1}) corresponds to a torsion of methyl groups. It is an (energetically) "easy" motion. The highest frequency mode (3306 cm^{-1}) corresponds to a combination of CH bond stretches. It is an (energetically) difficult motion.

P27.4) Chemists have a keen eye for what is stable and what is not. For example, they will easily recognize that cyclohexyl radical is more stable than cyclopentylmethyl radical, because they know that six-membered rings are more stable than five-membered rings and, more importantly, that secondary radicals are more stable than primary radicals. However, much important chemistry is not controlled by what is most stable (thermodynamics) but rather by what forms most readily (kinetics). For example, loss of bromine from 6-bromohexene leading initially to hex-5-enyl radical, results primarily in product from cyclopentylmethyl radical.



The two possible interpretations for the experimental result are that the reaction is thermochemically controlled but that our understanding of radical stability is wrong or that the reaction is kinetically controlled.

a) First, see if you can rule out the first possibility. Examine structures and total energies for cyclohexyl and cyclopentylmethyl radicals ("cyclohexyl, cyclopentylmethyl radicals"). Which radical, cyclohexyl or cyclopentylmethyl, is more stable (lower in energy)? Is the energy difference large enough such that only the more stable radical is likely to be observed? (Recall that at room temperature an energy difference of 12 kJ/mol

corresponds to a product ratio of >99:1.) Do you conclude that ring closure is under thermodynamic control?

(*cyclohexyl, cyclopentylmethyl radicals*) According to HF/6-31G* calculations, cyclohexyl radical is 33 kJ/mol lower in energy than cyclopentylmethyl radical. This corresponds to >99.99% favoring of the former. Ring closure cannot be under thermodynamic control.

b) The next objective is to establish which ring closure, to cyclohexyl radical or to cyclopentylmethyl radical, is easier; that is, which product, cyclohexane or methylcyclopentane, is the kinetic product? Bring up calculated structures and total energies for the transition states for the two ring closures (“to cyclohexyl, cyclopentylmethyl radicals”). Which radical, cyclohexyl or cyclopentylmethyl, is more easily formed?

(*to cyclohexyl, cyclopentylmethyl radicals*) According to the same calculations, the transition state for closure to cyclopentylmethyl radical is 10 kJ/mol lower in energy than that for closure to cyclohexyl radical.

c) Consider the following relationships between transition-state energy difference, ΔE^\ddagger , and the ratio of major to minor (kinetic) products, calculated from the Boltzmann distribution:

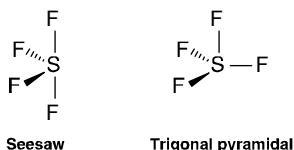
ΔE^\ddagger (kJ/mol)	Major : Minor (room temperature)
4	~90 : 10
8	~95 : 5
12	~99 : 1

What is the approximate ratio of products suggested by the calculations? How does this compare with what is observed? Do you conclude that ring closure is under kinetic control?

This corresponds to a (Boltzmann) distribution of 98:2 in favor of formation of cyclopentylmethyl radical, in qualitative agreement with the experimental preference. The ring closure reaction appears to be under kinetic control.

P27.5) VSEPR (valence state electron pair repulsion) theory was formulated to anticipate the local geometry about an atom in a molecule (see discussion in Section 25.1). All that is required is the number of electron pairs surrounding the atom, broken down into bonded pairs and nonbonded (lone) pairs. For example, the carbon in carbon tetrafluoride is surrounded by four electron pairs, all of them tied up in CF bonds, whereas the sulfur in sulfur tetrafluoride is surrounded by five electron pairs, four of which are tied up in SF bonds with the fifth being a lone pair.

VSEPR theory is grounded in two simple ideas. The first is that electron pairs (either lone pairs or bonds) will seek to avoid each other as much as possible. Thus, two electron pairs will lead to a linear geometry, three pairs to a trigonal planar geometry, four pairs to a tetrahedral geometry, five pairs to a trigonal bipyramidal geometry, and six pairs to an octahedral geometry. Although this knowledge is sufficient to assign a geometry for a molecule such as carbon tetrafluoride (tetrahedral), it is not sufficient to specify the geometry of a molecule such as sulfur tetrafluoride. Does the lone pair assume an *equatorial* position on the trigonal bipyramidal leading to a seesaw geometry, or an *axial* position leading to a trigonal pyramidal geometry?



The second rule, that lone pairs take up more space than bonds, clarifies the situation. The seesaw geometry in which the lone pair is 90° to two of the SF bonds and 120° to the other two bonds is preferable to the trigonal pyramidal geometry in which three bonds are 90° to the lone pair.

Although VSEPR theory is easy to apply, its results are strictly qualitative and often of limited value. For example, although the model tells us that sulfur tetrafluoride adopts a seesaw geometry, it does not reveal whether the trigonal pyramidal structure (or any other structure) is an energy minimum, and if it is, what its energy is relative to the seesaw form. Also it has little to say when more than six electron pairs are present. For example, VSEPR theory tells us that xenon hexafluoride is not octahedral, but it does not tell us what geometry the molecule actually assumes. Hartree-Fock molecular orbital calculations provide an alternative.

- Optimize the structure of SF_4 in a seesaw geometry (C_{2v} symmetry) using the HF/3-21G model and calculate vibrational frequencies (the infrared spectrum). This calculation is necessary to verify that the energy is at a minimum. Next, optimize the geometry of SF_4 in a trigonal pyramidal geometry and calculate its vibrational frequencies.

Is the seesaw structure an energy minimum? What leads you to your conclusion? Is it lower in energy than the corresponding trigonal pyramidal structure in accordance with VSEPR theory? What is the energy difference between the two forms? Is it small enough that both might actually be observed at room temperature? Is the trigonal pyramidal structure an energy minimum?

(*sulfur tetrafluoride*) The seesaw geometry for sulfur tetrafluoride is an energy minimum according to HF/3-21G calculations (no imaginary frequencies) whereas the trigonal pyramidal geometry is not an energy minimum (two imaginary frequencies). The difference in energy between the two forms is huge (143 kJ/mol) meaning that the trigonal pyramidal form would not likely be observed even were it an energy minimum.

b) Optimize the geometry of XeF_6 in an octahedral geometry (O_h symmetry) using the HF/3-21G model and calculate vibrational frequencies. Next, optimize XeF_6 in a geometry that is distorted from octahedral (preferably in C_1 symmetry) and calculate its vibrational frequencies. Is the octahedral form of XeF_6 an energy minimum? What leads you to your conclusion? Does distortion lead to a stable structure of lower energy?

(*xenon hexafluoride*) Octahedral xenon hexafluoride is not an energy minimum (three imaginary frequencies). A structure distorted to C_1 symmetry is 91 kJ/mol lower in energy according to HF/3-21G calculations.

P27.6) Each of the carbons in ethane is surrounded by four atoms in a roughly tetrahedral geometry; each carbon in ethene is surrounded by three atoms in a trigonal planar geometry and each carbon in acetylene by two atoms in a linear geometry. These structures can be rationalized by suggesting that the valence $2s$ and $2p$ orbitals of carbon are able to combine either to produce four equivalent sp^3 hybrids directed toward the four corners of a tetrahedron, or three equivalent sp^2 hybrids directed toward the corners of an equilateral triangle with a p orbital left over, or two equivalent sp hybrids directed along a line with two p orbitals left over. The $2p$ atomic orbitals extend farther from carbon than the $2s$ orbital. Therefore, sp^3 hybrids will extend farther than sp^2 hybrids, which in turn will extend farther than sp hybrids. As a consequence, bonds made with sp^3 hybrids should be longer than those made with sp^2 hybrids, which should in turn be longer than those made with sp hybrids.

a) Obtain equilibrium geometries for ethane, ethene, and acetylene using the HF/6-31G* model. Is the ordering in CH bond lengths what you expect on the basis of the hybridization arguments? Using the CH bond length in ethane as a standard, what is the percent reduction in CH bond lengths in ethene? In acetylene?

(*ethane, ethene, acetylene*) CH bond lengths from HF/6-31G* calculations and % reductions in CH bond lengths from that in ethane as a standard are as follows:

	<i>bond length (Å)</i>	<i>% reduction</i>
ethane	1.086	—
ethene	1.076	0.9%
acetylene	1.057	2.7%

The ordering of bond lengths is as expected from hybridization arguments.

b) Obtain equilibrium geometries for cyclopropane, cyclobutane, cyclopentane, and cyclohexane using the HF/6-31G* model. Are the CH bond lengths in each of these molecules consistent with their incorporating sp^3 -hybridized carbons? Note any exceptions.

(*cyclopropane, cyclobutane, cyclopentane, cyclohexane*) CH bond lengths from HF/

6-31G* calculations are as follows (values for cyclobutane, cyclopentane, and cyclohexane are averages).

	<i>bond lengths</i>
cyclopropane	1.076
cyclobutane	1.085
cyclopentane	1.086
cyclohexane	1.088

Except for cyclopropane, bond lengths in all cycloalkanes are consistent with sp^3 hybridization at carbon. CH bond lengths in cyclopropane are significantly shorter and more consistent with sp^2 hybridization at carbon (as in ethene).

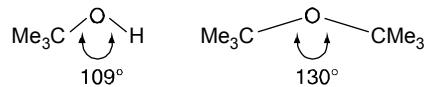
c) Obtain equilibrium geometries for propane, propene, and propyne using the HF/6-31G* model. Is the ordering of bond lengths the same as that observed for the CH bond lengths in ethane, ethene, and acetylene? Are the percent reductions in bond lengths from the standard (propane) similar ($\pm 10\%$) to those seen for ethene and acetylene (relative to ethane)?

(*propane, propene, propyne*) CC single bond lengths from HF/6-31G* calculations and % reductions in CC bond lengths from that in propane are as follows

	<i>bond length (Å)</i>	<i>% reduction</i>
propane	1.528	—
propene	1.503	1.7
propyne	1.468	4.1

The trends are the same as for CH bond lengths (part a) but the effects are larger.

P27.7) The bond angle about oxygen in alcohols and ethers is typically quite close to tetrahedral (109.5°), but opens up significantly in response to extreme steric crowding, for example, in going from *tert*-butyl alcohol to di-*tert*-butyl ether:



This is entirely consistent with the notion that while lone pairs take up space, but can be “squeezed” to relieve crowding. Another way to relieve unfavorable steric interactions (without changing the position of the lone pairs) is to increase the CO bond distance.

a) Build *tert*-butyl alcohol and di-*tert*-butyl ether and optimize the geometry of each using the HF/6-31G* model. Are the calculated bond angles involving oxygen in accord with the values given earlier, in particular with regard to the observed increase in bond angle? Do you see any lengthening of the CO bond in the ether over that in the alcohol? If not, or if the effect is very small ($<0.01 \text{ \AA}$), speculate why not.

(*tert*-butyl alcohol, *di-tert*-butyl ether) CO bond lengths and bond angles involving oxygen from HF/6-31G* calculations are as follows.

	<i>CO bond length (Å)</i>	<i>CO-X bond angle (°)</i>
<i>tert</i> -butyl alcohol	1.415	109.5
<i>di-tert</i> -butyl ether	1.420	129.9

CO bond lengths in the alcohol and ether are nearly identical but the central bond angle has opened up by 20°. Apparently angle bending is (energetically) much easier than bond stretching.

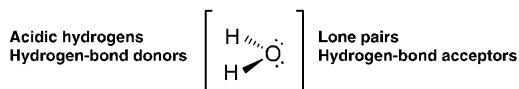
b) Next, consider the analogous trimethylsilyl compounds Me_3SiOH and $\text{Me}_3\text{SiOSiMe}_3$. Calculate their equilibrium geometries using the HF/6-31G* model. Point out any similarities and any differences between the calculated structures of these compounds and their *tert*-butyl analogues. In particular, do you see any widening of the bond angle involving oxygen in response to increased steric crowding? Do you see lengthening of the SiO bond in the ether over that of the alcohol? If not, rationalize what you do see.

(trimethylsilyl alcohol, *di(trimethylsilyl) ether*) SiO bond lengths and bond angles involving oxygen from HF/6-31G* calculations are as follows.

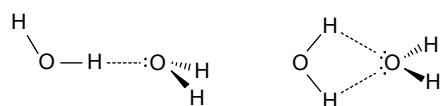
	<i>SiO bond length (Å)</i>	<i>SiOX bond angle (°)</i>
trimethylsilyl alcohol	1.661	118.7
<i>di(trimethylsilyl) ether</i>	1.635	178.5

The trend in central bond angle noted here in going from the alcohol to the ether is the same but exaggerated from that found in the carbon analogues. In fact, the SOSi bond angle is 180°. The SiO bond in the silyl ether is significantly shorter than the corresponding bond in the alcohol, not longer as steric considerations would suggest. This trend is different from that found in the carbon analogues. The most likely explanation for bond shortening is “back bonding” involving the two lone pairs on oxygen (pure p orbitals in a linear arrangement) and empty d-type orbitals on silicon.

P27.8) Water contains two acidic hydrogens that can act as hydrogen-bond donors and two lone pairs that can act as hydrogen-bond acceptors:



Given that all are tetrahedrally disposed around oxygen, this suggests two reasonable structures for the hydrogen-bonded dimer of water, $(\text{H}_2\text{O})_2$, one with a single hydrogen bond and one with two hydrogen bonds:

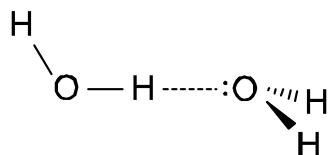


Whereas the second seems to make better use of water's attributes, in doing so, it imposes geometrical restrictions on the dimer.

Build the two dimer structures. Take into account that the hydrogen-bond distance ($\text{O}\dots\text{H}$) is typically on the order of 2 Å. Optimize the geometry of each using the HF/6-31G* model and, following this, calculate vibrational frequencies.

Which structure, singly or doubly hydrogen bonded, is more stable? Is the other (higher energy) structure also an energy minimum? Explain how you reached your conclusion. If the dimer with the single hydrogen bond is more stable, speculate what this has told you about the geometric requirements of hydrogen bonds. Based on your experience with water dimer, suggest a "structure" for liquid water.

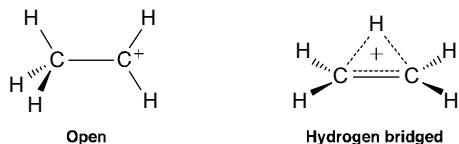
(water dimer) Only the singly-hydrogen-bonded structure



is an energy minimum according to HF/6-31G* calculations. The hydrogen bond ($\text{O}-\text{H}\cdots\text{H}$) is nearly linear (172°). This suggests that liquid water will exhibit only singly-hydrogen-bonded arrangements.

P27.9) For many years, a controversy raged concerning the structures of so-called "electron-deficient" molecules, that is, molecules with insufficient electrons to make normal two-atom, two-electron bonds. Typical is ethyl cation, C_2H_5^+ , formed from protonation of ethene.

Is ethyl cation best represented as an open Lewis structure with a full positive charge on one of the carbons, or as a hydrogen-bridged structure in which the charge is dispersed onto several atoms?



Build both open and hydrogen-bridged structures for ethyl cation. Optimize the geometry of each using the B3LYP/6-31G* model and calculate vibrational frequencies. Which structure is lower in energy, the open or hydrogen-bridged structure? Is the higher energy structure an energy minimum? Explain your answer.

(ethyl cation) Only hydrogen-bridged ethyl cation is an energy minimum according to B3LYP/6-31G* calculations. The open form (constrained to Cs symmetry) exhibits an

imaginary frequency corresponding to distortion away from symmetry and releasing this symmetry leads to the bridged structure.

P27.10) One of the most powerful attractions of quantum chemical calculations over experiments is their ability to deal with any molecular system, stable or unstable, real or imaginary. Take as an example the legendary (but imaginary) kryptonite molecule. Its very name gives us a formula, KrO_2^{2-} , and the fact that this species is isoelectronic with the known molecule, KrF_2 , suggests that it too should be linear.

a) Build KrF_2 as a linear molecule (F–Kr–F), optimize its geometry using the HF/6-31G* model, and calculate vibrational frequencies. Is the calculated KrF bond distance close to the experimental value (1.89 Å)? Does the molecule prefer to be linear or does it want to bend? Explain how you reached this conclusion.

(*krypton difluoride*) According to HF/6-31G*calculations, linear KrF_2 has a KrF bond length of 1.82 Å: All frequencies are real indicating that this arrangement corresponds to an energy minimum (the molecule does not want to bend).

b) Build KrO_2^{2-} as a linear molecule (or as a bent molecule if the preceding analysis has shown that KrF_2 is not linear), optimize its structure using the HF/6-31G* model, and calculate vibrational frequencies. What is the structure of KrO_2^{2-} ?

(*kryptonite*) Kryptonite also prefers a linear arrangement (all frequencies are real) with a KrO bond length of 1.97 Å.

(*krypton difluoride_B3LYP; krypton difluoride_MP2*) Extra: Electron correlation leads an increase in KrF bond length in krypton difluoride and to improved agreement with experiment. B3LYP/6-31G* calculations lead to a bond length of 1.93 Å and MP2/6-31G* calculations lead to a bond length of 1.90 Å.

P27.11) Discussion of the VSEPR model in Section 25.1 suggested a number of failures, in particular, in CaF_2 and SrCl_2 , which (according to the VSEPR) should be linear but which are apparently bent, and in SeF_6^{2-} and TeCl_6^{2-} , which should not be octahedral but apparently are. Are these really failures or does the discrepancy lie with the fact that the experimental structures correspond to the solid rather than the gas phase (isolated molecules)?

a) Obtain equilibrium geometries for linear CaF_2 and SrCl_2 and also calculate vibrational frequencies (infrared spectra). Use the HF/3-21G model, which has actually proven to be quite successful in describing the structures of main-group inorganic molecules. Are the linear structures for CaF_2 and SrCl_2 actually energy minima? Elaborate. If one or both are not, repeat your optimization starting with a bent geometry.

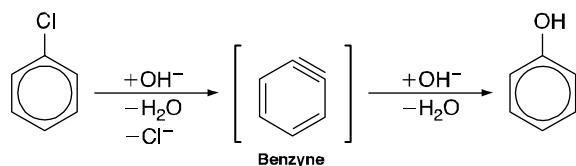
(*linear CaF2; linear SrF2; bent SrF2*) Linear CaF_2 is an energy minimum (all real frequencies). Linear SrCl_2 has two imaginary frequencies (corresponding to out-of-plane bending motions) and is not an energy minimum. The equilibrium structure has a bond

angle of 157° . Note that the energy difference between linear and bent structures (1 kJ/mol according to HF/3-21G calculations) is very small.

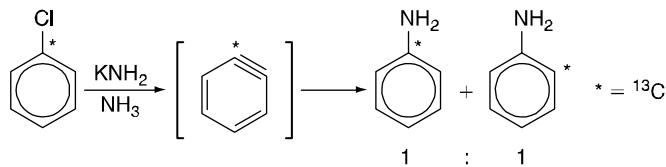
b) Obtain equilibrium geometries for octahedral SeF_6^{2-} and TeCl_6^{2-} and also calculate vibrational frequencies. Use the HF/3-21G model. Are the octahedral structures for SeF_6^{2-} and TeCl_6^{2-} actually energy minima? Elaborate. If one or both are not, repeat your optimization starting with distorted structures (preferably with C_1 symmetry).

(octahedral SeF_6 dianion; distorted octahedral SeF_6 dianion; octahedral TeF_6 dianion; distorted octahedral TeF_6 dianion) Both SeF_6^{2-} and TeF_6^{2-} distort from octahedral structures according to HF/3-21G calculations (octahedral structures for both molecules possess three imaginary frequencies). Note that energy differences between distorted and octahedral structures are quite large (50 kJ/mol and 130 kJ/mol for SeF_6^{2-} and TeF_6^{2-} , respectively).

P27.12) Benzyne has long been implicated as an intermediate in nucleophilic aromatic substitution, for example,



Although the geometry of benzyne has yet to be conclusively established, the results of a ^{13}C labeling experiment leave little doubt that two (adjacent) positions on the ring are equivalent.



There is a report, albeit controversial, that benzyne has been trapped in a low-temperature matrix and its infrared spectrum recorded. Furthermore, a line in the spectrum at 2085 cm^{-1} has been assigned to the stretching mode of the incorporated triple bond.

Optimize the geometry of benzyne using the HF/6-31G* model and calculate vibrational frequencies. For reference, perform the same calculations on 2-butyne. Locate the $\text{C}\equiv\text{C}$ stretching frequency in 2-butyne and determine an appropriate scaling factor to bring it into agreement with the corresponding experimental frequency (2240 cm^{-1}). Then, identify the vibration corresponding to the triple-bond stretch in benzyne and apply the same scaling factor to this frequency. Finally, plot the calculated infrared spectra of both benzyne and 2-butyne.

Does your calculated geometry for benzyne incorporate a fully formed triple bond? Compare with the bond in 2-butyne as a standard. Locate the vibrational motion in

benzyne corresponding to triple bond stretch. Is the corresponding (scaled) frequency significantly different ($> 100 \text{ cm}^{-1}$) from the frequency assigned in the experimental investigation? If it is, are you able to locate any frequencies from your calculation that would fit with the assignment of a benzyne mode at 2085 cm^{-1} ? Elaborate. Does your infrared plot provide further evidence for or against the experimental observation? (Hint: Look at the intensity of the triple-bond stretch in 2-butyne.)

(benzyne, 2-butyne, benzene) According to HF/6-31G* calculations, the $\text{C}\equiv\text{C}$ stretching frequency in 2-butyne is 2566 cm^{-1} . The scaling factor to bring this into agreement with the corresponding experimental frequency (2240 cm^{-1}) is 0.87. The calculated “triple bond” stretching frequency in benzyne is 2211 cm^{-1} . The scaled value is 1924 cm^{-1} which is significantly ($>100 \text{ cm}^{-1}$) smaller than the 2085 cm^{-1} line assigned to benzyne from the low-temperature matrix isolation study.

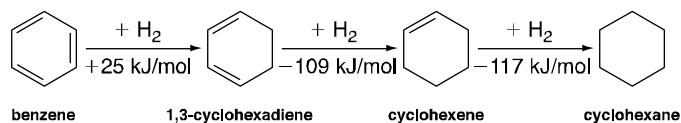
The triple bond stretch in 2-butyne is infrared inactive (it has zero intensity). While the corresponding stretching frequency in benzyne is “infrared active,” the calculation suggest a very low intensity.

On the basis of both frequency value and intensity, the calculations do not support the experimental claim that the infrared spectrum of benzyne has been recorded.

The calculated “triple” bond length in benzyne (1.223 \AA) is longer than that in 2-butyne (1.188 \AA) but significantly shorter than that in benzene (1.386 \AA). It can reasonably well be described as a triple bond.

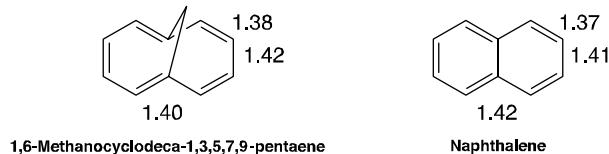
P27.13) All chemists know that benzene is unusually stable, that is, it is aromatic. They are also well aware that many other similar molecules are stabilized by aromaticity to some extent and, more often than not, can recognize aromatic molecules as those with delocalized bonding. What most chemists are unable to do, however, is to “put a number” on the aromatic stabilization afforded benzene or to quantify aromatic stabilization among different molecules. This is not to say that methods have not been proposed (for a discussion see Section 25.7), but rather that these methods have rarely been applied to real molecules.

Assigning a value to aromatic stabilization is actually quite straightforward. Consider a hypothetical reaction in which a molecule of hydrogen is added to benzene to yield 1,3-cyclohexadiene. Next, consider analogous hydrogenation reactions of 1,3-cyclohexadiene (leading to cyclohexene) and of cyclohexene (leading to cyclohexane):



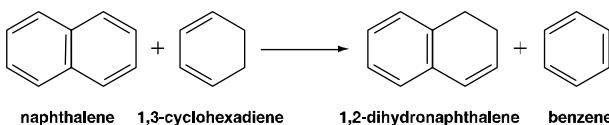
Addition of H_2 to benzene trades an $\text{H}-\text{H}$ bond and a $\text{C}-\text{C} \pi$ bond for two $\text{C}-\text{H}$ bonds, but in so doing destroys the aromaticity, whereas H_2 addition to either 1,3-cyclohexadiene or cyclohexene trades the same bonds but does not result in any loss of aromaticity (there is nothing to lose). Therefore, the difference in the heats of hydrogenation (134 kJ/mol referenced to 1,3-cyclohexadiene and 142 kJ/mol referenced to cyclohexene) is a measure of the aromaticity of benzene.

Reliable quantitative comparisons require accurate experimental data (heats of formation). These will generally be available only for very simple molecules and will almost never be available for novel interesting compounds. As a case in point, consider to what extent, if any, the 10 π -electron molecule 1,6-methanocyclodeca-1,3,5,7,9-pentaene (bridged naphthalene) is stabilized by aromaticity. Evidence that it is provided by the X-ray crystal structure suggests a fully delocalized π system. The 10 carbons that make up the base are very nearly coplanar and all CC bonds are intermediate in length between normal single and double linkages, just as they are in naphthalene.



Calculations provide a viable alternative to experiment for thermochemical data. Although absolute hydrogenation energies may be difficult to describe with currently practical models, hydrogenation energies relative to a closely related standard compound are much easier to accurately describe. In this case, the natural standard is benzene.

- a) Optimize the geometries of benzene, 1,3-cyclohexadiene, naphthalene, and 1,2-dihydronaphthalene using the HF/6-31G* model. Evaluate the energy of the following reaction, relating the energy of hydrogenation of naphthalene to that of benzene (as a standard):



On the basis of relative hydrogenation energies, would you say that naphthalene is stabilized (by aromaticity) to about the same extent as is benzene or to a lesser or greater extent? Try to explain your result.

(benzene, 1,3-cyclohexadiene, naphthalene, 1,2-dihydronaphthalene) According to HF/6-31G* calculations, the energy of hydrogenation of naphthalene relative to that of benzene, i.e.



is -53 kJ/mol. This implies that naphthalene is by this particular measure “less aromatic” than benzene by 53 kJ/mol. (For reference to calculations suggest a value of 134 kJ/mol for the aromatic stabilization of benzene.)

- b) Optimize the geometries of 1,6-methanocyclodeca-1,3,5,7,9-pentaene and its hydrogenation product using the HF/6-31G* model. Evaluate the energy of

hydrogenation relative to that of naphthalene. On the basis of relative hydrogenation energies, would you say that the bridged naphthalene is stabilized to about the same extent as is naphthalene or to a lesser or greater extent? Try to explain your result.

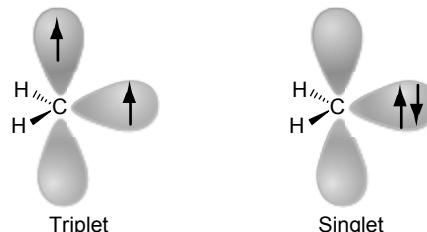
(naphthalene, 1,2-dihydronaphthalene, 1,6-methanonaphthalene, 2,3-dihydro-1,6-methanonaphthalene) The energy of hydrogenation of 1,6-methanonaphthalene relative to that of naphthalene, i.e.,



is 61 kJ/mol. This implies that 1,6-methanonaphthalene is 61 kJ/mol “less aromatic” than naphthalene, or 114 kJ/mol (53 + 61) “less aromatic” than benzene. Given that the aromatic stabilization of benzene is 134 kJ/mol by this measure, the conclusion is that 1,6-methanonaphthalene is not an aromatic molecule.

P27.14) Singlet and triplet carbenes exhibit different properties and show markedly different chemistry. For example, a singlet carbene will add to a *cis*-disubstituted alkene to produce only *cis*-disubstituted cyclopropane products (and to a *trans*-disubstituted alkene to produce only *trans*-disubstituted cyclopropane products), whereas a triplet carbene will add nonstereospecifically to produce a mixture of *cis* and *trans* products.

The origin of the difference lies in the fact that triplet carbenes are biradicals (or diradicals) and exhibit chemistry similar to that exhibited by radicals, whereas singlet carbenes incorporate both a nucleophilic site (a low-energy unfilled molecular orbital) and an electrophilic site (a high-energy filled molecular orbital); for example, for singlet and triplet methylene.



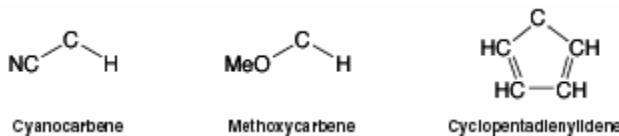
It should be possible to take advantage of what we know about stabilizing radical centers versus stabilizing empty orbitals and use that knowledge to design carbenes that will either be singlets or triplets. Additionally, it should be possible to say with confidence that a specific carbene of interest will either be a singlet or a triplet and, thus, to anticipate its chemistry.

The first step is to pick a model and then to establish the error in the calculated singlet–triplet energy separation in methylene where the triplet is known experimentally to be approximately 42 kJ/mol lower in energy than the singlet. This can then be applied as a correction for calculated singlet–triplet separations in other systems.

a) Optimize the structures of both the singlet and triplet states of methylene using both Hartree-Fock and B3LYP density functional models with the 6-31G* basis set. Which state (singlet or triplet) is found to be of lower energy according to the HF/6-31G* calculations? Is the singlet or the triplet unduly favored at this level of calculation? Rationalize your result. (*Hint:* Triplet methylene contains one fewer electron pair than singlet methylene.) What energy correction needs to be applied to calculated singlet–triplet energy separations? Which state (singlet or triplet) is found to be of lower energy according to the B3LYP/6-31G* calculations? What energy correction needs to be applied to calculated energy separations?

(*methylene_HF; methylene_B3LYP*) According to HF/6-31G* calculations triplet methylene is 129 kJ/mol lower in energy than singlet methylene. B3LYP/6-31G* calculations also assign a triplet ground state but the singlet triplet energy difference is much smaller (57 kJ/mol) and much closer to the difference estimated experimentally (42 kJ/mol). A correction factor of 87 kJ/mol (in favor of the singlet) would need to be applied to HF/6-31G* calculations and a correction factor of 15 kJ/mol (in favor of the singlet) would need to be applied to B3LYP/6-31G* calculations.

b) Proceed with either the HF/6-31G* or B3LYP/6-31G* model, depending on which leads to better agreement for the singlet–triplet energy separation in methylene. Optimize singlet and triplet states for cyanocarbene, methoxycarbene, and cyclopentadienylidene:



Apply the correction obtained in the previous step to estimate the singlet–triplet energy separation in each. For each of the three carbenes, assign the ground state as singlet or triplet.

Relative to hydrogen (in methylene), has the cyano substituent in cyanocarbene and the methoxy substituent in methoxycarbene led to favoring of the singlet or the triplet?

Rationalize your result by first characterizing cyano and methoxy substituents as π donors or π acceptors, and then speculating about how a donor or acceptor would stabilize or destabilize singlet and triplet methylene.

Has incorporation into a cyclopentadienyl ring led to increased preference for a singlet or triplet ground state (relative to the preference in methylene)? Rationalize your result.

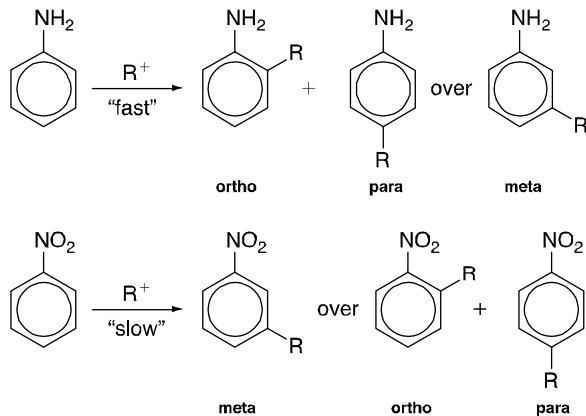
(*Hint:* Count the number of π electrons associated with the rings in both singlet and triplet states.)

(*cyanocarbene, methoxycarbene, cyclopentadienylidene_B3LYP*) Uncorrected and corrected singlet–triplet energy differences for substituted carbenes from B3LYP/6-31G* calculations are as follows (kJ/mol; favored state in parentheses).

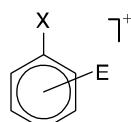
	<i>uncorrected</i>	<i>corrected</i>
cyanocarbene	68 (T)	53 (T)
methoxycarbene	103 (S)	118 (S)
cyclopentadienylidene	43 (T)	28 (T)

A cyano group (a “double” π acceptor) has little effect on the singlet-triplet energy separation in methylene. It can either act to delocalize lone pair in the singlet or to delocalize *both* unpaired electrons in the triplet. A small favoring of the triplet suggests that the latter is more effective. A methoxy group clearly favors singlet methylene. The (π) lone pair on oxygen be delocalized into the empty p orbital on the carbene center. This requires a planar skeleton (HCOC dihedral angle of 180°) which is what is found. Similar delocalization might be expected to occur in cyclopentadienylidene (π electrons from the two carbon-carbon double bonds into the empty p orbital), but this molecule is predicted to favor a triplet ground state (albeit less so than methylene itself). The obvious reason is that a delocalized cyclopentadienylidene incorporates a 4 π electron ring (it is “antiaromatic”). Note that the structure of the singlet is predicted to be non-planar to avoid this from being the case.

P27.15) Electron-donating groups on benzene promote electrophilic aromatic substitution and lead preferentially to so-called *ortho* and *para* products over *meta* products, whereas electron-withdrawing groups retard substitution and lead preferentially to *meta* products (over *ortho* and *para* products), for example, for electrophilic alkylation:



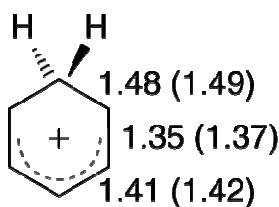
We can expect the first step in the substitution to be addition of the electrophile, leading to a positively charged adduct:



In fact, so-called benzenium ions have been characterized spectroscopically and X-ray crystal structures for several are known. Will the stabilities of benzenium ion intermediates anticipate product distribution?

a) Optimize the geometry of benzenium ion using the HF/3-21G model. A good guess is a planar six-membered ring comprising five sp^2 carbons and an sp^3 carbon with bond distances between sp^2 carbons intermediate in length between single and double bonds. It should have C_{2v} symmetry. In terms of ring bond distances, how does your calculated structure compare with the experimental X-ray geometry of heptamethylbenzenium ion?

(benzenium ion) Calculated bond lengths (HF/3-21G model) for benzenium ion are very similar to distances in heptamethylbenzenium ion obtained from X-ray crystallography (in parentheses)



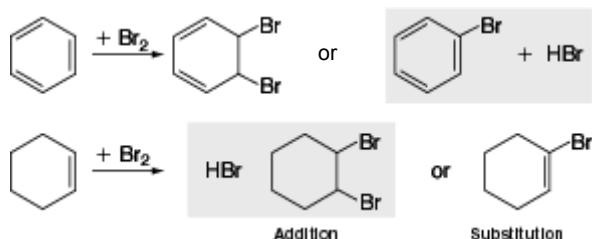
b) Optimize the geometries of benzene, aniline, and nitrobenzene using the HF/3-21G model. You will need their energies to ascertain the relative reactivities of the three substituted benzenes. Also, optimize the geometries of methyl cation adducts for benzene, aniline (*meta* and *para* isomers only), and nitrobenzene (*meta* and *para* isomers only) using the HF/3-21G model. Use the calculated structure of parent benzenium ion as a template. Which isomer, *meta* or *para*, of the aniline adduct is more stable? Which isomer of the nitrobenzene adduct is more stable? Considering only the lower energy isomer for each system, order the binding energies of methyl cation addition to benzene, aniline, and nitrobenzene, that is: E (substituted benzene methyl cation adduct) – E (substituted benzene) – E (methyl cation). You will need to calculate the energy of methyl cation using the HF/3-21G model. Which aromatic should be most reactive? Which should be least reactive? Taken as a whole, do your results provide support for the involvement of benzenium ion adducts in electrophilic aromatic substitution? Explain.

(benzene, aniline, nitrobenzene; methyl cation; benzene, aniline, nitrobenzene methyl cation adducts) The *para* methyl cation adduct is preferred for aniline (by 147 kJ/mol) while the *meta* adduct is preferred for nitrobenzene (by 31 kJ/mol). Both results are consistent with observed preferences in electrophilic aromatic substitution. Methyl cation binding energies (from the most stable adducts) are as follows.

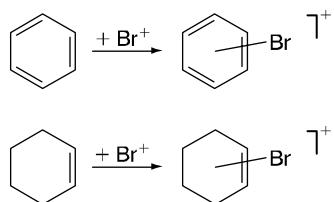
	binding-energy (kJ/mol)
benzene	309
aniline	456
nitrobenzene	233

Relative to benzene an amino group enhances reactivity while a nitro group retards reactivity. Both results are consistent with observed reaction rates in electrophilic aromatic substitution.

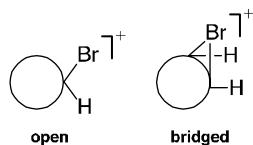
P27.16) Aromatics such as benzene typically undergo substitution when reacted with an electrophile such as Br₂, whereas alkenes such as cyclohexene most commonly undergo addition:



Both addition and substitution processes for both aromatics and alkenes are believed to initiate with attack of Br⁺, leading to a positively charged adduct:



Differentiation must, therefore, occur in the second step where Br⁻ either abstracts a hydrogen (leading to substitution) or itself adds (leading to addition). To decipher what is happening, you need to understand how the adducts for the aromatic and alkene differ. Optimize the geometries of Br⁺ adducts for both benzene and cyclohexene using the HF/3-21G model. You should consider two different forms for each (although only one is likely to be an energy minimum for each), open and bridged:



Br⁺ is associated with a single carbon in the former, whereas it straddles two carbons in the latter. Also, calculate vibrational frequencies for each (open or bridged) structure that you find.

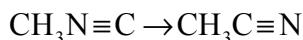
Which structure, open or bridged, is the more stable for the benzene adduct? Is the other structure an energy minimum? Explain. Which structure is the more stable for the cyclohexene adduct? Is the other structure an energy minimum? Explain. Speculate on the consequences of any differences you observe between the benzene and cyclohexene adducts with respect to their different modes of reaction.

(benzene bromonium; cyclohexene bromonium) The open form of benzene bromonium ion is 44 kJ/mol lower in energy than the (bromine) bridged form according to HF/3-21G calculations. To the contrary the bridged form of cyclohexene bromonium ion is 39

kJ/mol lower in energy than the open form. Bridged benzene brominium ion is not an energy minimum as evidenced by an imaginary frequency (corresponding to motion of the bromine away from a bridging position). Both bridged and open forms of cyclohexene bromonium ion are energy minima (all real frequencies).

P27.17) Evaluate the difference between change in energy at 0 K in the absence of zero point vibration and both change in enthalpy and in free energy for real molecules at 298 K. Consider both a unimolecular isomerization that does not lead to a net change in the number of molecules and a thermal decomposition reaction that leads to an increase in the number of molecules.

a) Calculate ΔU , ΔH (298), and ΔG (298) for the following isomerization reaction:



Obtain equilibrium geometries for both methyl isocyanide and acetonitrile using the B3LYP/6-31G* density functional model. Do the calculated values for ΔU and ΔH (298) differ significantly (by more than 10%)? If so, is the difference due primarily to the temperature correction or to the inclusion of zero point energy (or to a combination of both)? Is the calculated value for ΔG (298) significantly different from that of ΔH (298)?

(acetonitrile, methyl isocyanide) ΔU , $\Delta H(298)$ and $\Delta G(298)$ for isomerization of methyl isocyanide to acetonitrile from B3LYP/6-31G* calculations are as follows

$$\begin{aligned}\Delta U &= -100.8 \text{ kJ/mol} \\ \Delta H(298) &= -100.9 \text{ kJ/mol} \\ \Delta G(298) &= -99.9 \text{ kJ/mol}\end{aligned}$$

There is no significant difference among the three thermodynamic quantities.

b) Repeat your analysis (again using the B3LYP/6-31G* model) for the following pyrolysis reaction:



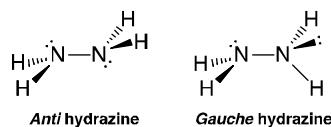
Do these two reactions provide a similar or a different picture as to the importance of relating experimental thermochemical data to calculated ΔG values rather than ΔU values? If different, explain your result.

(ethyl formate, ethene, formic acid) ΔU , $\Delta H(298)$ and $\Delta G(298)$ for pyrolysis of ethyl formate leading to formic acid and ethene from B3LYP/6-31G* calculations are as follows.

$$\begin{aligned}\Delta U &= -103.0 \text{ kJ/mol} \\ \Delta H(298) &= -91.0 \text{ kJ/mol} \\ \Delta G(298) &= -45.9 \text{ kJ/mol}\end{aligned}$$

There are significant differences among the three thermodynamic quantities primarily because of the different number of reactant and product molecules (1 vs. 2). One needs to be careful in using ΔU (instead of ΔH or better ΔG) in these situations, although accounting for different number of reactant and product molecules can be done more simply.

P27.18) Hydrazine would be expected to adopt a conformation in which the NH bonds stagger. There are two likely candidates, one with the lone pairs on nitrogen *anti* to each other and the other with the lone pairs *gauche*:

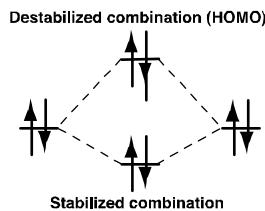


On the basis of the same arguments made in VSEPR theory (electron pairs take up more space than bonds) you might expect that *anti* hydrazine would be the preferred structure.

- a) Obtain energies for the *anti* and *gauche* conformers of hydrazine using the HF/6-31G* model. Which is the more stable conformer? Is your result in line with what you expect from VSEPR theory?

(*hydrazine*) According to HF/6-31G* calculations, *gauche* hydrazine is 12 kJ/mol lower in energy than *anti* hydrazine. This is not as expected from VSEPR theory in that the nitrogen lone pairs are “closer” in the *gauche* structure (120°) than in the *anti* structure (180°).

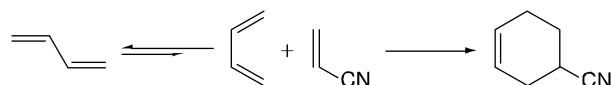
You can rationalize your result by recognizing that when electron pairs interact they form combinations, one of which is stabilized (relative to the original electron pairs) and one of which is destabilized. The extent of destabilization is greater than that of stabilization, meaning that overall interaction of two electron pairs is unfavorable energetically:



- b) Measure the energy of the highest occupied molecular orbital (the HOMO) for each of the two hydrazine conformers. This corresponds to the higher energy (destabilized) combination of electron pairs. Which hydrazine conformer (*anti* or *gauche*) has the higher HOMO energy? Is this also the higher energy conformer? If so, is the difference in HOMO energies comparable to the difference in total energies between the conformers?

The HOMO energy of the *anti* conformer is 1.37 eV (132 kJ/mol) higher than that of the *gauche* conformer. The direction is expected (the more destabilized lone pair combination is associated with the higher-energy conformer) but the difference in HOMO energies is an order of magnitude of greater than the difference in conformer energies.

P27.19) Diels-Alder cycloaddition of 1,3-butadiene with acrylonitrile requires that the diene be in a *cis* (or *cis*-like) conformation:



In fact, the diene exists primarily in a *trans* conformation, the *cis* conformer being approximately 9 kJ/mol less stable and separated from the *trans* conformer by a low-energy barrier. At room temperature, only about 5% of butadiene molecules will be in a *cis* conformation. Clearly, rotation into a *cis* conformation is required before reaction can proceed.

Conduct a search for a substituted 1,3-butadiene that actually prefers to exist in a *cis* (or *cis*-like) conformation as opposed to a *trans* conformation. The only restriction you need to be aware of is that the diene needs to be electron rich in order to be reactive. Restrict your search to alkyl and alkoxy substituents as well as halogen. Use the HF/3-21G model. Report your successes and provide rationales.

(*1,3-butadiene; 2-methyl-1,3-butadiene, 2-tert-butyl-1,3-butadiene; 2-cyano-1,3-butadiene*) The “search” has been restricted to a single group on the “internal” (C_2) carbon in 1,3-butadiene. Calculated (HF/3-21G) *cis-trans* energy differences (kJ/mol, favored conformer in parentheses) are as follows.

1,3-butadiene	11	(T)
2-methyl-1,3-butadiene	8	(T)
2-tert-butyl-1,3-butadiene	13	(C)
2-cyano-1,3-butadiene	10	(T)

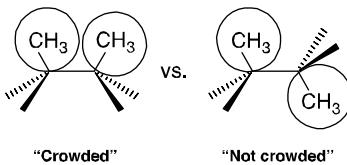
Methyl and cyano groups in the 2-position do not change the favoring for a *trans* arrangements of double bonds seen in the parent system and have very little effect on the *cis-trans* energy difference. Only incorporation of a *tert*-butyl group in this position reverses the preference. Inspection of *cis* and *trans* conformers suggests that crowding (steric) effects are to cause.

P27.20) The energy of rotation about a single bond is a periodic function of the torsion angle, ϕ , and is, therefore, appropriately described in terms of a truncated Fourier series, the simplest acceptable form of which is given by

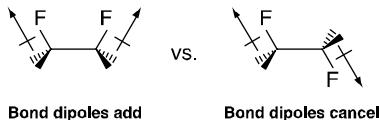
$$\begin{aligned} V(\phi) &= \frac{1}{2}V_1(1 - \cos\phi) + \frac{1}{2}V_2(1 - \cos 2\phi) + \frac{1}{2}V_3(1 - \cos 3\phi) \\ &= V_1(\phi) + V_2(\phi) + V_3(\phi) \end{aligned}$$

Here, V_1 is the onefold component (periodic in 360°), V_2 is the twofold component (periodic in 180°), and V_3 is the threefold component (periodic in 120°).

A Fourier series is an example of an orthogonal polynomial, meaning that the individual terms which it comprises are independent of each other. It should be possible, therefore, to dissect a complex rotational energy profile into a series of N -fold components and to interpret each of these components independent of all others. The one-fold component is quite easy to rationalize. For example, the onefold term for rotation about the central bond in *n*-butane no doubt reflects the crowding of methyl groups,



whereas the onefold term in 1,2-difluoroethane probably reflects differences in electrostatic interactions as represented by bond dipoles:

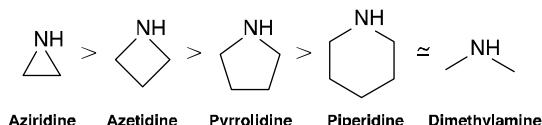


The threefold component is perhaps the most familiar to chemists, because it represents the difference in energy between eclipsed and staggered arrangements about a single bond. However, the twofold component is perhaps the most interesting of the three and is what concerns us here. It relates to the difference in energy between planar and perpendicular arrangements.

Optimize the geometry of dimethyl peroxide (CH_3OOCH_3) subject to the COOC dihedral being held at $0^\circ, 20^\circ, 40^\circ, \dots, 180^\circ$ (10 optimizations in total). Use the B3LYP/6-31G* density functional model. Construct a plot of energy versus dihedral angle and fit this to a three-term Fourier series. Does the Fourier series provide a good fit to your data? If so, what is the dominant term? Rationalize it. What is the second most important term? Rationalize your result.

(dimethylperoxide) The Fourier fit is excellent. One-fold ($\cos(x)$) and two-fold ($\cos(2x)$) terms dominate the fit. The one-fold term (*syn* vs. *anti*) reflects the desire to position the methyl group as far apart as possible. The two-fold term (*syn/anti* vs *perpendicular*) reflects the desire for the high-energy π lone pairs on oxygen to be orthogonal and not interact.

P27.21) Pyramidal inversion in the cyclic amine aziridine is significantly more difficult than inversion in an acyclic amine, for example, 80 versus 23 kJ/mol in dimethylamine according to HF/6-31G* calculations. One plausible explanation is that the transition state for inversion needs to incorporate a planar trigonal nitrogen center, which is obviously more difficult to achieve in aziridine, where one bond angle is constrained to a value of around 60°, than it is in dimethylamine. Such an interpretation suggests that the barriers to inversion in the corresponding four- and five-membered ring amines (azetidine and pyrrolidine) should also be larger than normal and that the inversion barrier in the six-membered ring amine (piperidine) should be quite close to that for the acyclic.



Optimize the geometries of aziridine, azetidine, pyrrolidine, and piperidine using the HF/6-31G* model. Starting from these optimized structures, provide guesses at the respective inversion transition states by replacing the tetrahedral nitrogen center with a trigonal center. Obtain transition states using the same Hartree-Fock model and calculate inversion barriers. Calculate vibrational frequencies to verify that you have actually located the appropriate inversion transition states.

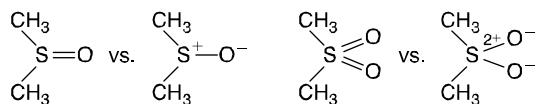
Do the calculated inversion barriers follow the order suggested in the preceding figure? If not, which molecule(s) appear to be anomalous? Rationalize your observations by considering other changes in geometry from the amine to the transition state.

(dimethylamine; aziridine, azetidine, pyrrolidine, piperidine; dimethylamine inversion transition state; aziridine, azetidine, pyrrolidine, piperidine inversion transition states;) Nitrogen inversion barriers (kJ/mol) from HF/3-21G* calculations for cyclic amines are as follows. Dimethylamine is included as a “standard.”

aziridine	81
azetidine	27
pyrrolidine	17
piperidine	26
dimethylamine	23

Except for pyrrolidine, results are as expected: the inversion barrier in aziridine is much greater than that for the “standard” (dimethylamine) while the barriers in azetidine and piperidine are only slightly greater. Pyrrolidine is anomalous in that it shows a smaller than expected inversion barrier.

P27.22) Molecules such as dimethylsulfoxide and dimethylsulfone can either be represented as *hypervalent*, that is, with more than the normal complement of eight valence electrons around sulfur, or as *zwitterions*, in which sulfur bears a positive charge:



Atomic charges obtained from quantum chemical calculations can help to decide which representation is more appropriate.

- a) Obtain equilibrium geometries for dimethylsulfide, $(\text{CH}_3)_2\text{S}$, and dimethylsulfoxide using the HF/3-21G model and obtain charges at sulfur based on fits to the electrostatic potential. Is the charge on sulfur in dimethylsulfoxide about the same as that on sulfur in dimethylsulfide (normal sulfur), or has it increased by one unit, or is it somewhere between? Would you conclude that dimethylsulfoxide is best represented as a hypervalent molecule, as a zwitterion, or something between? See if you can support your conclusion with other evidence (geometries, dipole moments, and so on).

(dimethylsulfide, dimethylsulfoxide, dimethylsulfone) Charges (in electrons) at sulfur and at oxygen and dipole moments (debyes) from HF/3-21G calculations are as follows.

	charge at S	Charge at O	dipole moment
dimethylsulfide	-0.1	—	1.8
dimethylsulfoxide	+0.5	-0.5	4.3
dimethylsulfone	+1.7	-0.7	5.0

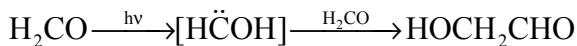
- b) Repeat your analysis for dimethylsulfone. Compare your results for the charge at sulfur to those for dimethylsulfide and dimethylsulfoxide.

These suggest a partial zwitterionic description for dimethylsulfoxide and nearly a full zwitterionic description for dimethylsulfone. This is supported by the large dipole moments in these two compounds (4.3 and 5.0 debyes for the sulfoxide and sulfone, respectively) compared to a dipole moment of 1.8 debyes in dimethylsulfide.

P27.23) Hydroxymethylene has never actually been observed, although it is believed to be an intermediate both in the photofragmentation of formaldehyde to hydrogen and carbon monoxide,



and in the photodimerization of formaldehyde in an argon matrix:



Does hydroxymethylene actually exist? To have a chance “at life,” it must be separated from both its rearrangement product (formaldehyde) and from its dissociation product

(hydrogen and carbon monoxide) by a sizable energy barrier (>80 kJ/mol). Of course, it must also actually be a minimum on the potential energy surface.

- a) First calculate the energy difference between formaldehyde and hydroxymethylene and compare your result to the indirect experimental estimate of 230 kJ/mol. Try two different models, B3LYP/6-31G* and MP2/6-31G*. Following calculation of the equilibrium geometry for hydroxymethylene, obtain vibrational frequencies. Is hydroxymethylene an energy minimum? How do you know? Is the energy difference inferred from experiment reasonably well reproduced with one or both of the two models?

(formaldehyde, hydroxymethylene_B3LYP; formaldehyde, hydroxymethylene_MP2)
According to B3LYP/6-31G* calculations, hydroxymethylene is 240 kJ/mol higher in energy than formaldehyde, in good agreement with the experimental estimate of 230 kJ/mol. MP2/6-31G * calculations suggest that the energy difference is slightly larger (256 kJ/mol). Hydroxymethylene is an energy minimum according to both B3LYP/6-31G* and MP2/6-31G * calculations (all vibrational frequencies are real).

- b) Proceed with the model that gives the better energy difference and try to locate transition states both for isomerization of hydroxymethylene to formaldehyde and for dissociation to hydrogen and carbon monoxide. Be certain to calculate vibrational frequencies for the two transition states. On the basis of transition states you have located, would you expect that both isomerization and dissociation reactions are available to hydroxymethylene? Explain. Do both suggest that hydroxymethylene is in a deep enough energy well to actually be observed?

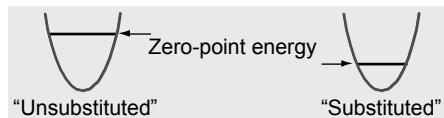
(hydroxymethylene isomerization, dissociation transition states_B3LYP) According to B3LYP/6-31G * calculations, isomerization of hydroxymethylene to formaldehyde requires 141 kJ/mol activation while dissociation of hydroxymethylene to carbon monoxide and hydrogen requires 134 kJ/mol activation. Both of these barriers are sufficiently high that it should be possible to observe hydroxymethylene.

P27.24) The Born-Oppenheimer approximation completely removes nuclear mass from the Schrödinger equation. How then is it possible to explain observed mass dependencies? The clue is that a molecule's infrared spectrum depends on mass. For example, the three vibrational frequencies in H₂O (1595, 3657, and 3756 cm⁻¹) are all much larger than the corresponding frequencies in D₂O (1178, 2671, and 2788 cm⁻¹). This follows from the fact that vibrational frequency is given by the square root of a (mass-independent) quantity, which relates to the curvature of the energy surface at the minima, divided by a quantity that depends on the masses of the atoms involved in the motion.

As discussed in Section 27.8.4, vibrational frequencies enter into both terms required to relate the energy obtained from a quantum chemical calculation (stationary nuclei at 0 K) to the enthalpy obtained experimentally (vibrating nuclei at finite temperature), as well as the entropy required to relate enthalpies to free energies. For the present purpose, focus is

entirely on the so-called zero point energy term, that is, the energy required to account for the latent vibrational energy of a molecule at 0 K.

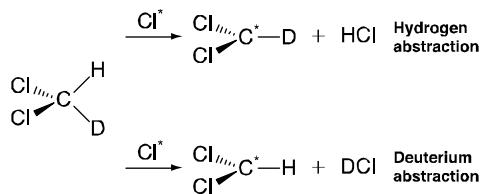
The zero point energy is given simply as the sum over individual vibrational energies (frequencies). Thus, the zero point energy for a molecule in which isotopic substitution has resulted in an increase in mass will be reduced from that in the unsubstituted molecule:



A direct consequence of this is that enthalpies of bond dissociation for isotopically substituted molecules (light to heavy) are smaller than those for unsubstituted molecules.

a) Perform B3LYP/6-31G* calculations on HCl and on its dissociation products, chlorine atom and hydrogen atom. Following geometry optimization on HCl, calculate the vibrational frequency for both HCl and DCl and evaluate the zero point energy for each. In terms of a percentage of the total bond dissociation energy, what is the change noted in going from HCl to DCl?

d_1 -Methylene chloride can react with chlorine atoms in either of two ways: by hydrogen abstraction (producing HCl) or by deuterium abstraction (producing DCl):



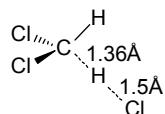
Which pathway is favored on the basis of thermodynamics and which is favored on the basis of kinetics?

(hydrogen chloride, chlorine, hydrogen atoms) The bond dissociation energy for hydrogen chloride from B3LYP/6-31G * calculations is 418 kJ/mol. Zero point energies for hydrogen chloride and deuterium chloride are 18 kJ/mol and 13 kJ/mol, respectively. Thus, the difference in zero-point energies (5 kJ/mol) is only slightly more than 1% of the bond dissociation energy.

b) Obtain the equilibrium geometry for dichloromethyl radical using the B3LYP/6-31G* model. Also obtain vibrational frequencies for both the unsubstituted and the deuterium-substituted radical and calculate zero point energies for the two abstraction pathways (you already have zero point energies for HCl and DCl). Which pathway is favored on the basis of thermodynamics? What would you expect the (thermodynamic) product ratio to be at room temperature?

(dichloromethyl radical) The zero-point energy of the products of hydrogen abstraction ($\text{DCCl}_2 + \text{HCl}$) is 51 kJ/mol and that of the products of deuterium abstraction ($\text{HCCl}_2 + \text{DCl}$) is 54 kJ/mol. Thus, hydrogen abstraction is favored thermodynamically. The Boltzmann ratio of hydrogen to deuterium abstraction products is roughly 90:10 at room temperature.

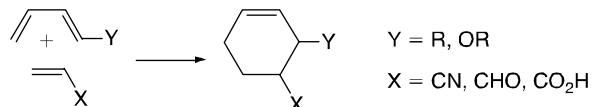
c) Obtain the transition state for hydrogen abstraction from methylene chloride using the B3LYP/6-31G* model. A reasonable guess is shown here:



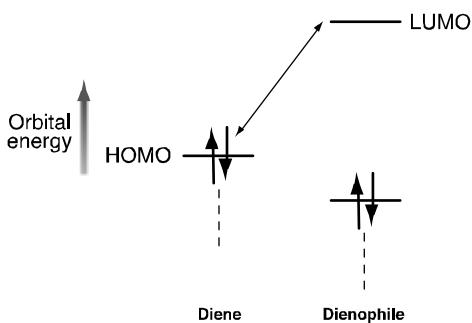
Calculate vibrational frequencies for the two possible structures with one deuterium and evaluate the zero point energies for these two structures. (For the purpose of zero point energy calculation, ignore the imaginary frequency corresponding to the reaction coordinate.) Which pathway is favored on the basis of kinetics? Is it the same or different from the thermodynamic pathway? What would you expect the (kinetic) product ratio to be at room temperature?

(methylene chloride + hydrogen atom to dichloromethyl radical + hydrogen chloride)
The zero point energy for the transition state for hydrogen abstraction from d_1 -methylene chloride is 51 kJ/mol, and that for deuterium abstraction is 56 kJ/mol. Thus hydrogen abstraction is favored kinetically. The kinetic ratio of hydrogen to deuterium abstraction products is roughly 90:10 at room temperature.

P27.25) Diels-Alder reactions commonly involve electron-rich dienes and electron-deficient dienophiles:

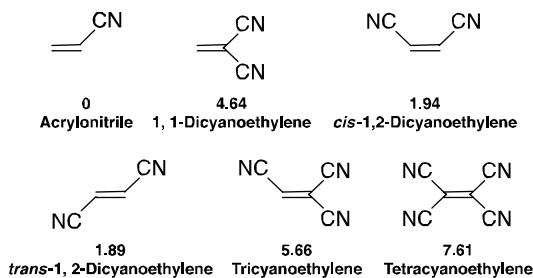


The rate of these reactions generally increases with the π -donor ability of the diene substituent, Y, and with the π -acceptor ability of the dienophile substituent, X. The usual interpretation is that electron donors will push up the energy of the HOMO on the diene and that electron acceptors will push down the energy of the LUMO on the dienophile:



The resulting decrease in the HOMO–LUMO gap leads to a stronger interaction between diene and dienophile and to a decrease in the activation barrier.

- a) Obtain equilibrium geometries for acrylonitrile, 1,1-dicyanoethylene, *cis*- and *trans*-1,2-dicyanoethylene, tricyanoethylene, and tetracyanoethylene using the HF/3-21G model.



(acrylonitrile, 1,1-, *cis*, *trans*-1, 2-dicyanoethylene, tricyanoethylene, tetracyanoethylene)
Plot the LUMO energy for each dienophile versus the log of the observed relative rate for its addition to cyclopentadiene (listed below the structures in the preceding figure). Is there a reasonable correlation between LUMO energy and relative rate?

LUMO energies (eV) from HF/3-21G calculations are as follows:

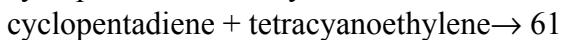
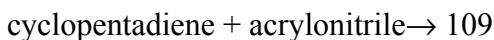
acrylonitrile	2.85
1,1-dicyanoethylene	1.40
<i>cis</i> -1,2-dicyanoethylene	1.16
<i>trans</i> -1,2-dicyanoethylene	1.09
tricyanoethylene	0.12
tetracyanoethylene	-1.24

These correlate reasonably well with the observed relative rates.

- b) Obtain transition-state geometries for Diels-Alder cycloadditions of acrylonitrile and cyclopentadiene and tetracyanoethylene and cyclopentadiene using the HF/3-21G model. Also obtain a geometry for cyclopentadiene. Calculate activation energies for the two reactions.

How does the calculated difference in activation energies compare with the experimental difference (based on a value of 7.61 for the difference in the log of the rates and assuming 298 K)?

(cyclopentadiene; cyclopentadiene+acrylonitrile, tetracyanoethylene) Calculated activation energies (kJ/mol) for the two Diels-Alder reactions are as follows.



The difference in activation energies (48 kJ/mol) leads to a difference in the log of relative rates of 19 log units is larger than the experimental estimate (7.6 log units).

P27.26) It is well known that cyanide acts as a “carbon” and not a “nitrogen” nucleophile in S_N2 reactions, for example,



How can this behavior be rationalized with the notion that nitrogen is in fact more electronegative than carbon and, therefore, would be expected to hold any excess electrons?

a) Optimize the geometry of cyanide using the HF/3-21G model and examine the HOMO. Describe the shape of the HOMO of cyanide. Is it more concentrated on carbon or nitrogen? Does it support the picture of cyanide acting as a carbon nucleophile? If so, explain why your result is not at odds with the relative electronegativities of carbon and nitrogen.

Why does iodide leave following nucleophilic attack by cyanide on methyl iodide?

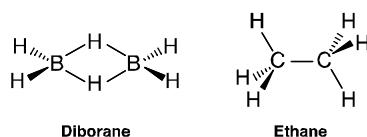
(cyanide anion) The HOMO of cyanide shows greater amplitude on carbon than on nitrogen, consistent with it behaving as a carbon nucleophile. This result is not at odds with the fact that nitrogen is more electronegative than carbon. The greater the electronegativity, the greater the desire to hold onto electrons, that is, the less likely to be a nucleophile.

b) Optimize the geometry of methyl iodide using the HF/3-21G model and examine the LUMO. Describe the shape of the LUMO of methyl iodide. Does it anticipate the loss of iodide following attack by cyanide? Explain.

(methyl iodide) The LUMO of cyanide is made up of p orbitals on carbon and on iodine. It does not involve the hydrogens. The LUMO is antibonding (between carbon and iodine) meaning, that were it to become occupied (the result of attack by a nucleophile), the CI bond would weaken. This is exactly what happens.

As an aside, note that the LUMO has amplitude on both the carbon (the site of nucleophilic attack) and on iodine. This suggests another possible reaction, leading to ICN and CH₃⁻.

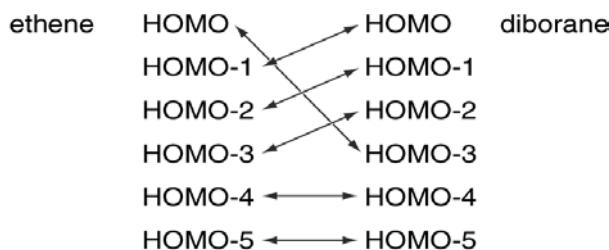
P27.27) At first glance, the structure of diborane would seem unusual. Why shouldn't the molecule assume the same geometry as ethane, which after all has the same number of heavy atoms and the same number of hydrogens?



The important difference between the two molecules is that diborane has two fewer electrons than ethane and is not able to make the same number of bonds. In fact, it is ethene which shares the same number of electrons, to which diborane is structurally related.

Obtain equilibrium geometries for both diborane and ethene using the HF/6-31G* model and draw the six valence molecular orbitals for each. As best you can, associate each valence orbital in ethene with its counterpart in diborane. Focus on similarities in the structure of the orbitals and not on their position in the lists of orbitals. To which orbital in diborane does the π orbital in ethylene (the HOMO) best relate? How would you describe this orbital in diborane? Is it B–B bonding, B–H bonding, or both?

(*ethene, diborane*) Associations among the six occupied valence molecular orbitals of ethene and diborane are as follows (HOMO - x means “x” orbitals below the HOMO in energy).



The HOMO in ethylene relates closely to the HOMO-3 in diborane. This orbital is B–B bonding because it is B–H bonding.

P27.28) Molecular orbitals are most commonly delocalized throughout the molecule and exhibit distinct bonding or antibonding character. Loss of an electron from a specific molecular orbital from excitation by light or by ionization would, therefore, be expected to lead to distinct changes in bonding and changes in molecular geometry.

a) Obtain equilibrium geometries for ethene, formaldimine, and formaldehyde using the HF/6-31G* model and display the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) for each. What would happen to the geometry around carbon (remain planar versus pyramidalize), to the C=X bond length, and (for formaldimine) to the C=NH bond angle if an electron were to be removed from the HOMO of ethene, formaldimine, and formaldehyde?

(*ethene, formaldimine, formaldehyde*) Based on the shape and nodal structure of the HOMO, the geometry of ethene, formaldimine, and formaldehyde would be expected to change as follows in response to removal of an electron (ionization).

ethene: CC bond lengthens, CH₂ groups pyramidalize

formaldimine: little change to CN bond

formaldehyde: little change to CO bond

b) Obtain equilibrium geometries for radical cations of ethene, formaldimine, and formaldehyde using the HF/6-31G* model. Are the calculated geometries of these species, in which an electron has been removed from the corresponding neutral molecule, in line with your predictions based on the shape and nodal structure of the HOMO?

(ethene, formaldimine, formaldehyde radical cations) Calculated structures for radical cations (removal of one electron) show the following changes in geometry (from the corresponding neutral molecules).

ethene: CC bond lengthens by 0.09Å; no pyramidalization of CH₂ groups

formaldimine: no significant change in CN bond length; HCN angle opened by 37°

formaldehyde: CO bond lengthens by 0.03Å

The HOMO is only modestly successful in anticipating detailed changes caused by electron removal.

c) Unoccupied molecular orbitals are also delocalized and also show distinct bonding or antibonding character. Normally, this is of no consequence. However, were these orbitals to become occupied (from excitation or from capture of an electron), then changes in molecular geometry would also be expected. What would happen around carbon, to the C=X bond length, and (for formaldimine) to the C=NH bond angle, if an electron were to be added to the LUMO of ethene, formaldimine, and formaldehyde?

Based on the shape and nodal structure of the LUMO, the geometry of ethene, formaldimine, and formaldehyde would be expected to change as follows in response to addition of an electron.

ethene: CC bond lengthens; CH₂ groups pyramidalize

formaldimine: CN bond lengthens; CH₂ group pyramidalizes

formaldehyde: CO bond lengthens; CH₂ group pyramidalizes

d) Obtain equilibrium geometries for the radical anions of ethene, formaldimine, and formaldehyde using the HF/6-31G* model. Are the calculated geometries of these species, in which an electron has been added to the corresponding neutral molecule, in line with your predictions based on the shape and nodal structure of LUMO?

(ethene, formaldimine, formaldehyde radical anions) Calculated structures for the radical anions (addition of one electron) show the following changes in geometry (from the corresponding neutral molecules).

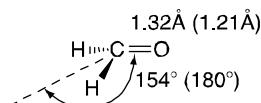
ethene: CC bond lengthens by 0.13 Å; CH₂ groups pyramidalize

formaldimine: CN bond lengthens by 0.12 Å; CH₂ group pyramidalizes

formaldehyde: CO bond lengthens by 0.10 Å; CH₂ group pyramidalizes

The LUMO is quite successful in anticipating detailed changes caused by electron addition.

- e) The first excited state of formaldehyde (the so-called $n \rightarrow \pi^*$ state) can be thought of as arising from the promotion of one electron from the HOMO (in the ground state of formaldehyde) to the LUMO. The experimental equilibrium geometry of the molecule shows lengthening of the CO bond and a pyramidal carbon (ground-state values are shown in parentheses):



Rationalize this experimental result on the basis of what you know about the HOMO and LUMO in formaldehyde and your experience with calculations on the radical cation and radical anion of formaldehyde.

This structure is in qualitative agreement with the results of calculations on the radical cation and radical anion (relative to that on the neutral). Both the radical cation and radical anion show CO bond lengthening (relative to the neutral molecule). The radical anion shows pyramidalization of the CH₂ group. Both features are found in the first excited state of formaldehyde.

P27.29) BeH₂ is linear, whereas CH₂ with two additional electrons and H₂O with four additional electrons are both bent to a similar degree. Could these changes in geometry have been anticipated by examining the shapes of the bonding molecular orbitals?

- a) Perform a series of geometry optimizations on BeH₂ with the bond angle constrained at 90°, 100°, 110°, . . . , 180° (10 optimizations in total). Use the HF/6-31G* model. Plot the total energy, along with the HOMO and LUMO energies versus bond angle. Also, display the HOMO and LUMO for one of your structures of intermediate bond angle.

Does the energy of the HOMO of BeH₂ increase (more positive) or decrease in going from a bent to a linear structure, or does it remain constant, or is the energy at a minimum or maximum somewhere between? Rationalize your result by reference to the shape and nodal structure of the HOMO. Given that BeH₂ has only two valence electrons (in the HOMO), would you expect the molecule to be linear or bent? Is your conclusion consistent with the total energy curve you plotted?

Does the energy of the LUMO of BeH₂ increase or decrease with increase in bond angle, or does it remain constant, or is the energy at a minimum or maximum somewhere between? Rationalize your result by reference to the shape and nodal structure of the LUMO. What do you anticipate would happen to the geometry of BeH₂ as electrons are added to the LUMO? Take a guess at the structure of BH₂[•] (one electron added to the LUMO) and singlet CH₂ (two electrons added to the LUMO).

(BeH₂ angle variation) A plot of total energy vs. bond angle (white line) shows that BeH₂ prefers a linear geometry. The HOMO energy (red line) closely parallels the total energy in that it decreases monotonically in going from a bent to a linear geometry. This behavior is consistent with the shape and nodal structure of the HOMO which is BeH bonding but has a node between the two BeH bonds.

The LUMO energy (blue line) increases monotonically in going from a bent to a linear geometry (the opposite behavior to that exhibited by the HOMO). The orbital is heavily localized on beryllium in the highly bent structures but with a bonding component between the two hydrogens. In the limit of a linear structure it is a pure p orbital (with no bonding between the hydrogens). Adding one electron to BeH₂ should lead to a decrease in bond angle (from 180°) and adding a second electron should lead to a further decrease, i.e., BeH₂ > BH₂ > CH₂.

b) Optimize the geometries of (singlet) BH₂• and CH₂ using the HF/6-31G* model. Are the results of the quantum chemical calculations in line with your qualitative arguments?

(BH₂, CH₂) According to the HF/6-31G* calculations, the bond angle in BH₂ is 127° and the bond angle in CH₂ is 103°. This lends support to the qualitative arguments based on the energy of the LUMO as a function of bond angle.

c) Perform a series of geometry optimizations on singlet CH₂ with the bond angle constrained to 90°, 100°, 110°, . . . , 180°. Plot the total energy as a function of the angle as well as the HOMO and LUMO energies.

Display the LUMO for some intermediate structure. Does the plot of HOMO energy versus angle in CH₂ mirror the plot of LUMO energy versus angle in BeH₂? Rationalize your answer. Does the energy of the LUMO in CH₂ increase, decrease, or remain constant with increase in bond angle (or is it at a minimum or maximum somewhere between)? Is the change in LUMO energy smaller, larger, or about the same as the change in the energy of the HOMO over the same range of bond angles? Rationalize these two observations by reference to the shape and nodal structure of the LUMO. What do you anticipate would happen to the geometry of CH₂ as electrons are added to the LUMO?

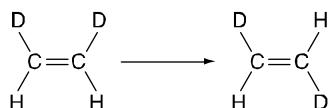
Take a guess at the structure of NH₂• (one electron added to the LUMO) and H₂O (two electrons added to the LUMO).

(CH₂ angle variation) A plot of total energy vs. bond angle (white line) shows that CH₂ prefers a bond angle of 103° (see part b). The HOMO energy (red line) roughly parallels the total energy although (unlike the total energy) it increases monotonically over the range of angles investigated (it does not exhibit a minimum). This behavior is consistent with the shape and nodal structure of the HOMO which is essentially a lone pair on carbon in the highly bent structures but with a bonding component between the two hydrogens. In the limit of linear CH₂ it is a pure p orbital (with no bonding between the hydrogens). The LUMO energy (blue line) does not vary significantly with change in bond angle. The orbital is a pure p function. Adding one or two electrons to this orbital should lead to little change in geometry, i.e., CH₂ ≈ NH₂ ≈ OH₂.

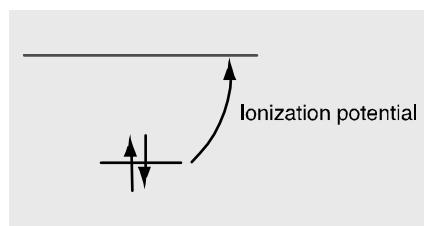
d) Optimize the geometries of NH_2^\bullet and H_2O using the HF/6-31G* model. Are the results of the quantum chemical calculations in line with your qualitative arguments?

($\text{NH}_2, \text{H}_2\text{O}$) According to HF/6-31G* calculations the bond angle in NH_2^\bullet is 104° and that in water is 105° . Both are close to the bond angle in CH_2 (103°). This lends support to the qualitative arguments based on the lack of variation in energy of the LUMO in CH_2 .

P27.30) Olefins assume planar (or nearly planar) geometries wherever possible. This ensures maximum overlap between p orbitals and maximum π -bond strength. Any distortion away from planarity should reduce orbital overlap and bond strength. In principle, π -bond strength can be determined experimentally, by measuring the activation energy required for *cis-trans* isomerization, for example, in *cis*-1,2-dideuteroethylene:



Another measure of π -bond strength, at least π -bond strength relative to a standard, is the energy required to remove an electron from the π orbital, or the ionization potential.



Non-planar olefins might be expected to result from incorporation to a *trans* double bond into a small ring. Small-ring cycloalkenes prefer *cis* double bonds, and the smallest *trans* cycloalkene to actually have been isolated is cyclooctene. It is known experimentally to be approximately 39 kJ/mol less stable than *cis*-cyclooctene. Is this a measure of reduction in π bond strength?

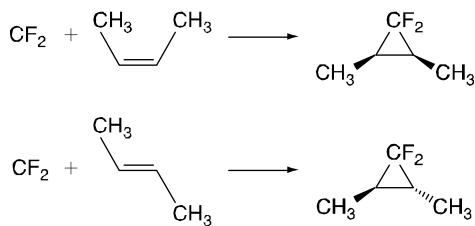
Optimize the geometries of both *cis*- and *trans*-cyclooctene using the HF/3-21G model. (You should first examine the possible conformers available to each of the molecules.) Finally, calculate and display the HOMO for each molecule.

Is the double bond in *trans*-cyclooctene significantly distorted from its ideal planar geometry? If so, would you characterize the distortion as puckering of the double bond carbons or as twisting around the bond, or both? Does the HOMO in *trans*-cyclooctene show evidence of distortion? Elaborate. Is the energy of the HOMO in *trans*-cyclooctene significantly higher (less negative) than that in *cis*-cyclooctene? How does the energy difference compare to the experimentally measured difference in ionization potentials

between the two isomers (0.29 eV)? How does the difference in HOMO energies (ionization potentials) relate to the calculated (measured) difference in isomer energies?

(cyclooctene) The double bond in *trans*-cyclooctene is both twisted (CC=CC dihedral angle = 140°) and the alkene carbons have pyramidalized. This is reflected in the HOMO in which the upper and lower lobes are skewed relative to each other. The HOMO energy for *trans* cyclooctene is 0.28 eV (27 kJ/mol) higher than that for the *cis* isomer. This is nearly identical to the measured difference in ionization potentials of the two conformers (0.29 eV) and of similar magnitude to the difference in total energies (40 kJ/mol favoring *cis*-cyclooctene).

P27.31) Singlet carbenes add to alkenes to yield cyclopropanes. Stereochemistry is maintained, meaning that *cis*- and *trans*-substituted alkenes give *cis*- and *trans*-substituted cyclopropanes, respectively; for example:



This implies that the two σ bonds are formed more or less simultaneously, without the intervention of an intermediate that would allow *cis-trans* isomerization.

Locate the transition state for addition of singlet difluorocarbene and ethene using the HF/3-21G model and, following this, calculate vibrational frequencies. When completed, verify that you have in fact found a transition state and that it appears to be on the way to the correct product.

What is the orientation of the carbene relative to ethene in your transition state? Is it the same orientation as adopted in the product (1,1-difluorocyclopropane)? If not, what is the reason for the difference? (Hint: Consider that the π electrons on ethene need to go into a low-lying unoccupied molecular orbital on the carbene. Build difluorocarbene and optimize its geometry using the HF/3-21G model and display the LUMO.)

(difluorocarbene; difluorocarbene+ethene) The FCF plane (in difluorocarbene) lies above and nearly parallel to the plane of ethene. This is quite far from the “perpendicular orientation” in the product (1,1- difluorocyclopropane). The reason for this is that it is the LUMO in difluorocarbene, which is a p orbital out of the FCF plane, that needs to interact with the ethene π bond. Positioning difluorocarbene in its final (product) geometry would minimize this favorable interaction and would maximize unfavorable interaction involving the HOMO on the carbene (an electron pair localized on carbon).

P27.32) Further information about the mechanism of the ethyl formate pyrolysis reaction can be obtained by replacing the static picture with a movie, that is, an animation

along the reaction coordinate. Bring up “ethyl formate pyrolysis” and examine the change in electron density as the reaction proceeds. Do hydrogen migration and CO bond cleavage appear to occur in concert or is one leading the other?

(*ethyl formate pyrolysis*) Examination of the change in electron density as a function of the reaction coordinate for pyrolysis of ethyl formate clearly shows that hydrogen migration and CO bond cleavage occur in concert. However, bond cleavage is ahead of migration.

P27.33) Do related molecules with the same number of electrons occupy the same amount of space, or are other factors (beyond electron count) of importance when dictating overall size requirements? Obtain equilibrium geometries for methyl anion, ammonia, and hydronium cation using the HF/6-31G* model and examine electron density surfaces. Do the three molecules take up the same amount of space? If not, why not?

(*methyl anion, ammonia, hydronium cation*) These three molecules share the same number of electrons (10), but differ in nuclear charge. The electron density surface for methyl anion which has the smallest nuclear charge is much larger than that for hydronium cation which has the largest nuclear charge. Ammonia is in between, both in terms of the size of the density surface and in its nuclear charge. The underlying “glue” which holds molecules together is Coulombic attraction between positively charged nuclei and negatively charged electrons. Electrons will be held more and more tightly (closely) as nuclear charge increases.

P27.34) Lithium provides a very simple example of the effect of oxidation state on overall size. Perform HF/6-31G* calculations on lithium cation, lithium atom, and lithium anion, and compare the three electron density surfaces. Which is smallest? Which is largest? How does the size of lithium relate to the number of electrons? Which surface most closely resembles a conventional space-filling model? What, if anything does this tell you about the kinds of molecules that were used to establish the space-filling radius for lithium?

(*lithium cation, atom, anion*) According to calculated (HF/6-31G*) electron density surfaces, lithium cation is smaller than lithium atom which in turn is smaller than lithium atom. This parallels an increase in the number of electrons (for a fixed nuclear charge) in going from the cation to the anion. The fewer the number of electrons the tighter (closer) they will be held to the nucleus and the smaller the density. The conventional space filling model is closest in size to the electron density surface of lithium cation (and much smaller than the surfaces corresponding to the atom and anion), reflecting the fact that lithium is most commonly “ionic” in its compounds.

P27.35) A surface for which the electrostatic potential is negative delineates regions in a molecule that are subject to electrophilic attack. It can help you to rationalize the widely different chemistry of molecules that are structurally similar.

Optimize the geometries of benzene and pyridine using the HF/3-21G model and examine electrostatic potential surfaces. Describe the potential surface for each molecule. Use it to rationalize the following experimental observations: (1) Benzene and its derivatives undergo electrophilic aromatic substitution far more readily than do pyridine and its derivatives; (2) protonation of perdeuterobenzene (C_6D_6) leads to loss of deuterium, whereas protonation of perdeuteropyridine (C_5D_5N) does not lead to loss of deuterium; and (3) benzene typically forms π -type complexes with transition models, whereas pyridine typically forms σ -type complexes.

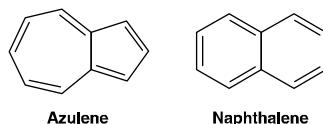
(benzene, pyridine) The surfaces correspond to regions in benzene and pyridine for which the electrostatic potential is a constant negative value. This means that an electrophile will be attracted to these regions.

In benzene, the regions are above and below the plane of the ring, that is the π system. This is consistent with the fact that electrophiles will attack benzene in the π system, “electrophilic aromatic substitution.” It is also consistent with the fact that benzene will bind “face on” to electron-deficient transition metal centers (making π complexes).

Where the electrophile is H^+ , electrophilic attack onto perdeuterobenzene will lead to an intermediate (“benzenium ion”) in which the incoming proton (the electrophile) and one of the deuteriums are in chemically equivalent environment. Loss of D^+ from this intermediate is equally probably to loss of H^+ .

In pyridine, the region of negative potential is away from the nitrogen in the plane of the ring. This corresponds to the lone pair on pyridine. The fact that the potential above and below the plane of the ring (the π system) is not as negative as that in benzene suggests that pyridine will not be as reactive as benzene toward electrophilic aromatic substitution. No “benzenium type” ions will form and no loss of deulenum (from perdeuteropyridine) will result. Pyridine will bond “end on” to electron-deficient transition metal centers (making σ complexes).

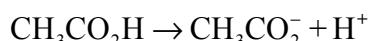
P27.36) Hydrocarbons are generally considered to be nonpolar or weakly polar at best, characterized by dipole moments that are typically only a few tenths of a debye. For comparison, dipole moments for molecules of comparable size with heteroatoms are commonly several debyes. One recognizable exception is azulene, which has a dipole moment of 0.8 debye:



Optimize the geometry of azulene using the HF/6-31G* model and calculate an electrostatic potential map. For reference, perform the same calculations on naphthalene, a nonpolar isomer of azulene. Display the two electrostatic potential maps side by side and on the same (color) scale. According to its electrostatic potential map, is one ring in azulene more negative (relative to naphthalene as a standard) and one ring more positive? If so, which is which? Is this result consistent with the direction of the dipole moment in azulene? Rationalize your result. (Hint: Count the number of π electrons.)

(azulene, naphthalene) Relative to naphthalene as a standard, the seven-membered ring in azulene is more positive and the five-membered ring is more negative. This is consistent with the sign of the dipole moment. The simplest interpretation is that azulene is the fusing of two 6π electrons aromatic rings, cycloheptatrienyl (tropylium) cation and cyclopentadienyl anion.

P27.37) Chemists know that nitric and sulfuric acids are strong acids and that acetic acid is a weak acid. They would also agree that ethanol is at best a very weak acid. Acid strength is given directly by the energetics of deprotonation (heterolytic bond dissociation); for example, for acetic acid.

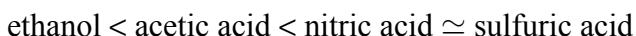


As written, this is a highly *endothermic* process, because not only is a bond broken but two charged molecules are created from the natural acid. It occurs readily in solution only because the solvent acts to disperse charge.

Acid strength can be calculated simply as the difference in energy between the acid and its conjugate base (the energy of the proton is 0). In fact, acid strength comparisons among closely related systems, for example, carboxylic acids, are quite well described with practical quantum chemical models. This is consistent with the ability of the same models to correctly account for relative base strengths (see discussion in Section 27.8.3). Another possible measure of acid strength is the degree of positive charge on the acidic hydrogen as measured by the electrostatic potential. It is reasonable to expect that the more positive the potential in the vicinity of the hydrogen, the more easily it will dissociate and the stronger the acid. This kind of measure, were it to prove successful, offers an advantage over the calculation of reaction energy, in that only the acid (and not the conjugate base) needs to be considered.

- a) Obtain equilibrium geometries for nitric acid, sulfuric acid, acetic acid, and ethanol using the HF/3-21G model, and compare electrostatic potential maps. Be certain to choose the same (color) scale for the four acids. For which acid is the electrostatic potential in the vicinity of (the acidic) hydrogen most positive? For which is it least positive? Do electrostatic potential maps provide a qualitatively correct account of the relative acid strength of these four compounds?

(ethanol, acetic, sulfuric, nitric acids) The electrostatic potential (in the vicinity of the acidic hydrogen) in sulfuric and nitric acids are similar and more positive than that in acetic acid which is in turn more positive than the electrostatic potential in ethanol. This parallels the relative acidities of these compounds:



- b) Obtain equilibrium geometries for several of the carboxylic acids found in the following table using the HF/3-21G model and display an electrostatic potential map for each.

Acid	pK _a	Acid	pK _a
Cl ₃ CCO ₂ H	0.7	HCO ₂ H	3.75
HO ₂ CCCO ₂ H	1.23	<i>trans</i> -ClCH=CHCO ₂ H	3.79
Cl ₂ CHCO ₂ H	1.48	C ₆ H ₅ CO ₂ H	4.19
NCCH ₂ CO ₂ H	2.45	<i>p</i> -ClC ₆ H ₄ CH=CHCO ₂ H	4.41
ClCH ₂ CO ₂ H	2.85	<i>trans</i> -CH ₃ CH=CHCO ₂ H	4.70
<i>trans</i> -HO ₂ CCH=CHCO ₂ H	3.10	CH ₃ CO ₂ H	4.75
<i>p</i> -HO ₂ CC ₆ H ₄ CO ₂ H	3.51	(CH ₃) ₃ CCO ₂ H	5.03

“Measure” the most positive value of the electrostatic potential associated with the acidic hydrogen in each of these compounds and plot this against experimental pK_a (given in the preceding table). Is there a reasonable correlation between acid strengths and electrostatic potential at hydrogen in this closely related series of acids?

(carboxylic acids) Maximum (most positive) values of the electrostatic potential (at the acidic hydrogen) for different carboxylic acids are as follows.

trichloroacetic acid	83.9
oxalic acid	79.8
dichloroacetic acid	80.9
cyanoacetic acid	78.0
chloroacetic acid	77.9
fumaric acid	75.2
terephthalic acid	72.5
formic acid	73.3
(E)-3-chloroacrylic acid	73.9
benzoic acid	67.6
(E)-3-(<i>p</i> -chlorophenyl) acrylic acid	69.0
crotonic acid	65.6
acetic acid	68.8
pivalic acid	66.1

A plot of these maximum values vs. pK_a yields a reasonable correlation.

Chapter 28: Molecular Symmetry

Questions on Concepts

Q28.1) What is the difference between a symmetry element and a symmetry operation?

A symmetry element is a geometrical entity such as a rotation axis or a mirror plane. A symmetry operation is a rotation through a certain angle or a reflection through the mirror plane that leaves the molecule in a position that is indistinguishable from the original position.

Q28.2) Why are all one-dimensional representations irreducible?

A representation is reducible if its dimension can be reduced. As there is no dimension lower than one, a one-dimensional representation is irreducible.

Q28.3) Why does the C_{3v} group have a two-dimensional irreducible representation? Answer this question by referring to the form of the matrices that represent the operations of the group.

If x' and/or $y' = f(x, y)$ for a representation, then the basis will be (x, y) and the dimension of that irreducible representation will be two. An example is the C_3 rotation of the C_{3v} group, and consequently, one of the representations of the C_{3v} group has the dimension two.

Q28.4) Some symmetry operations can be carried out physically using a ball-and-stick model of a molecule and others can only be imagined. Give two examples of each category.

Rotations and reflections through a mirror plane can be carried out physically using a ball-and-stick model of a molecule. By contrast, inversion through a center of symmetry and a rotation-reflection can only be imagined.

Q28.5) Which of the three normal modes of H_2O in Figure 28.8 is best described as a bending mode? Does the bond angle remain unchanged in any of the modes? Which requires less energy, bond bending or bond stretching?

The 1595 cm^{-1} mode does not involve significant changes in bond length, and is therefore largely a change in bond angle. The bond angle changes in all modes, but most significantly in the 1595 cm^{-1} mode. Less energy is required to bend the bond as can be seen from the fact that this mode has the lowest energy.

Q28.6) Why does the list of elements for the D_{6h} group in Table 28.2 not list the elements S_6^2 , S_6^3 , and S_6^4 ?

S_6^2 is not listed because it is identical to S_3 . S_6^3 is not listed because it is identical to i . S_6^4 is not listed because it is identical to S_3^2 .

Q28.7) Why does the list of elements for the D_{6h} group in Table 28.2 not list the elements C_6^2 , C_6^3 , and C_6^4 ?

C_6^2 is not listed because it is identical to C_3 . C_6^3 is not listed because it is identical to C_2 . C_6^4 is not listed because it is identical to C_3^2 .

Q28.8) How are quantum mechanical calculations in the LCAO-MO model simplified through the construction of symmetry-adapted MOs?

If symmetry is not considered, the coefficient of each atomic orbital in the basis set must be assumed to be different from zero and from one another. This would require 12 coefficients for ethene as discussed in Section 28.8. However, taking the symmetry of the molecule into account reduces the number of coefficients that are different or nonzero from 12 to 3.

Q28.9) Explain why only two peaks are observed in the infrared spectrum of methane although six of the nine normal modes are infrared active.

The infrared active modes of vibration of benzene all belong to three dimensional representations. Because all modes that belong to the same representation have the same frequency, the 6 infrared active modes give rise to only two frequencies.

Q28.10) Explain why the overlap integral between two combinations of AOs is nonzero only if the combinations belong to the same representation.

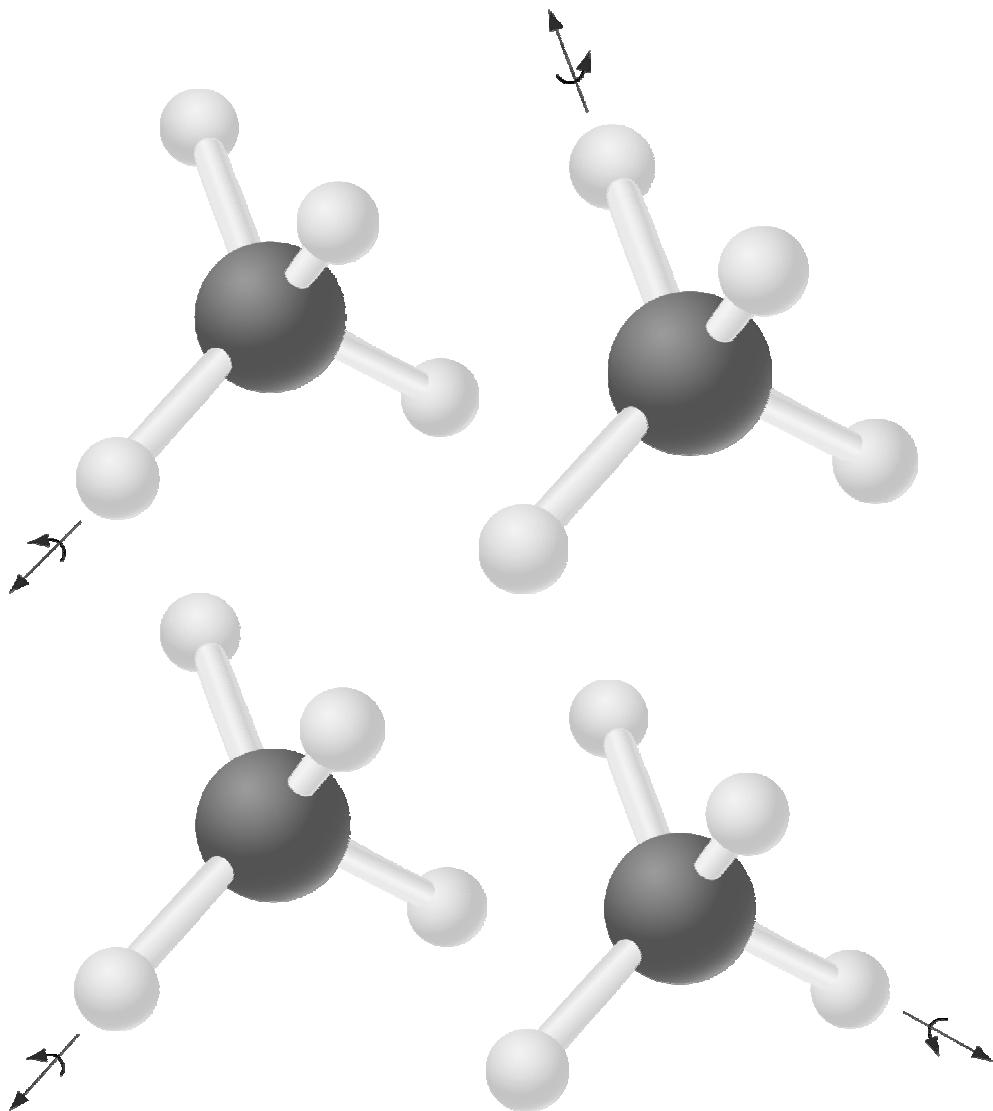
Because S_{ij} is just a number, it can't change upon applying any of the operators of the group to which the molecule belongs to the integral. In other words, S_{ij} belongs to the A_1 representation. The same must be true of the integrand, and therefore, the integrand must also belong to the A_1 representation. This requires that each character of the representation formed from the direct product of the combinations of the AOs is equal to one. This is only the case if the combinations belong to the same representation.

Problems

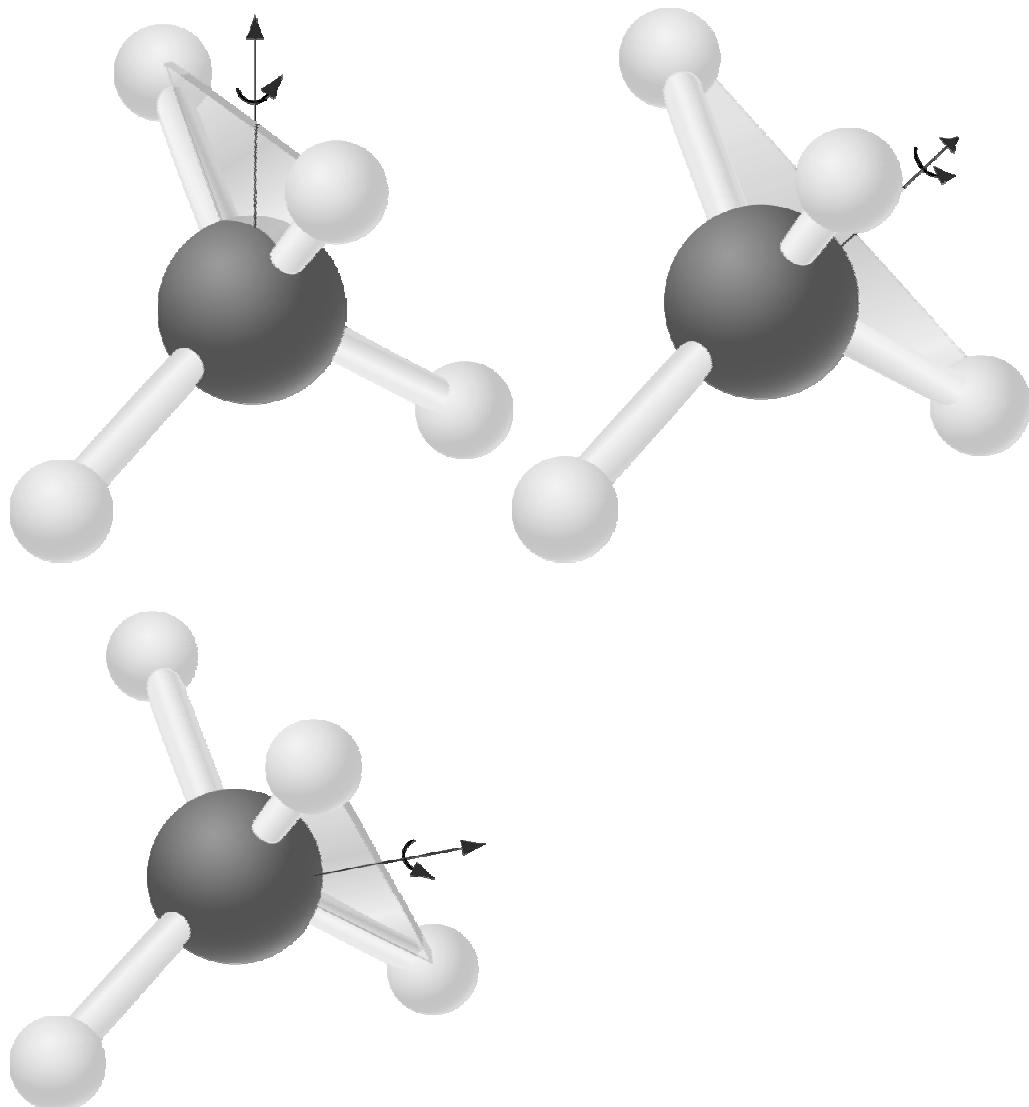
P28.1) CH_4 belongs to the T_d point group with the following symmetry elements: E , $4C_3$, $4C_3^2$, $3C_2$, $3S_4$, $3S_4^3$, and 6σ . Make a drawing similar to Figure 28.1 showing these elements.

The symmetry elements are shown in the figures below. The identity element is not depicted..

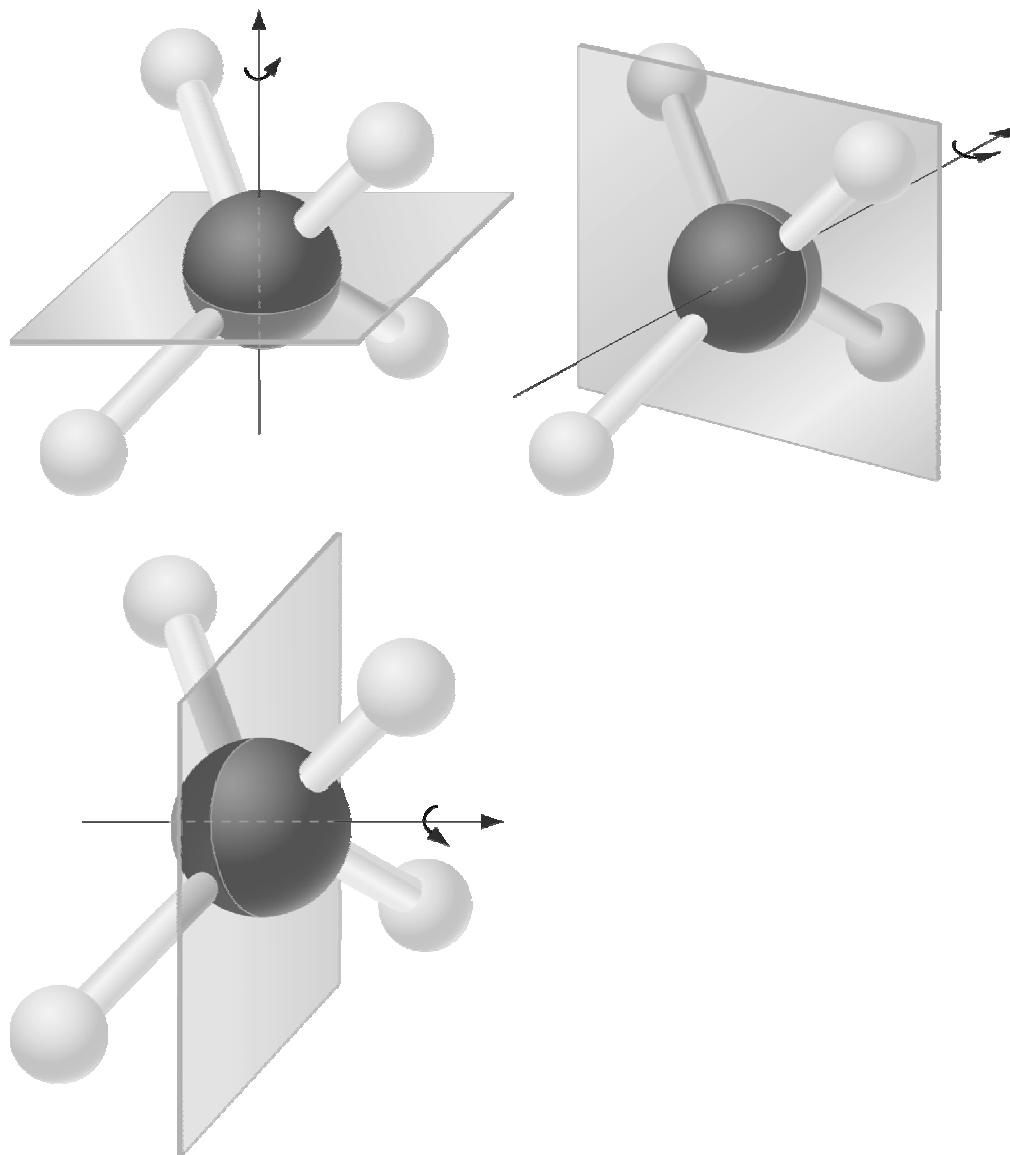
There are four 3-fold axes on each of the C–H bonds. These give rise to the $4C_3$ and $4C_3^2$ operations.



There are three 2-fold axes that lie in a H–C–H plane. The rotation axis bisects this angle. They give rise to the $3C_2$ operations.

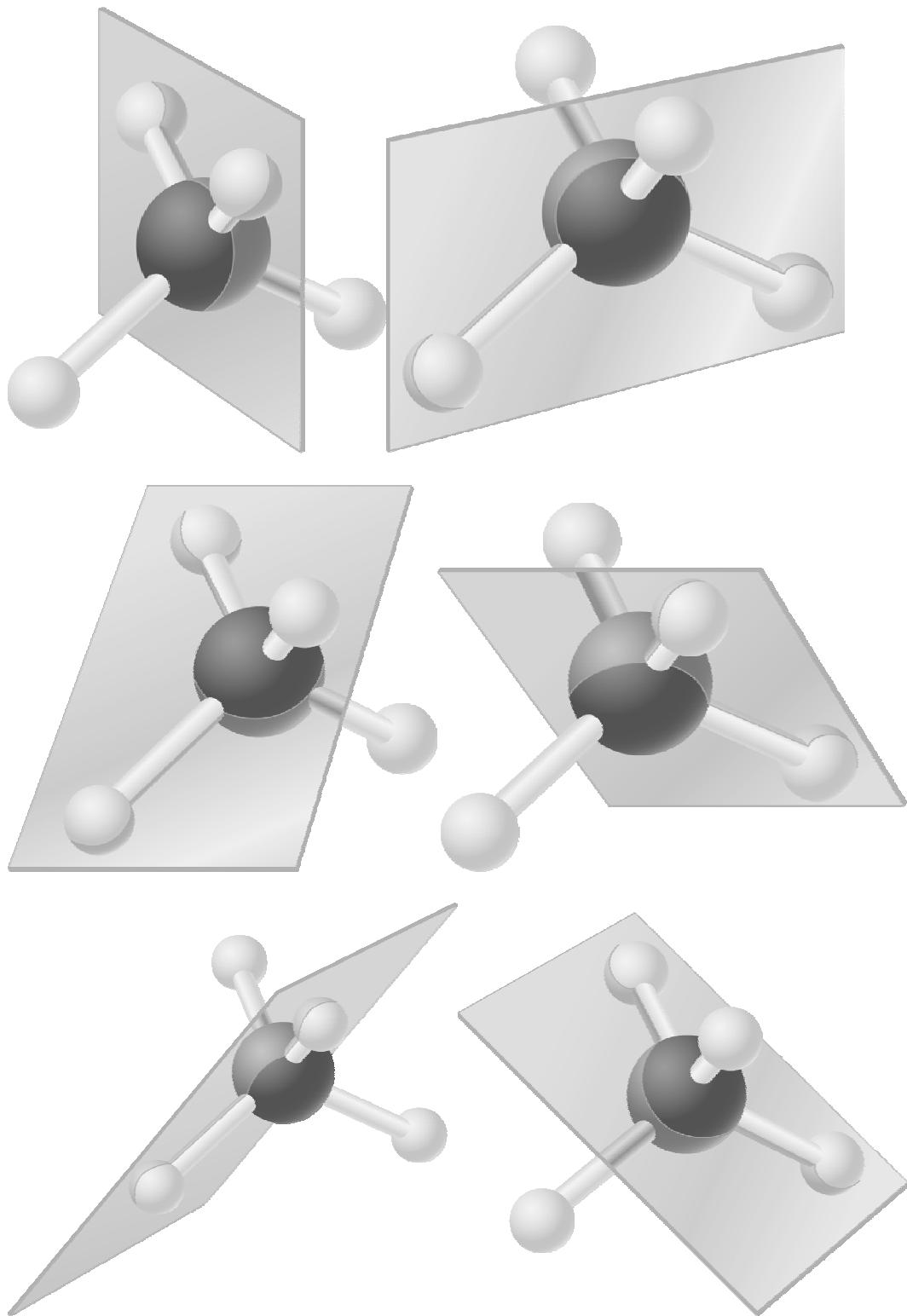


There are three mutually perpendicular S_4 -axes as shown below.



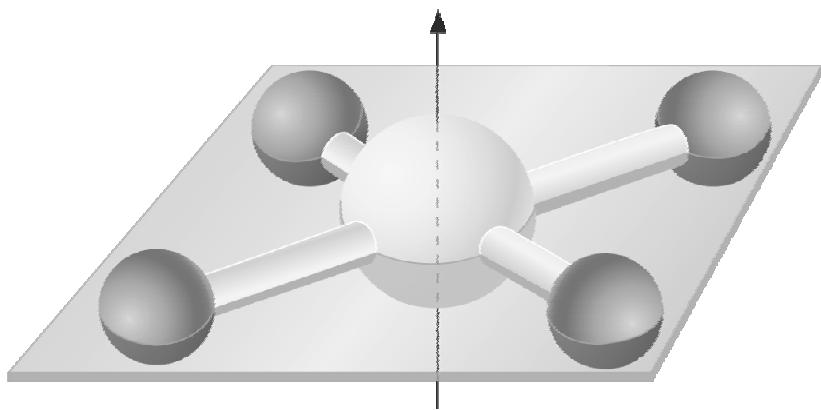
Chapter 28/Molecular Symmetry

There are six mirror planes, each of which contains a H–C–H.

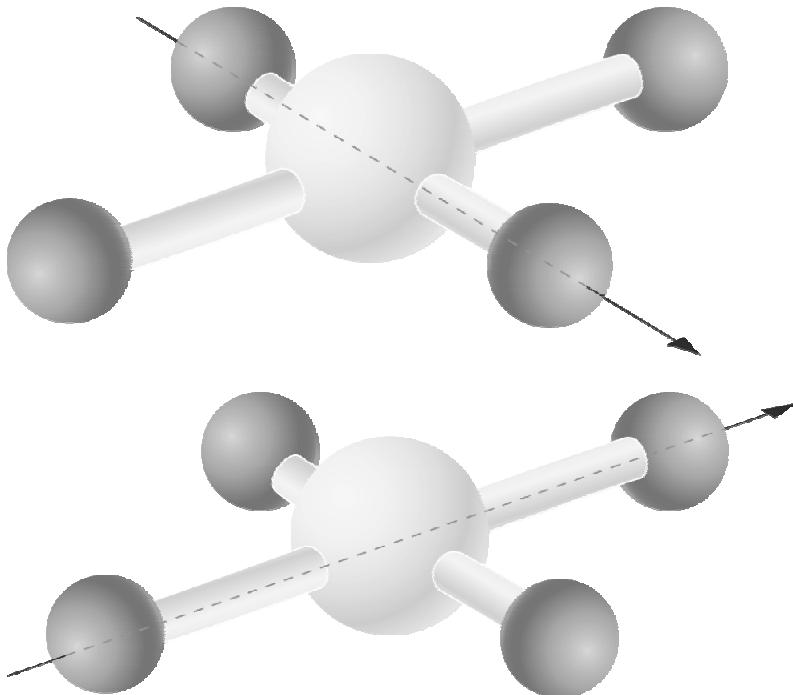


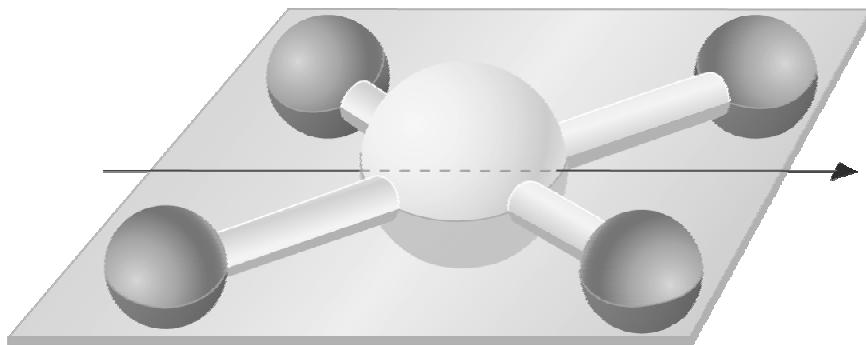
P28.2) XeF_4 belongs to the D_{4h} point group with the following symmetry elements: E , C_4 , C_4^2 , C_2 , C_2' , C_2'' , i , S_4 , S_4^2 , σ , $2\sigma'$, and $2\sigma''$. Make a drawing similar to Figure 28.1 showing these elements.

The 4-fold axis is perpendicular to the plane of the molecule.

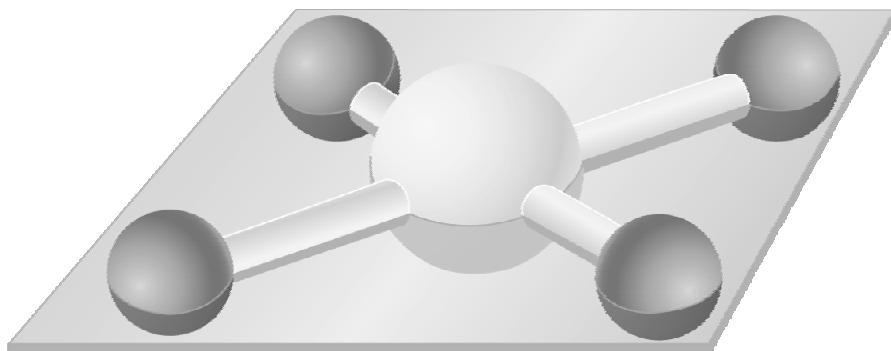


There are three 2-fold axes, as shown below. Two pass through the opposed F atoms, and the third bisects the F-Xe-F angle.

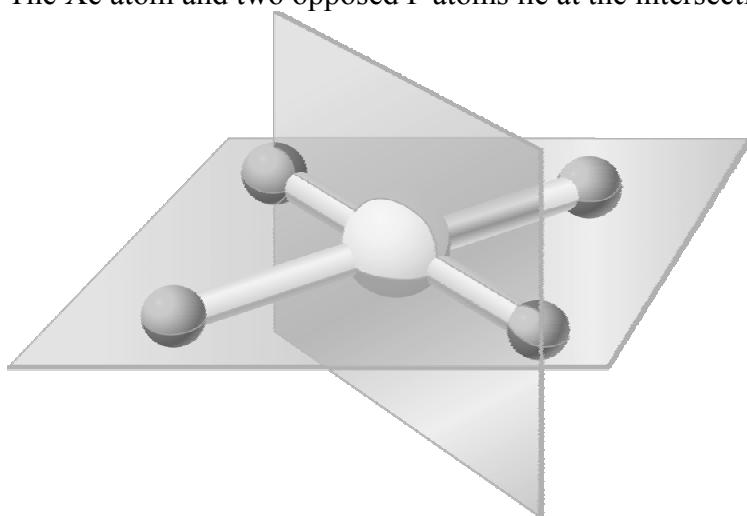


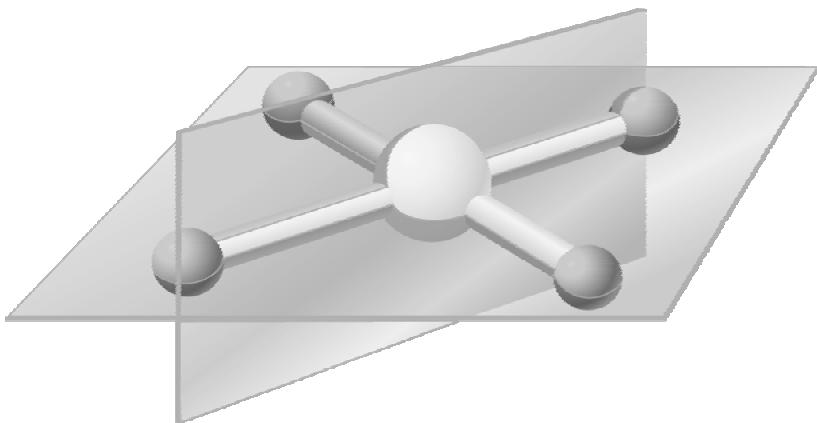


The mirror plane denoted σ lies in the plane of the molecule.

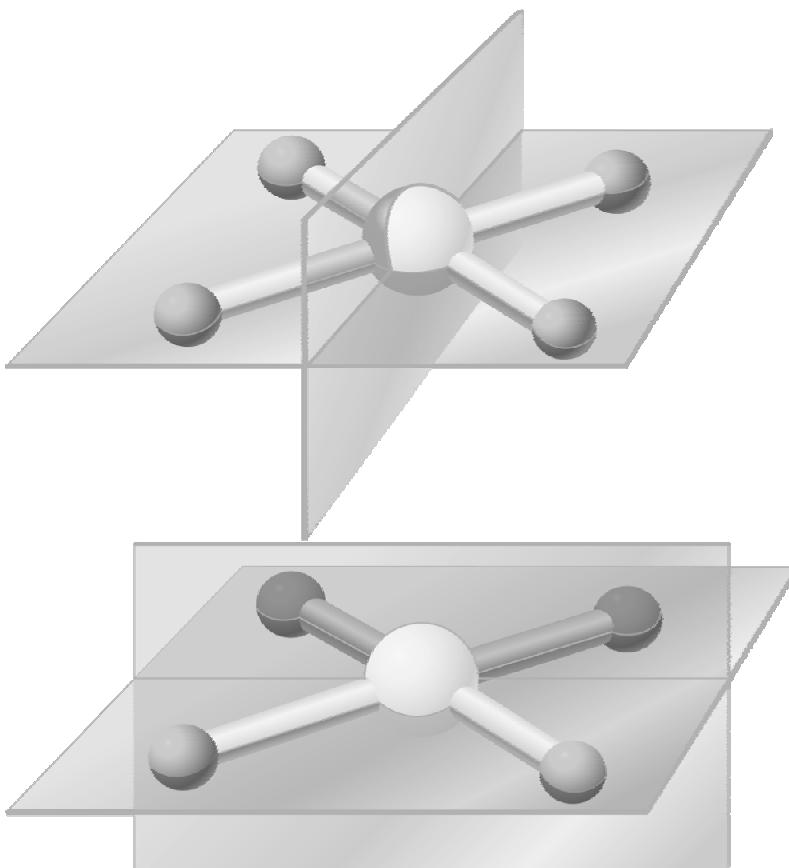


The two mirror planes denoted σ' are mutually perpendicular, and are perpendicular to σ .
The Xe atom and two opposed F atoms lie at the intersection of σ' with σ .





The two mutually perpendicular mirror planes σ'' contain the Xe, but no F atoms.



The Xe atom is the invasion center. This element is not depicted.

P28.3) Use the logic diagram of Figure 28.2 to determine the point group for allene. Indicate your decision-making process as was done in the text for NH₃.

a) allene

1) linear?	No
2) C_n axis?	Yes C_2 axis $\Rightarrow z$ axis
3) more than 1 C_n axis?	Yes
3) more than 1 C_n axis, $n > 2$?	No
4) σ plane?	Yes
5) $\sigma \perp$ to C_2 ?	No

We conclude that the point group is D_{2d} .

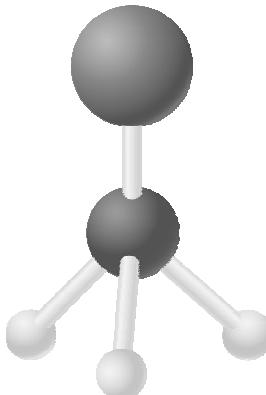
P28.4) Use the logic diagram of Figure 28.2 to determine the point group for PCl_5 . Indicate your decision-making process as was done in the text for NH_3 .

1) linear?	No
2) C_n axis?	Yes C_3 axis $\Rightarrow z$ axis
3) more than 1 C_n axis	Yes
3) more than 1 C_n axis, $n > 2$?	No
4) σ plane?	Yes
5) $\sigma \perp$ to C_3 ?	Yes

We conclude that the point group is D_{3h} .

P28.5) Use the logic diagram of Figure 28.2 to determine the point group for CH_3Cl . Indicate your decision-making process as was done in the text for NH_3 .

The molecule is depicted below.

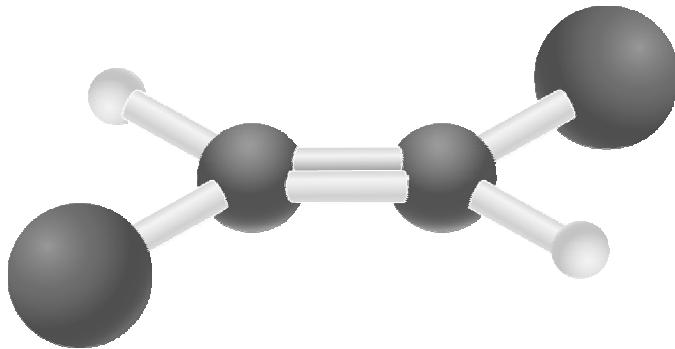


1) linear?	No
2) C_n axis?	Yes
3) more than 1 C_n axis?	No
4) σ plane?	Yes
5) C_3 lies in σ ?	Yes

We conclude that the point group is C_{3v} .

P28.6) Use the logic diagram of Figure 28.2 to determine the point group for the planar molecule *trans*-HBrC=CBrH. Indicate your decision-making process as was done in the text for NH₃.

The molecule is depicted below.

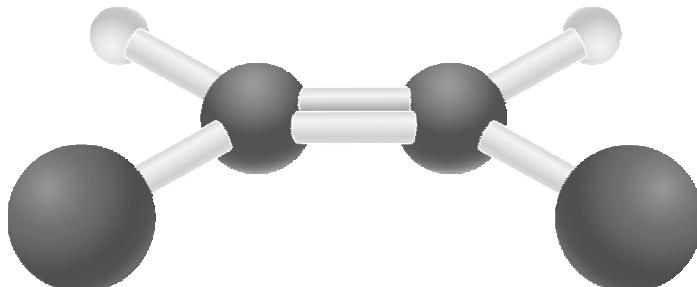


- | | |
|-------------------------------------|-----|
| 1) linear? | No |
| 2) C _n axis? | Yes |
| 3) more than 1 C _n axis? | No |
| 4) σ plane? | Yes |
| 5) C ₂ lies in σ? | No |

We conclude that the point group is C_{2h}.

P28.7) Use the logic diagram of Figure 28.2 to determine the point group for the planar molecule *cis*-HBrC=CClH. Indicate your decision-making process as was done in the text for NH₃.

The molecule is depicted below.



- | | |
|-------------------------------------|-----|
| 1) linear? | No |
| 2) C _n axis? | Yes |
| 3) more than 1 C _n axis? | No |
| 4) σ plane? | Yes |
| 5) C ₂ lies in σ? | Yes |

We conclude that the point group is C_{2v}.

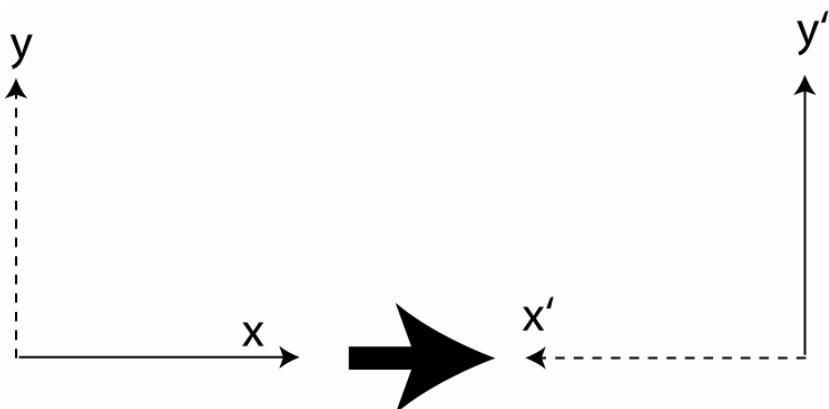
P28.8) Use the method illustrated in Example Problem 28.1 to generate a 3×3 matrix for the following:

a) \hat{C}_6 operator The \hat{C}_6 operator is a 6-fold rotation, $360 \div 6 = 60^\circ$.

$$\hat{C}_6 = \begin{pmatrix} \cos(60^\circ) & -\sin(60^\circ) & 0 \\ \sin(60^\circ) & \cos(60^\circ) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\hat{C}_6 = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

b) \hat{S}_4 operator. This is a 4-fold counterclockwise rotation ($\theta = 90^\circ$) about the z axis followed by a reflection through the x-y plane. The ($\theta = 90^\circ$) rotation is depicted in the following drawing.



We see that $x' = -y$ and $y' = x$. The subsequent reflection in the mirror plane leaves x and y unchanged but $z' = -z$. This transformation is described by

$$\hat{S}_4 \begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} -y \\ x \\ -z \end{pmatrix}$$

Thus, the matrix can be derived as

$$\begin{pmatrix} a & b & c \\ d & e & f \\ g & h & j \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -y \\ x \\ -z \end{pmatrix}$$

or

$$\begin{aligned} ax + by + cz &= -y && \text{Therefore } a = 0, b = -1, c = 0 \\ dx + ey + fz &= x && \text{Therefore } d = 1, e = 0, f = 0 \\ gx + hy + jz &= -z && \text{Therefore } g = 0, h = 0, j = -1 \end{aligned}$$

These equations are described by the matrix

$$\hat{S}_4 = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

c) \hat{i} operator. The inversion is described by $(x,y,z) \rightarrow (-x,-y,-z)$ or

$$i = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \rightarrow \begin{pmatrix} -x \\ -y \\ -z \end{pmatrix}$$

The matrix for this transformation is described by

$$\begin{pmatrix} a & b & c \\ d & e & f \\ g & h & j \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ -z \end{pmatrix}$$

$$\begin{aligned} ax + by + cz &= -x && \text{Therefore } a = -1, b = 0, c = 0 \\ dx + ey + fz &= -y && \text{Therefore } d = 0, e = -1, f = 0 \\ gx + hy + jz &= -z && \text{Therefore } g = 0, h = 0, j = -1 \end{aligned}$$

$$\hat{i} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

P28.9) Use the 3×3 matrices for the C_{2v} group in Equation (28.2) to verify the group multiplication table for the following successive operations:

- a) $\hat{\sigma}_v \hat{\sigma}'_v$ b) $\hat{\sigma}_v \hat{C}_2$ c) $\hat{C}_2 \hat{C}_2$

$$\hat{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \hat{C}_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\hat{\sigma}_v = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \hat{\sigma}'_v = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

a)

$$\hat{\sigma}_v \hat{\sigma}'_v = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\hat{\sigma}_v \hat{\sigma}'_v = \hat{C}_2$$

b)

$$\hat{\sigma}_v \hat{C}_2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\hat{\sigma}_v \hat{C}_2 = \hat{\sigma}'_v$$

c)

$$\hat{C}_2 \hat{C}_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\hat{C}_2 \hat{C}_2 = \hat{E}$$

P28.10) Use the 3×3 matrices for the C_{2v} group in Equation (28.2) to verify the associative property for the following successive operations:

$$a) \hat{\sigma}_v (\hat{\sigma}'_v \hat{C}_2) = (\hat{\sigma}_v \hat{\sigma}'_v) \hat{C}_2 \quad b) (\hat{\sigma}_v \hat{E}) \hat{C}_2 = \hat{\sigma}_v (\hat{E} \hat{C}_2)$$

See the above problem for matrices.

a)

$$\hat{\sigma}_v(\hat{\sigma}'_v \hat{C}_2) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \left[\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right] \\ = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\hat{\sigma}_v(\hat{\sigma}'_v \hat{C}_2) = \hat{E}$$

$$(\hat{\sigma}_v \hat{\sigma}'_v) \hat{C}_2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \left[\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right] \\ = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$(\hat{\sigma}_v \hat{\sigma}'_v) \hat{C}_2 = \hat{E}$$

$$\text{Thus } (\hat{\sigma}_v \hat{\sigma}'_v) \hat{C}_2 = \hat{\sigma}_v(\hat{\sigma}'_v \hat{C}_2)$$

b)

$$(\hat{\sigma}_v \hat{E}) \hat{C}_2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \left[\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right] \\ = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$(\hat{\sigma}_v \hat{E}) \hat{C}_2 = \hat{\sigma}'_v$$

$$\begin{aligned}\hat{\sigma}_v(\hat{E}\hat{C}_2) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \left[\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right] \\ &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\end{aligned}$$

$$\hat{\sigma}_v(\hat{E}\hat{C}_2) = \hat{\sigma}'_v$$

$$\text{Thus } (\hat{\sigma}_v\hat{E})\hat{C}_2 = \hat{\sigma}_v(\hat{E}\hat{C}_2)$$

P28.11) The D_3 group has the following classes: E , $2C_3$, and $3C_2$. How many irreducible representations does this group have and what is the dimensionality of each?

The D_3 group has three classes and six elements ($1E$, $2C_3$, $3C_2$).

There are three irreducible representations because there are three classes. Their dimensions are determined by the equation

$$d_1^2 + d_2^2 + d_3^2 = 6$$

This can only be satisfied by $d_1 = 2$, $d_2 = 1$, $d_3 = 1$. Thus

3 irreducible representations; two 1-dimensional and one 2-dimensional.

P28.12) The C_{4v} group has the following classes: E , $2C_4$, C_2 , $2\sigma_v$, and $2\sigma_d$. How many irreducible representations does this group have and what is the dimensionality of each?

The C_{4v} group has five classes and eight elements ($1E$, $2C_4$, $1C_2$, $2\sigma_v$ and $2\sigma_d$).

There are five irreducible representations because there are five classes. Their dimensions are determined by the equation

$$d_1^2 + d_2^2 + d_3^2 + d_4^2 + d_5^2 = 8$$

This can only be satisfied if $d_1 = 2$, $d_2 = d_3 = d_4 = d_5 = 1$. Thus

5 irreducible representations; four 1-dimensional and one 2-dimensional.

P28.13) Use the 2×2 matrices of Equation (28.10) to derive the multiplication table for the C_{3v} group.

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad C_3 = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \quad C_3^2 = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

$$\sigma_v = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \quad \sigma'_v = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \quad \sigma''_v = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

$$E \cdot E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = E$$

$$E \cdot C_3 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = C_3$$

$$E \cdot C_3^2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = C_3^2$$

$$E \cdot \sigma_v = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} = \sigma_v$$

$$E \cdot \sigma'_v = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \sigma'_v$$

$$E \cdot \sigma''_v = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \sigma''_v$$

$$C_3 \cdot E = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = C_3$$

$$C_3 \cdot C_3 = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = C_3^2$$

$$C_3 \cdot C_3^2 = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = E$$

$$C_3 \cdot \sigma_v = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \sigma_v''$$

$$C_3 \cdot \sigma'_v = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} = \sigma_v$$

$$C_3 \cdot \sigma''_v = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \sigma'_v$$

$$C_3^2 \cdot E = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = C_3^2$$

$$C_3^2 \cdot C_3 = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = E$$

$$C_3^2 \cdot C_3^2 = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = C_3$$

$$C_3^2 \cdot \sigma_v = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \sigma'_v$$

$$C_3^2 \cdot \sigma'_v = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \sigma''_v$$

$$C_3^2 \cdot \sigma''_v = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} = \sigma_v$$

$$\sigma_v \cdot E = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} = \sigma_v$$

$$\sigma_v \cdot C_3 = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \sigma'_v$$

$$\sigma_v \cdot C_3^2 = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \sigma''_v$$

$$\sigma_v \cdot \sigma_v = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = E$$

$$\sigma_v \cdot \sigma'_v = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = C_3$$

$$\sigma_v \cdot \sigma''_v = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = C_3^2$$

$$\sigma'_v \cdot E = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \sigma'_v$$

$$\sigma'_v \cdot C_3 = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \sigma''_v$$

$$\sigma'_v \cdot C_3^2 = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} = \sigma_v$$

$$\sigma'_v \cdot \sigma_v = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} = C_3^2$$

$$\sigma'_v \cdot \sigma'_v = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = E$$

$$\sigma'_v \cdot \sigma''_v = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = C_3$$

$$\sigma''_v \cdot E = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \sigma''_v$$

$$\sigma''_v \cdot C_3 = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} = \sigma_v$$

$$\sigma''_v \cdot C_3^2 = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \sigma'_v$$

$$\sigma_v'' \cdot \sigma_v = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = C_3$$

$$\sigma_v'' \cdot \sigma_v' = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = C_3^2$$

$$\sigma_v'' \cdot \sigma_v'' = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = E$$

Thus, the multiplication table takes the following form. The first column represents the first operation, and successive columns represent the second operation.

C_{3v}	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
C_3	C_3	C_3^2	E	σ_v''	σ_v	σ_v'
C_3^2	C_3^2	E	C_3	σ_v'	σ_v''	σ_v
σ_v	σ_v	σ_v'	σ_v''	E	C_3	C_3^2
σ_v'	σ_v'	σ_v''	σ_v	C_3^2	E	C_3
σ_v''	σ_v''	σ_v	σ_v'	C_3	C_3^2	E

P28.14) Show that z is a basis for the A_1 representation and that R_z is a basis for the A_2 representation of the C_{3v} group.

All of the operations of the C_{3v} group are described by the matrix equation

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \pm 1 & 0 & 0 \\ 0 & \pm 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \pm x \\ \pm y \\ z \end{pmatrix}$$

The signs of at least one of x and y are changed by the operations other than E, but it is always the case that $z' = z$. Therefore, the character of each operation on z is 1, which makes z a basis for the A_1 representation.

For a rotation about the z axis, the character is +1 if the direction of rotation is unchanged, and -1 if the direction of the rotation is changed. Because the identity

operator does not change the direction of the rotation, the character is +1. The same is true of the \hat{C}_2 operator. However, reflection if both the σ_v and σ'_v planes changes the direction of rotation because the rotation axis lies in the plane. Therefore the character for these operations is -1. The sequence of these characters correspond to the A_2 representation.

P28.15) Decompose the following reducible representation into irreducible representations of the C_{2v} group:

E	C_2	σ_v	σ'_v
4	0	0	0

We set up the following table and apply Equation (28.22). The reducible representation is in the first row.

	E	C_2	σ_v	σ'_v
Red	4	0	0	0
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

$$n_{A_1} = \frac{1}{4} [(1 \times 4 \times 1) + (1 \times 0 \times 1) + (1 \times 0 \times 1) + (1 \times 0 \times 1)] = 1$$

$$n_{A_2} = \frac{1}{4} [(1 \times 4 \times 1) + (1 \times 0 \times 1) + (1 \times 0 \times -1) + (1 \times 0 \times -1)] = 1$$

$$n_{B_1} = \frac{1}{4} [(1 \times 4 \times 1) + (1 \times 0 \times -1) + (1 \times 0 \times 1) + (1 \times 0 \times -1)] = 1$$

$$n_{B_2} = \frac{1}{4} [(1 \times 4 \times 1) + (1 \times 0 \times -1) + (1 \times 0 \times -1) + (1 \times 0 \times 1)] = 1$$

Thus: $\Gamma_{\text{red}} = A_1 + A_2 + B_1 + B_2$

P28.16) Decompose the following reducible representation into irreducible representations of the C_{3v} group:

E	$2C_3$	$3\sigma_v$
5	2	-1

We proceed as in Problem P28.15.

	E	$2C_3$	$3\sigma_v$
Red	5	2	-1
A ₁	1	1	2
A ₂	1	1	-1
E	2	-1	0

$$n_{A_1} = \frac{1}{6} [(1 \times 5 \times 1) + (2 \times 2 \cdot 1) + (3 \times (-1) \times 1)] = 1$$

$$n_{A_2} = \frac{1}{6} [(1 \times 5 \times 1) + (2 \times 2 \times 1) + (3 \times (-1) \times (-1))] = 1$$

$$n_E = \frac{1}{6} [(1 \times 5 \times 1) + (2 \times 2 \times 1) + (3 \times (-1) \times (0))] = 1$$

Thus: $\Gamma_{\text{red}} = A_1 + A_2 + E$

P28.17) Methane belongs to the T_d group, which has the following character table. The reducible representation for the vibrational modes is $\Gamma_{\text{reducible}} = A_1 + E + T_2$.

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
A_1	1	1	1	1	1	$x^2+y^2+z^2$
A_2	1	1	1	-1	-1	
E	2	-1	2	0	0	$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)
T_2	3	0	-1	-1	1	(x, y, z)
						(xy, xz, yz)

a) Show that the A_2 and T_1 representations are orthogonal to each other and to the other representations in the table.

b) What is the symmetry of each of the vibrational modes that gives rise to Raman activity? Are any of the Raman active modes degenerate in energy?

a)

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_2	1	1	1	-1	-1
T_1	3	0	-1	1	-1

To test if the representations are orthogonal, we treat them as vectors and take the scalar product as described in Section 28.5.

$$\begin{aligned}\Gamma_{A_2} \cdot \Gamma_{T_1} &= [(1 \times 1 \times 3) + (8 \times 1 \times 0) + (3 \times 1 \times (-1)) + (6 \times (-1) \times 1) + (6 \times (-1) \times (-1))] \\ &= [3 + 0 + (-3) + (-6) + 6]\end{aligned}$$

$$\Gamma_{A_2} \cdot \Gamma_{T_1} = 0$$

Because the scalar product is zero, the representations are orthogonal.

- b) The normal modes of a molecule are Raman active if the bases of the representation to which the normal mode belongs are the x^2, y^2, z^2, xy, yz , or xz functions. Both the A_1 and the T_2 modes are active in Raman. The A_1 mode is not degenerate. The T_2 mode has a three-fold degeneracy.

P28.18) To determine the symmetry of the normal modes of methane, an analysis of the transformation of individual coordinate systems on the five atoms is carried out, as shown in Figure 28.11 for H_2O . After the rotational and translational representations are removed, the following reducible representation $\chi_{reducible}$ is obtained for the vibrational modes:

$$\begin{array}{ccccc} E & 8C_3 & 3C_2 & 6S_4 & 6\sigma_d \\ 9 & 0 & 1 & -1 & 3 \end{array}$$

Using the character table for the T_d group from Problem P28.19, verify that

$$\Gamma_{reducible} = A_1 + E + 2T_2.$$

	E	8C ₃	3C ₂	6S ₄	6σ _d
Red	9	0	1	-1	3
A_1	1	2	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

$$n_{A_1} = \frac{1}{24} [(1 \times 9 \times 1) + (8 \times 0 \times 1) + (3 \times 1 \times 1) + (6 \times (-1) \times 1) + (6 \times 3 \times 1)] = 1$$

$$n_{A_2} = \frac{1}{24} [(1 \times 9 \times 1) + (8 \times 0 \times 1) + (3 \times 1 \times 1) + (6 \times (-1) \times (-1)) + (6 \times 3 \times (-1))] = 0$$

$$n_E = \frac{1}{24} [(1 \times 9 \times 2) + (8 \times 0 \times 1) + (3 \times 1 \times 2) + (6 \times (-1) \times 0) + (6 \times 3 \times 0)] = 1$$

$$n_{T_1} = \frac{1}{24} [(1 \times 9 \times 3) + (8 \times 0 \times 0) + (3 \times 1 \times (-1)) + (6 \times (-1) \times (+1)) + (6 \times 3 \times (-1))] = 0$$

$$n_{T_2} = \frac{1}{24} [(1 \times 9 \times 3) + (8 \times 0 \times 0) + (3 \times 1 \times (11)) + (6 \times (-1) \times (-1)) + (6 \times 3 \times (1))] = 2$$

$$\Gamma_{reducible} = A_1 + E + 2T_2$$

P28.19) NH_3 belongs to the C_{3v} group. The character table for this group is shown here. The reducible representation for the vibrational modes is $\Gamma_{reducible} = 2A_1 + 2E$.

$$\begin{array}{ccccc} E & 2C_3 & 3\sigma_v \end{array}$$

A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y), (R_x, R_y)$	$(x^2-y^2, xy), (xz, yz)$

- a) How many vibrational modes does NH_3 have?
- b) How many of these modes are infrared active and to which representation do they belong?
- c) Are any of the infrared active modes degenerate in energy?
- d) How many of these modes are Raman active and to which representation do they belong?
- e) Are any of the Raman active modes degenerate in energy?
- f) How many modes are both infrared and Raman active?
-
- a) NH_3 has $3n - 6 = 6$ normal modes.
- b) The requirement that a normal mode is infrared active is it must have x, y , or z as a basis. The IR active modes are of A_1 and E symmetry. All of the normal modes are IR active.
- c) There are 2 infrared active modes with one frequency (A_1) and 4 modes with a second frequency (E).
- d) The normal modes of a molecule are Raman active if the bases of the representation to which the normal mode belongs are the x^2, y^2, z^2, xy, yz , or xz functions. All of the normal modes are Raman active.
- e) There are 2 Raman active modes with one frequency (A_1) and 4 modes with a second frequency (E).
- f) All of the modes are both Raman and infrared active.

P28.20) Benzene, C_6H_6 , belongs to the D_{6h} group. The character table for this group is shown in Appendix B. The reducible representation for the vibrational modes is

$$\Gamma_{\text{reducible}} = 2A_{1g} + A_{2g} + A_{2u} + 2B_{1u} + 2B_{2g} + 2B_{2u} + E_{1g} + 3E_{1u} + 4E_{2g} + 2E_{2u}$$

- a) How many vibrational modes does benzene have?
- b) How many of these modes are infrared active and to which representation do they belong?
- c) Which of the infrared active modes are degenerate in energy and what is the degeneracy for each?
- d) How many of these modes are Raman active and to which representation do they belong?
- e) Which of the Raman active modes are degenerate in energy and what is the degeneracy for each?
- f) Which of the infrared modes are also Raman active?

$$\Gamma_{red} = 2A_{1g} + A_{2g} + A_{2u} + 2B_{1u} + 2B_{2g} + 2B_{2u} + E_{1g} + 3E_{1u} + 4E_{2g} + 2E_{2u}$$

↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓

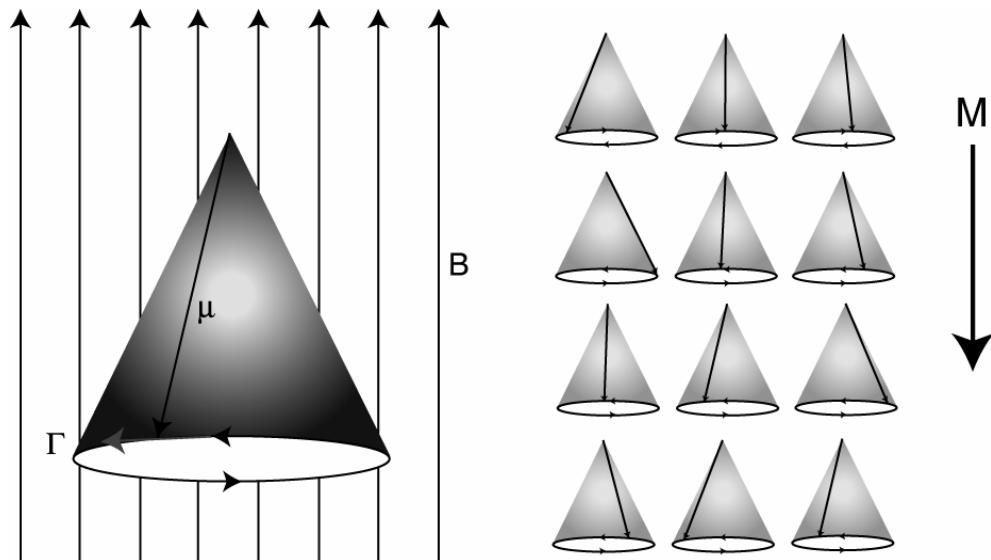
dimension	1	1	1	1	1	1	2	2	2	2
-----------	---	---	---	---	---	---	---	---	---	---

- a) Benzene has $3n - 6 = 30$ normal modes.
- b) The requirement that a normal mode is infrared active is it must have x, y , or z as a basis. The IR active modes must belong to the E_{1u} representation (of which there are three) and the A_{2u} representation. Thus there are $1(1) + 3(2) = 7$ infrared active modes.
- c) Each of the E_{1u} representations is degenerate, with a two-fold degeneracy. There are seven infrared active normal modes, but only four distinct vibrational frequencies.
- d) The Raman active modes are A_{1g}, E_{1g} , and E_{2g} . Thus there are
 $2(1) + 1(2) + 4(2) = 12$ Raman active modes.
- e) The E_{1g} and E_{2g} modes are both doubly degenerate. There are 7 distinct frequencies (4 E_{2g} , E_{1g} , and 2 A_{1g}).
- f) None of the IR modes are Raman active.

Chapter 29: Nuclear Magnetic Resonance Spectroscopy

Questions on Concepts

Q29.1) Redraw Figure 29.2 for β spins. What is the direction of precession for the spins and for the macroscopic magnetic moment?



The \mathbf{M} vector is anti-parallel to the field and does not precess. The direction of precession for the β spins is the same as for the α spins. This is the case because $\Gamma = \mu \times \mathbf{B}_0$ does not change sign between 0 and 180° .

Q29.2) Explain why two magnetic fields, a static field, and a radio-frequency field are needed to carry out NMR experiments. Why must the two field directions be perpendicular?

The static magnetic field causes the splitting in the energy of the nuclear spin states corresponding to different projections of the magnetic moment on the static field axis, which we designate as the z axis. The radio-frequency field is required to stimulate the transition between magnetic states.

Q29.3) Why do magnetic field inhomogeneities of only a few parts per million pose difficulties in NMR experiments?

The chemical shifts observed in NMR measurements are on the order of several parts per million. Therefore, if the magnetic field suffers from inhomogeneities of a few parts per million, the changes in the Larmor frequency that result from the field inhomogeneities are similar to those arising from a chemical shift.

Q29.4) Why is it useful to define the chemical shift relative to a reference compound as follows?

$$\delta = 10^6 \frac{(\nu - \nu_{ref})}{\nu_{ref}}$$

The nuclear spin splitting depends on the static magnetic field. Thus, measuring the same sample on two NMR spectrometers with different field strengths will result in different chemical shifts. This is corrected by including an internal standard (tetramethylsilane). Even if the absolute chemical shifts change from instrument to instrument, the chemical shift relative to the shift produced by the internal standard will remain constant from instrument to instrument.

Note the numbering jump.

In solution, the direct dipole-dipole coupling between spins is averaged to zero due to anisotropic tumbling of the molecule, resulting in a net zero induced magnetic field. In the solid state, the crystalline structure of the solid prevents the anisotropic movement, resulting in a net non-zero dipole induced magnetic field.

Q29.5) Order the molecules CH₃I, CH₃Br, CH₃Cl, and CH₃F in terms of increasing chemical shift for ¹H. Explain your answer.

Chemical shift increases as the electron withdrawing character of the substrate increases. Thus, the more electronegative the halogen, the greater the chemical shift for the methyl protons. Therefore, the ordering will be CH₃I < CH₃Br < CH₃Cl < CH₃F.

Q29.6) Why do neighboring groups lead to a net induced magnetic field at a given spin in a molecule in the solid state, but not for the same molecule in solution?

In liquids, the only coupling that determined the splitting is the scalar coupling. The scalar coupling is independent of the external magnetic field. Therefore, the splitting is independent of the external magnetic field.

Q29.7) Explain the difference in the mechanism that gives rise to through-space dipole-dipole coupling and through-bond coupling.

The mechanism of through-bond coupling involves transmission of nuclear coupling through bonding electrons. The nuclear and electronic spins are coupled; an α spin nucleus has a lower energy in the presence of a β spin electron rather than an α spin electron. This polarizes the chemical bond, forcing the α electron towards the neighboring nucleus, resulting in a β spin nucleus.

The dipole-dipole coupling arises due to the magnetic vector field that is produced by the induced dipoles formed when a nucleus experiences an external magnetic field. The field

lines from one nucleus will produce net forces on neighboring nuclei, and as one is perturbed, the other is correspondingly perturbed.

Q29.8) Why is the multiplet splitting for coupled spins independent of the static magnetic field?

The multiplet splitting is determined by the coupling constant, J_{12} , rather than by the static magnetic field. Therefore, it is independent of the static magnetic field.

Q29.9) Why can the signal loss resulting from spin dephasing caused by magnetic field inhomogeneities and chemical shift be recovered in the spin-echo experiment?

The signal decays as a function of time, given as e^{-t/T_2} , where t is the time and T_2 is the spin-spin relaxation time. Thus, by knowing t and T_2 and the signal strength at t , the original signal strength can be calculated. In the spin-echo method, the echo that occurs at a known time, t , can be measured to determine T_2 , which can then be used to calculate the original signal strength.

Q29.10) Why is the measurement time in NMR experiments reduced by using Fourier transform techniques?

By employing Fourier transform NMR, a number of resonance frequencies can be probed in a single measurement and deconvoluted into a single spectrum. Without Fourier transform capabilities, an individual measurement must be made for each resonance frequency.

Q29.11) Why does NMR lead to a higher contrast in the medical imaging of soft tissues than X-ray techniques?

The signal to noise ratio of scattering measurements (such as X-ray measurements) is generally very small, because the scattered intensity is generally very small in comparison to the incident radiation. NMR techniques have greater resolution because the properties measured do not suffer from interference from the incident radiation. These include properties such as chemical shifts and relaxation times.

Problems

P29.1) For a fixed frequency of the radio frequency field, ^1H , ^{13}C , and ^{31}P will be in resonance at different values of the static magnetic field. Calculate the value of \mathbf{B}_0 for these nuclei to be in resonance if the radio frequency field has a frequency of 250 MHz.

The condition for resonance is

$$\hbar\nu = \gamma\hbar B_0; B_0 = \frac{\hbar\nu}{\gamma} = \frac{2\pi\nu}{\gamma}$$

Using the appropriate value of γ from Table 29.1, we carry out the calculation for ^1H :

$$B_0 = \frac{h\nu}{\gamma\hbar} = \frac{2\pi\nu}{\gamma} = \frac{2\pi \times 250 \times 10^6 \text{ s}^{-1}}{26.75 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}} = 5.87 \text{ T}$$

The values for ^{13}C and ^{31}P are 23.3 and 14.5 T, respectively.

P29.2) Calculate the spin energy eigenvalues for the wave functions

$\psi_1 = \alpha(1)\alpha(2)$, $\psi_3 = \alpha(1)\beta(2)$, and $\psi_4 = \beta(1)\beta(2)$ [Equation (29.15)] for noninteracting spins.

$$\psi_1 = \alpha(1)\alpha(2)$$

$$\begin{aligned} H\psi_1 &= \left[-\gamma B_0 (1 - \sigma_1) \hat{I}_{z_1} - \gamma B_0 (1 - \sigma_2) \hat{I}_{z_2} \right] \psi_1 \\ &= -\gamma B_0 \left[(1 - \sigma_1) \hat{I}_{z_1} \alpha(1) \alpha(2) + (1 - \sigma_2) \hat{I}_{z_2} \alpha(1) \alpha(2) \right] \\ &= -\gamma B_0 \left[(1 - \sigma_1) \frac{\hbar}{2} \alpha(1) \alpha(2) + (1 - \sigma_2) \frac{\hbar}{2} \alpha(1) \alpha(2) \right] \\ &= -\gamma B_0 \frac{\hbar}{2} \left[(1 - \sigma_1) + (1 - \sigma_2) \right] \alpha(1) \alpha(2) \\ &= -\gamma B_0 \frac{\hbar}{2} [2 - \sigma_1 - \sigma_2] \psi_1 \end{aligned}$$

$$H\psi_1 = -\hbar\gamma B_0 \left[1 - \frac{\sigma_1 + \sigma_2}{2} \right] \psi_1$$

Thus, the eigenvalue is

$$E_1 = -\hbar\gamma B_0 \left[1 - \frac{\sigma_1 + \sigma_2}{2} \right]$$

$$\psi_3 = \alpha(1)\beta(2)$$

$$\begin{aligned} H\psi_3 &= \left[-\gamma B_0 (1 - \sigma_1) \hat{I}_{z_1} - \gamma B_0 (1 - \sigma_2) \hat{I}_{z_2} \right] \psi_3 \\ &= -\gamma B_0 \left[(1 - \sigma_1) \hat{I}_{z_1} \alpha(1) \beta(2) + \gamma B_0 (1 - \sigma_2) \hat{I}_{z_2} \alpha(1) \beta(2) \right] \\ &= -\gamma B_0 \left[(1 - \sigma_1) \frac{\hbar}{2} \alpha(1) \beta(2) + \gamma B_0 (1 - \sigma_2) \alpha(1) \left(-\frac{\hbar}{2} \right) \beta(2) \right] \\ &= -\gamma B_0 \frac{\hbar}{2} \left[(1 - \sigma_1) - (1 - \sigma_2) \right] \alpha(1) \beta(2) \\ &= -\gamma B_0 \frac{\hbar}{2} [-\sigma_1 + \sigma_2] \psi_3 \end{aligned}$$

$$H\psi_3 = \hbar\gamma B_0 \left[\frac{\sigma_1 - \sigma_2}{2} \right] \psi_3$$

Thus, the eigenvalue is

$$E_3 = \hbar\gamma B_0 \left[\frac{\sigma_1 - \sigma_2}{2} \right]$$

$$\psi_4 = \beta(1)\beta(2)$$

$$\begin{aligned} H\psi_4 &= \left[-\gamma B_0 (1 - \sigma_1) \hat{I}_{z_2} - \gamma B (1 - \sigma_2) \hat{I}_{z_2} \right] \psi_3 \\ &= -\gamma B_0 \left[(1 - \sigma_1) \hat{I}_{z_2} \beta(1) \beta(2) + (1 - \sigma_2) \hat{I}_{z_2} \beta(1) \beta(1) \right] \\ &= -\gamma B_0 \left[\left(1 - \sigma_2 \left(-\frac{\hbar}{2} \right) \beta(1) \beta(2) + (1 - \sigma_2) \beta(1) \left(-\frac{\hbar}{2} \right) \beta(2) \right) \right] \\ &= \gamma B_0 \frac{\hbar}{2} [(1 - \sigma_1) + (1 - \sigma_2)] \beta(1) \beta(2) \\ &= \gamma B_0 \frac{\hbar}{2} [2 - \sigma_1 - \sigma_2] \psi_4 \\ H\psi_4 &= \hbar\gamma B_0 \left[1 - \frac{\sigma_1 + \sigma_2}{2} \right] \psi_4 \end{aligned}$$

Thus the eigenvalue is

$$E_4 = \hbar\gamma B_0 \left[1 - \frac{\sigma_1 + \sigma_2}{2} \right]$$

P29.3) A 250 MHz ^1H spectrum of a compound shows two peaks. The frequency of one peak is 510 Hz higher than that of the reference compound (tetramethylsilane) and the second peak is at a frequency 280 Hz lower than that of the reference compound. What chemical shift should be assigned to these two peaks?

The chemical shift is negative if the frequency is higher than that of the reference compound, and positive if the frequency is lower.

$$\delta = \frac{\Delta\nu}{\nu_0} = -\frac{510 \text{ s}^{-1}}{250 \times 10^6 \text{ s}^{-1}} = -2.04 \text{ ppm}$$

$$\delta = \frac{\Delta\nu}{\nu_0} = \frac{280 \text{ s}^{-1}}{250 \times 10^6 \text{ s}^{-1}} = 1.12 \text{ ppm}$$

P29.4) Consider the first-order correction to the energy of interacting spins illustrated in Example Problem 29.3 for ψ_2 . Calculate the energy correction to the wave functions $\psi_1 = \alpha(1)\alpha(2)$, $\psi_2 = \beta(1)\alpha(2)$, and $\psi_4 = \beta(1)\beta(2)$. Show that your results are consistent with $\Delta E = m_1 m_2 \hbar J_{12}$ with m_1 and $m_2 = +1/2$ for α and $-1/2$ for β .

Chapter 29/Nuclear Magnetic Resonance Spectroscopy

$$\psi_1 = \alpha(1) \alpha(2)$$

$$\begin{aligned}
\Delta E_1 &= \frac{4\pi^2}{h} J_{12} \int \int \alpha^*(1) \alpha^*(2) [\hat{I}_{x_1} \hat{I}_{x_2} + \hat{I}_{y_1} \hat{I}_{y_2} + \hat{I}_{z_1} \hat{I}_{z_2}] \alpha(1) \alpha(2) d_{\tau_1} d_{\tau_2} \\
&= \frac{4\pi^2}{h} J_{12} \left[\int \int \alpha^*(1) \alpha^*(2) \hat{I}_{x_1} \hat{I}_{x_2} \alpha(1) \alpha(2) d_{\tau_1} d_{\tau_2} + \int \int \alpha^*(1) \alpha^*(2) \hat{I}_{y_1} \hat{I}_{y_2} \alpha(1) \alpha(2) d_{\tau_1} d_{\tau_2} \right. \\
&\quad \left. + \int \int \alpha^*(1) \alpha^*(2) \hat{I}_{z_1} \hat{I}_{z_2} \alpha(1) \alpha(2) d_{\tau_1} d_{\tau_2} \right] \\
&= \frac{4\pi^2}{h} J_{12} \left[\int \int \alpha^*(1) \alpha^*(2) \left(\frac{\hbar}{2}\right)^2 \beta(1) \beta(2) d_{\tau_1} d_{\tau_2} + \int \int \alpha^*(1) \alpha^*(2) \left(\frac{E^h}{2}\right)^2 \beta(1) \beta(2) d_{\tau_1} d_{\tau_2} \right. \\
&\quad \left. + \int \int \alpha^*(1) \alpha^*(2) \left(\frac{\hbar}{2}\right)^2 \alpha(2) \alpha(2) d_{\tau_1} d_{\tau_2} \right] \\
&= J_{12} \frac{4\pi^2}{h} \left[\frac{\hbar^2}{4} \int \alpha^*(1) \beta(1) d_{\tau_1} \int \alpha^*(2) \beta(2) d_{\tau_2} + \left(\frac{-\hbar^2}{2}\right) \int \alpha^*(1) \beta(1) d_{\tau_1} \int \alpha^*(2) \beta(2) d_{\tau_2} \right. \\
&\quad \left. + \frac{\hbar^2}{4} \int \alpha^*(1) \beta(1) d_{\tau_1} \int \alpha^*(2) \beta(2) d_{\tau_2} \right] \\
&= J_{12} \frac{4\pi^2}{h} \left[\frac{\hbar^2}{4} \right] \\
&= J_{12} \frac{4\pi^2}{h} \times \frac{\hbar^2}{16\pi^2}
\end{aligned}$$

$$\Delta E_1 = \frac{h}{4} J_{12} \Rightarrow \Delta E_1 = m_1 m_2 h J_{12} = \frac{1}{2} \times \frac{1}{2} h J_{12} = \frac{h J_{12}}{4}$$

$$\begin{aligned}
 \psi_2 &= \beta(1) \alpha(2) \\
 \Delta E_2 &= \frac{4\pi^2}{2} J_{12} \iiint \beta^*(1) \alpha^*(2) [\hat{I}_{x_1} \hat{I}_{x_2} + \hat{I}_{y_1} \hat{I}_{y_2} + \hat{I}_{z_1} \hat{I}_{z_2}] \beta(1) \alpha(1) d_{\tau_1} d_{\tau_2} \\
 &= \frac{4\pi^2}{h} J_{12} \left[\iint \beta^*(1) \alpha^*(2) \hat{I}_{x_1} \hat{I}_{x_2} \beta(1) \alpha(2) d_{\tau_1} d_{\tau_2} + \iint \beta^*(1) \alpha^*(2) \hat{I}_{y_1} \hat{I}_{y_2} \beta(1) \alpha(2) d_{\tau_1} d_{\tau_2} \right. \\
 &\quad + \iint \alpha^*(1) \alpha^*(2) \hat{I}_{y_1} \hat{I}_{y_2} \alpha(1) \alpha(2) d_{\tau_1} d_{\tau_2} \\
 &\quad \left. + \iint \beta^*(1) \alpha^*(2) \hat{I}_{z_1} \hat{I}_{z_2} \beta(1) \alpha(2) d_{\tau_1} d_{\tau_2} \right] \\
 &= h J_{12} \left[\iint \beta^*(1) \alpha^*(2) \left(\frac{\hbar}{2}\right)^2 \alpha(1) \beta(2) d_{\tau_1} d_{\tau_2} + \iint \beta^*(1) \alpha^*(2) \left(-\frac{i\hbar}{2} \cdot \frac{i\hbar}{2}\right) \alpha(1) \beta(2) d_{\tau_1} d_{\tau_2} \right. \\
 &\quad \left. + \iint \beta^*(1) \alpha^*(2) \left(-\frac{\hbar}{2} \cdot \frac{\hbar}{2}\right)^2 \beta(1) \alpha(2) d_{\tau_1} d_{\tau_2} \right] \\
 &= \frac{4\pi^2}{h} J_{12} \left[\frac{\hbar^2}{4} \int \beta^*(1) \alpha(1) d_{\tau_1} \int \alpha^*(2) \beta(2) d_{\tau_2} + \left(\frac{\hbar^2}{2}\right) \int \beta^*(1) \alpha(1) d_{\tau_1} \int \alpha^*(1) \beta(1) d_{\tau_2} \right. \\
 &\quad \left. - \frac{\hbar^2}{4} \int \beta^*(1) \beta(1) d_{\tau_1} \int \alpha^*(2) \alpha(2) d_{\tau_2} \right] \\
 &= \frac{4\pi^2}{h} J_{12} \left(-\frac{\hbar^2}{4} \right) \\
 &= -\frac{\pi^2 J_{12}}{h} \times \frac{h^2}{4\pi^2} \\
 \Delta E_2 &= -\frac{hJ_{12}}{4} \Rightarrow \Delta E_2 = m_1 m_2 h J_{12} = -\frac{1}{2} \times \frac{1}{2} h \cdot J_{12} = -\frac{hJ_{12}}{4}
 \end{aligned}$$

$$\psi_4 = \beta(1)\beta(2)$$

$$\begin{aligned}
 \Delta E_4 &= J_{12} \frac{4\pi^2}{h} \left[\int \int \beta^*(1) \beta^*(2) \left[\hat{I}_{x_1} \hat{I}_{x_2} + \hat{I}_{y_1} \hat{I}_{y_2} + \hat{I}_{z_1} \hat{I}_{z_2} \right] \beta(1) \beta(2) d_{\tau_1} d_{\tau_2} \right] \\
 &= \frac{4\pi^2}{h} J_{12} \left[\int \int \beta^*(1) \beta^*(2) \hat{I}_{x_1} \hat{I}_{x_2} \beta(1) \beta(2) d_{\tau_1} d_{\tau_2} + \int \int \beta^*(1) \beta^*(2) \hat{I}_{y_1} \hat{I}_{y_2} \beta(1) \beta(2) d_{\tau_1} d_{\tau_2} \right. \\
 &\quad \left. + \int \int \beta^*(1) \beta^*(2) \hat{I}_{z_1} \hat{I}_{z_2} \beta(1) \beta(2) d_{\tau_1} d_{\tau_2} \right] \\
 &= \frac{4\pi^2}{h} J_{12} \left[\int \int \beta^*(1) \beta^*(2) \left(\frac{\hbar}{2} \right)^2 \alpha(1) \alpha(2) d_{\tau_1} d_{\tau_2} + \int \int \beta^*(1) \beta^*(2) \left(-\frac{i\hbar}{2} \right)^2 \alpha(1) \alpha(2) d_{\tau_1} d_{\tau_2} \right. \\
 &\quad \left. + \int \int \beta^*(1) \beta^*(2) \left(-\frac{\hbar}{2} \right)^4 \beta(1) \beta(2) d_{\tau_1} d_{\tau_2} \right] \\
 &= \frac{4\pi^2}{4} J_{12} \left[\frac{\hbar^2}{4} \int \beta^*(1) \alpha(1) d_{\tau_1} \int \beta^*(2) \alpha(2) d_{\tau_2} + \frac{\hbar^2}{4} \int \beta^*(1) \alpha(1) d_{\tau_1} \int \beta^*(1) \alpha(1) d_{\tau_2} \right. \\
 &\quad \left. + \frac{\hbar^2}{4} \int \beta^*(1) \beta(1) d_{\tau_1} \int \beta^*(2) \beta(2) d_{\tau_2} \right] \\
 &= \frac{4\pi^2}{4} J_{12} \frac{\hbar^2}{4} \\
 &= \frac{4\pi^2}{4} J_{12} \frac{\hbar^2}{16\pi^2} \\
 \Delta E_4 &= -\frac{hJ_{12}}{4} \Rightarrow \Delta E_4 = m_1 m_2 h J_{12} = \frac{1}{2} \times \frac{1}{2} h J_{12} = \frac{h J_{12}}{4}
 \end{aligned}$$

P29.5) Using your results from the previous problems, show that there are four possible transitions between the energy levels of two interacting spins and that the frequencies are given by

$$\begin{aligned}
 \nu_{12} &= \frac{\gamma B (1 - \sigma_1)}{2\pi} - \frac{J_{12}}{2} \\
 \nu_{34} &= \frac{\gamma B (1 - \sigma_1)}{2\pi} + \frac{J_{12}}{2} \\
 \nu_{13} &= \frac{\gamma B (1 - \sigma_2)}{2\pi} - \frac{J_{12}}{2} \\
 \nu_{24} &= \frac{\gamma B (1 - \sigma_2)}{2\pi} + \frac{J_{12}}{2}
 \end{aligned}$$

The relevant energies, with corrections, are

$$E_1 = -\hbar\gamma B_0 \left(1 - \frac{\sigma_1 + \sigma_2}{2}\right) + \frac{h}{4} J_{12} \quad E_2 = -\frac{1}{2} \hbar\gamma B_0 (\sigma_1 - \sigma_2) - \frac{h}{4} J_{12}$$

$$E_3 = \frac{1}{2} \hbar\gamma B_0 (\sigma_1 - \sigma_2) - \frac{h}{4} J_{12} \quad E_4 = \hbar\gamma B_0 \left(1 - \frac{\sigma_1 + \sigma_2}{2}\right) + \frac{h}{4} J_{12}$$

and the frequencies are defined as

$$\begin{aligned}
 \nu_{ab} &= \frac{E_b - E_a}{h} \\
 \nu_{12} &= \frac{1}{h} \left[-\frac{1}{2} \hbar \gamma B_0 (\sigma_1 - \sigma_2) - \frac{\hbar}{4} J_{12} - \left(-\hbar \gamma B_0 \left(1 - \frac{\sigma_1 - \sigma_2}{2} \right) + \frac{\hbar}{4} J_{12} \right) \right] \\
 &= \frac{1}{h} \left[-\hbar \gamma B_0 \left(\frac{\sigma_1}{2} - \frac{\sigma_2}{2} - 1 + \frac{\sigma_1}{2} + \frac{\sigma_2}{2} \right) - \frac{\hbar}{2} J_{12} \right] \\
 &= \frac{1}{h} \left[-\frac{\hbar \gamma B_0}{2\pi} (-1 + \sigma_1) - \frac{\hbar}{2} J_{12} \right] \\
 \nu_{12} &= \frac{\gamma B_0}{2\pi} (1 - \sigma_1) - \frac{J_{12}}{2} \\
 \nu_{34} &= \frac{1}{h} \left[\hbar \gamma B_0 \left(1 - \frac{\sigma_1 + \sigma_2}{2} \right) + \frac{\hbar}{4} J_{12} - \frac{1}{2} \hbar \gamma B_0 (\sigma_1 - \sigma_2) + \frac{\hbar}{4} J_{12} \right] \\
 &= \frac{1}{h} \left[\hbar \gamma B_0 \left(1 - \frac{\sigma_1}{2} - \frac{\sigma_2}{2} - \frac{\sigma_1}{2} + \frac{\sigma_2}{2} \right) + \frac{\hbar}{2} J_{12} \right] \\
 &= \frac{1}{h} \left[-\frac{\hbar \gamma B_0}{2\pi} (1 - \sigma_1) + \frac{\hbar}{2} J_{12} \right] \\
 \nu_{34} &= \frac{\gamma B_0}{2\pi} (1 - \sigma_1) + \frac{J_{12}}{2} \\
 \nu_{13} &= \frac{1}{h} \left[\frac{1}{2} \hbar \gamma B_0 (\sigma_1 - \sigma_2) - \frac{\hbar}{4} J_{12} - \left(-\hbar \gamma B_0 \left(1 - \frac{\sigma_1 + \sigma_2}{2} \right) + \frac{\hbar}{4} J_{12} \right) \right] \\
 &= \frac{1}{h} \left[\hbar \gamma B_0 \left(\frac{\sigma_1}{2} - \frac{\sigma_2}{2} + 1 - \frac{\sigma_1}{2} - \frac{\sigma_2}{2} \right) - \frac{\hbar}{2} J_{12} \right] \\
 &= \frac{1}{h} \left[\frac{\hbar \gamma B_0}{2\pi} (1 - \sigma_2) - \frac{\hbar}{2} J_{12} \right] \\
 \nu_{13} &= \frac{\gamma B_0}{2\pi} (1 - \sigma_2) - \frac{J_{12}}{2} \\
 \nu_{24} &= \frac{1}{h} \left[\hbar \gamma B_0 \left(1 - \frac{\sigma_1 + \sigma_2}{2} \right) + \frac{\hbar}{4} J_{12} - \left(-\frac{1}{2} \hbar \gamma B_0 (\sigma_1 - \sigma_2) - \frac{\hbar}{4} J_{12} \right) \right] \\
 &= \frac{1}{h} \left[\hbar \gamma B_0 \left(1 - \frac{\sigma_1}{2} - \frac{\sigma_2}{2} + \frac{\sigma_1}{2} - \frac{\sigma_2}{2} \right) + \frac{\hbar J_{12}}{2} \right] \\
 &= \frac{1}{h} \left[-\frac{\hbar \gamma B_0}{2\pi} (1 - \sigma_1) + \frac{\hbar J_{12}}{2} \right] \\
 \nu_{24} &= \frac{\gamma B_0}{2\pi} (1 - \sigma_2) + \frac{J_{12}}{2}
 \end{aligned}$$

P29.6) The nuclear spin operators can be represented as 2×2 matrices in the form and α and β can be represented as column vectors in the form $\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. Given

that $\hat{I}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, $\hat{I}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$, $\hat{I}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$, and $\hat{I}^2 = \left(\frac{\hbar}{2}\right)^2 \begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix}$, show that

$$\hat{I}^2 \alpha = \frac{1}{2} \left(\frac{1}{2} + 1 \right) \hbar^2 \alpha, \quad \hat{I}_z \alpha = +\frac{1}{2} \hbar \alpha, \quad \hat{I}^2 \beta = \frac{1}{2} \left(\frac{1}{2} + 1 \right) \hbar^2 \beta, \quad \text{and} \quad \hat{I}_z \beta = -\frac{1}{2} \hbar \beta.$$

$$\hat{I}^2 \alpha = \left(\frac{\hbar}{2}\right)^2 \begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \left(\frac{\hbar}{2}\right)^2 \begin{pmatrix} 3+0 \\ 0+3 \end{pmatrix} = \frac{3\hbar^2}{4} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$= \frac{3\hbar^2}{4} \alpha = \left(\frac{1}{4} + \frac{1}{2}\right) \hbar^2 \alpha = \frac{1}{2} \left(\frac{1}{2} + 1\right) \hbar^2 \alpha$$

$$\hat{I}_z \alpha = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1+0 \\ 0+0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{2} \hbar \alpha$$

$$\hat{I}^2 \beta = \left(\frac{\hbar^2}{2}\right)^2 \begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \left(\frac{\hbar^2}{2}\right)^2 \begin{pmatrix} 0+0 \\ 0+3 \end{pmatrix} = \frac{3\hbar^2}{4} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$= \frac{3\hbar^2}{4} \beta = \left(\frac{1}{4} + \frac{1}{2}\right) \hbar^2 \beta = \frac{1}{2} \left(\frac{1}{2} + 1\right) \hbar^2 \beta$$

$$\hat{I}_z \beta = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0+0 \\ 0-1 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0 \\ -1 \end{pmatrix} = -\frac{\hbar}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{1}{2} \hbar \beta$$

P29.7) Using the matrix representation of the operators and spin eigenfunctions of Problem P29.6, show that the relationships listed in Equation (29.20) are obeyed.

$$\hat{I}_x \alpha = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0+0 \\ 1+0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2} \beta$$

$$\hat{I}_x \beta = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0+1 \\ 0+0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \alpha$$

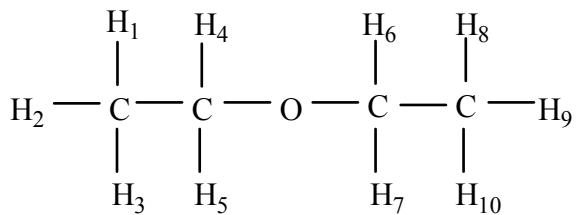
$$\hat{I}_y \alpha = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0+0 \\ i+0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0 \\ i \end{pmatrix} = \frac{i\hbar}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{i\hbar}{2} \beta$$

$$\hat{I}_y \beta = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0-i \\ 0+0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} -i \\ 0 \end{pmatrix} = \frac{-i\hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{-i\hbar}{2} \alpha$$

$$\hat{I}_z \alpha = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1+0 \\ 0+0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{2} \hbar \alpha$$

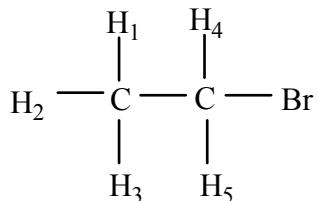
$$\hat{I}_z \beta = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0+0 \\ 0-1 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0 \\ -1 \end{pmatrix} = -\frac{\hbar}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{1}{2} \hbar \beta$$

P29.8) Predict the number of chemically shifted ^1H peaks and the multiplet splitting of each peak that you would observe for diethyl ether. Justify your answer.



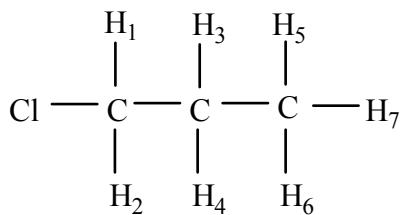
There are two sets of equivalent protons. Set A consists of H_1 , H_2 , H_3 , H_8 , H_9 , and H_{10} and has 2 neighboring protons, yielding a multiplicity of 3. Set B consists of H_4 , H_5 , H_6 , and H_7 and has 3 neighboring protons, giving a multiplicity of 4.

P29.9) Predict the number of chemically shifted ^1H peaks and the multiplet splitting of each peak that you would observe for bromoethane. Justify your answer.



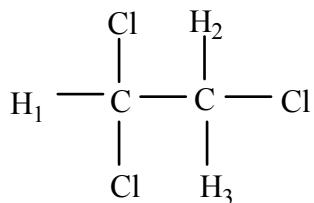
There are two equivalent sets of protons. Set A consists of H_1 , H_2 , H_3 and has 2 neighboring protons, giving a multiplicity of 3. Set B consists of H_4 , H_5 , and has 3 neighboring protons, giving a multiplicity of 4.

P29.10) Predict the number of chemically shifted ^1H peaks and the multiplet splitting of each peak that you would observe for 1-chloropropane. Justify your answer.



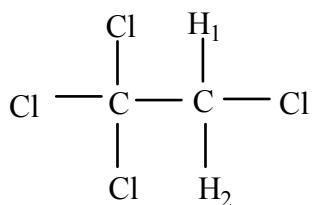
There are three sets of equivalent protons. Set A consists of H_1 and H_2 and has 2 neighboring protons, yielding a multiplicity of 3. Set B consists of H_3 and H_4 and has 5 neighboring protons (2 and 3) giving a multiplicity of $3 \times 4 = 12$. Set C consists of H_5 , H_6 , H_7 and has 2 neighboring protons, giving a multiplicity of 3.

P29.11) Predict the number of chemically shifted ^1H peaks and the multiplet splitting of each peak that you would observe for 1,1,2-trichloroethane. Justify your answer.



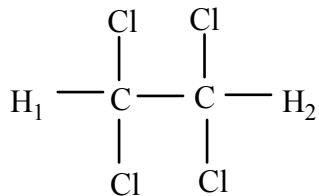
There are two sets of equivalent protons. Set A consists of H_1 and has 2 neighboring protons, giving a multiplicity of 3. Set B consists of H_2 and H_3 and has 1 neighboring proton, giving a multiplicity of 2.

P29.12) Predict the number of chemically shifted ^1H peaks and the multiplet splitting of each peak that you would observe for 1,1,1,2-tetrachloroethane. Justify your answer.



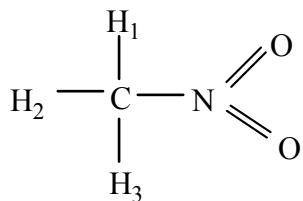
There is only one set of equivalent protons. They are H_1 and H_2 . There are no neighboring protons, so the multiplicity is 1.

P29.13) Predict the number of chemically shifted ^1H peaks and the multiplet splitting of each peak that you would observe for 1,1,2,2-tetrachloroethane. Justify your answer.



There is only one set of equivalent protons. They are H_1 and H_2 . Each proton has one neighboring proton, yielding a multiplicity of 2.

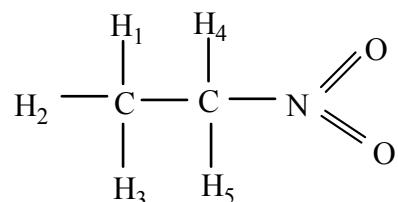
P29.14) Predict the number of chemically shifted ^1H peaks and the multiplet splitting of each peak that you would observe for nitromethane. Justify your answer.



Chapter 29/Nuclear Magnetic Resonance Spectroscopy

There is only one set of equivalent protons (H_1, H_2, H_3). There are no neighboring protons, and so the multiplicity is 1.

P29.15) Predict the number of chemically shifted 1H peaks and the multiplet splitting of each peak that you would observe for nitroethane. Justify your answer.



There are two sets of equivalent protons. Set A consists of H_1, H_2, H_3 and has 2 neighboring protons, giving a multiplicity of 3. Set B consists of H_4, H_5 and has 3 neighboring protons, giving a multiplicity of 4.

Chapter 30: Probability

Problem numbers in italics indicate that the solution is included in the *Student's Solutions Manual*.

Questions on Concepts

Q30.1) What is the difference between a configuration and a permutation?

A configuration is an unordered arrangement of objects. A permutation is a specific order of an arrangement of objects.

Q30.2) What are the elements of a probability model, and how do they differ for continuous and discrete variables?

A probability model consists of a sample space containing the possible values for a variable, and the corresponding probabilities that the variable will assume a value in the sample space. In the discrete case, the sample space consists of a set of specific values a variable can assume, whereas in the continuous case there is a range of values the variable can assume.

Q30.3) How does Figure 30.2 change if one is concerned with two versus three colored-ball configurations and permutations?

For the case where two balls are chosen from the 4-ball set, the number of possible configurations is:

$$C(4,2) = \frac{4!}{2!2!} = 6$$

Therefore in Figure 30.2, there will be six rows in the left column corresponding to the 6 possible configurations, with each configuration having two associated permutations.

Q30.4) What must the outcome of a binomial experiment be if $P_E = 1$?

If the probability of a successful trial is unity, the probability of observing j successful trials out of n total trials is unity. That is, every trial will be successful.

Q30.5) Why is normalization of a probability distribution important? What would one have to consider when working with a probability distribution that was not normalized?

A variable will always assume some value from the sample set; therefore, normalization of a probability distribution ensures that the sum of probabilities for the variable assuming values contained in the sample set is equal to unity. If the

probability distribution is not normalized, then each individual probability should be divided by the sum of all probabilities.

Q30.6) What properties of atomic and molecular systems could you imagine describing using probability distributions?

Electron orbital densities, distributions of bond lengths or molecular geometries, locations of particles in space, etc. In quantum mechanics, the square modulus of the wavefunction is simply a statement of a probability distribution.

Q30.7) When is the higher moment of a probability distribution more useful as a benchmark value as opposed to simply using the mean of the distribution?

When the spread or width of the distribution is of interest in addition to the average value. Particle velocity distributions serve as a good example of this issue. Consider motion in a single dimension. Since particles are just as likely to be moving in the positive and negative direction, the average velocity is equal to zero (see Problem P30.23); however, the width of the velocity distribution will be finite, as can be judged by considering higher moments of the distribution.

Problems

P30.1) Suppose that you draw a card from a standard deck of 52 cards. What is the probability of drawing:

- a) an ace of any suit?
- b) the ace of spades?
- c) How would your answers to parts (a) and (b) change if you were allowed to draw three times, replacing the card drawn back into the deck after each draw?

a) In a deck of 52 cards there are four aces, therefore:

$$P_E = \frac{E}{N} = \frac{4}{52}$$

b) There is only one card that corresponds to the event of interest, therefore:

$$P_E = \frac{E}{N} = \frac{1}{52}$$

c) By replacing the card, the probability for each drawing is independent, and the total probability is the sum of probabilities for each event. Therefore, the probability will be $3P_E$ with P_E as given above.

P30.2) You are dealt a hand consisting of 5 cards from a standard deck of 52 cards. Determine the probability of obtaining the following hands:

- a) a flush (five cards of the same suit)
- b) a king, queen, jack, ten, and ace of the same suit (a “royal flush”)
- a) The first card specifies the suit, and the remaining four cards must be of that suit in order to obtain a flush:

$$P = \left(\frac{52}{52} \right) \left(\frac{12}{51} \right) \left(\frac{11}{50} \right) \left(\frac{10}{49} \right) \left(\frac{9}{48} \right) \cong 0.002$$

- b) A royal flush requires that one receive a K, Q, J, 10, or A of any suit in the first card. If that card is obtained, only the other four cards of the suit will result in a royal flush:

$$P = \left(\frac{20}{52} \right) \left(\frac{4}{51} \right) \left(\frac{3}{50} \right) \left(\frac{2}{49} \right) \left(\frac{1}{48} \right) \cong 1.52 \times 10^{-6}$$

P30.3) A pair of standard dice are rolled. What is the probability of observing the following:

- a) The sum of the dice is equal to 7.
- b) The sum of the dice is equal to 9.
- c) The sum of the dice is less than or equal to 7.

a) We are interested in the outcome where the sum of two dice is equal to 7. If any side of a die has an equal probability of being observed, then the probability of any number appearing is 1/6.

$$\begin{aligned} P_{sum=7} &= [2 \times (P_1 \times P_6)] + [2 \times (P_2 \times P_5)] + [2 \times (P_3 \times P_4)] \\ &= 3 \left[\frac{2}{36} \right] = \frac{1}{6} \end{aligned}$$

b) Using the nomenclature developed above:

$$\begin{aligned} P_{sum=9} &= [2 \times (P_3 \times P_6)] + [2 \times (P_4 \times P_5)] \\ &= 2 \left[\frac{2}{36} \right] = \frac{1}{18} \end{aligned}$$

c) Now, one has to sum all the probabilities that correspond to the event of interest:

$$\begin{aligned} P_{sum<7} &= [(P_1 \times P_1)] + [2 \times (P_1 \times P_2)] + [2 \times (P_1 \times P_3)] + [2 \times (P_1 \times P_4)] + [2 \times (P_1 \times P_5)] + [2 \times (P_1 \times P_6)] \\ &\quad + [(P_2 \times P_2)] + [2 \times (P_2 \times P_3)] + [2 \times (P_2 \times P_4)] + [2 \times (P_2 \times P_5)] + [(P_3 \times P_3)] + [2 \times (P_3 \times P_4)] \\ &= 21 \left[\frac{1}{36} \right] = \frac{21}{36} \end{aligned}$$

P30.4) Answer Problem P30.3 assuming that “shaved” dice are used so that the number 6 appears twice as often as any other number.

a) If the number 6 is twice, the new probabilities (with renormalization) are:

$$P_1, P_2, P_3, P_4, P_5 = \frac{1}{7}$$

$$P_6 = \frac{2}{7}$$

Proceeding as described in Problem P30.3:

$$\begin{aligned} P_{sum=7} &= [2 \times (P_1 \times P_6)] + [2 \times (P_2 \times P_5)] + [2 \times (P_3 \times P_4)] \\ &= \left[2 \times \left(\frac{1}{7} \times \frac{2}{7} \right) \right] + 2 \left[2 \times \left(\frac{1}{7} \times \frac{1}{7} \right) \right] = \frac{8}{49} \end{aligned}$$

b)

$$\begin{aligned} P_{sum=9} &= [2 \times (P_3 \times P_6)] + [2 \times (P_4 \times P_5)] \\ &= \left[2 \times \left(\frac{1}{7} \times \frac{2}{7} \right) \right] + \left[2 \times \left(\frac{1}{7} \times \frac{1}{7} \right) \right] = \frac{6}{49} \end{aligned}$$

c)

$$\begin{aligned} P_{sum<7} &= [(P_1 \times P_1)] + [2 \times (P_1 \times P_2)] + [2 \times (P_1 \times P_3)] + [2 \times (P_1 \times P_4)] + [2 \times (P_1 \times P_5)] + [2 \times (P_1 \times P_6)] \\ &\quad + [(P_2 \times P_2)] + [2 \times (P_2 \times P_3)] + [2 \times (P_2 \times P_4)] + [2 \times (P_2 \times P_5)] + [(P_3 \times P_3)] + [2 \times (P_3 \times P_4)] \\ &= \left[19 \times \left(\frac{1}{7} \times \frac{1}{7} \right) \right] + \left[2 \times \left(\frac{1}{7} \times \frac{2}{7} \right) \right] = \frac{23}{49} \end{aligned}$$

P30.5) Evaluate the following:

- a) The number of permutations employing all objects in a six-object set
- b) The number of permutations employing 4 objects from a six-object set
- c) The number of permutations employing no objects from a six-object set
- d) $P(50,10)$

$$a) P(n, j) = P(6, 6) = \binom{n!}{(n-j)!} = \frac{6!}{0!} = 720$$

$$b) P(n, j) = P(6, 4) = \binom{n!}{(n-j)!} = \frac{6!}{2!} = 360$$

$$c) P(n, j) = P(6, 0) = \binom{n!}{(n-j)!} = \frac{6!}{6!} = 1$$

$$d) P(n, j) = P(50, 10) = \binom{n!}{(n-j)!} = \frac{50!}{40!} \approx 3.73 \times 10^{16}$$

P30.6) Determine the number of permutations of size 3 that can be made from the set $\{1,2,3,4,5,6\}$. Write down all of the permutations.

There are 6 objects in the set, and we are interested in the number of permutations that can be made using 3 objects from the set:

$$P(n, j) = P(6, 3) = \left(\frac{n!}{(n-j)!} \right) = \frac{6!}{3!} = 120$$

To write down all of the permutations using three objects, consider the following example using “1”, “2”, and “3” as three objects from the set. The six possible permutations are:

$$\{1, 2, 3\} = 123, 132, 213, 231, 312, 321$$

Similar permutations can be constructed using the following 19 subsets in addition to the $\{1,2,3\}$ subset discussed above:

$$\begin{aligned} & \{1, 2, 4\}, \{1, 2, 5\}, \{1, 2, 6\}, \{1, 3, 4\}, \{1, 3, 5\}, \{1, 3, 6\} \\ & \{1, 4, 5\}, \{1, 4, 6\}, \{1, 5, 6\}, \{2, 3, 4\}, \{2, 3, 5\}, \{2, 3, 6\} \\ & \{2, 4, 5\}, \{2, 4, 6\}, \{2, 5, 6\}, \{3, 4, 5\}, \{3, 4, 6\}, \{3, 5, 6\}, \{4, 5, 6\} \end{aligned}$$

P30.7) Determine the numerical values for the following:

- a) The number of configurations employing all objects in a six-object set
- b) The number of configurations employing 4 objects from a six-object set
- c) The number of configurations employing no objects from a six-object set
- d) $C(50, 10)$

$$a) C(n, j) = C(6, 6) = \left(\frac{n!}{j!(n-j)!} \right) = \frac{6!}{6!0!} = 1$$

$$b) C(n, j) = C(6, 4) = \left(\frac{n!}{j!(n-j)!} \right) = \frac{6!}{4!2!} = 15$$

$$c) C(n, j) = C(6, 0) = \left(\frac{n!}{j!(n-j)!} \right) = \frac{6!}{0!6!} = 1$$

$$d) P(n, j) = P(50, 10) = \left(\frac{n!}{j!(n-j)!} \right) = \frac{50!}{10!40!} \cong 1.03 \times 10^{10}$$

P30.8) Radio station call letters consist of four letters (for example, KUOW).

- a) How many different station call letters are possible using the 26 letters in the English alphabet?
- b) Stations west of the Mississippi River must use the letter K as the first call letter. Given this requirement, how many different station call letters are possible if repetition is allowed for any of the remaining letters?

c) How many different station call letters are possible if repetition is not allowed for any of the letters?

a) There are 26 choices for each letter; therefore, the number of possible radio call letter combinations is:

$$N_{total} = (26)^4 \cong 4.57 \times 10^5$$

b) In this case, the first letter is defined, but the remaining three letters can assume any of 26 values. Therefore, the total number of radio call letter combinations having K as the first letter is:

$$N_{total} = (26)^3 \cong 1.76 \times 10^4$$

c) The question is asking for the number of permutations possible using four objects from a set of 26 objects:

$$P(n, j) = P(26, 4) = \left(\frac{n!}{(n-j)!} \right) = \frac{26!}{22!} \cong 3.59 \times 10^5$$

P30.9) Four bases (A, C, T, and G) appear in DNA. Assume that the appearance of each base in a DNA sequence is random.

- a) What is the probability of observing the sequence AAGACATGCA?
- b) What is the probability of finding the sequence GGGGGAAAAA?
- c) How do your answers to parts (a) and (b) change if the probability of observing A is twice that of the probabilities used in parts (a) and (b) of this question when the preceding base is G?

a) There are four choices for each base, and the probability of observing any base is equal. Therefore, for a decamer the number of possible sequences is:

$$N_{total} = (4)^{10} \cong 1.05 \times 10^6$$

Since there is only one sequence that corresponds to the event of interest:

$$P_E = \frac{E}{N} \cong \frac{1}{1.05 \times 10^6} \cong 9.54 \times 10^{-7}$$

a) Identical to part (a).

b) In this case, the probability of observing a base at a given location is dependent on which base is present. If G appears in the sequence, then the probability of observing A is 1/2 while the probability of observing any other base is 1/6 (watch the normalization!). Therefore, the probability of observing the sequence in part (a) is:

$$P = \left(\frac{1}{4}\right)^3 \left(\frac{1}{2}\right) \left(\frac{1}{4}\right)^4 \left(\frac{1}{6}\right) \left(\frac{1}{4}\right) \cong 1.27 \times 10^{-6}$$

and the probability for the sequence in part (b) is:

$$P = \left(\frac{1}{4}\right)\left(\frac{1}{6}\right)^4\left(\frac{1}{2}\right)\left(\frac{1}{4}\right)^4 \cong 3.77 \times 10^{-7}$$

P30.10) In the neck of the flask depicted in the following figure, five white balls rest on five black balls. Suppose the balls are tipped back into the flask, shaken, and the flask is reinverted. What's the probability that the order depicted in the figure will be seen?

There are five ways out of 10 to get the black ball in the first location, four ways out of nine to get a black ball in the second location, and so forth:

$$P = \left(\frac{5}{10}\right)\left(\frac{4}{9}\right)\left(\frac{3}{8}\right)\left(\frac{2}{7}\right)\left(\frac{1}{6}\right) \cong 0.004$$

This problem can also be solved by realizing that the order shown corresponds to one possible configuration of five objects from a set of 10 total objects:

$$P = [C(10,5)]^{-1} = \left(\frac{10!}{5!5!}\right)^{-1} \cong 0.004$$

P30.11) The Washington State Lottery consists of drawing five balls numbered 1 to 43, and a single ball numbered 1 to 23 from a separate machine.

- a) What is the probability of hitting the jackpot in which the values for all six balls are correctly predicted?
- b) What is the probability of predicting just the first five balls correctly?
- c) What is the probability of predicting the first five balls in the exact order they are picked?

a) The total probability is the product of probabilities for the five-ball outcome and the one-ball outcome. The five-ball outcome is derived by considering the configurations possible using five objects from a set of 43 total objects:

$$P_{\text{fiveball}} = [C(43,5)]^{-1} = \left(\frac{43!}{5!38!}\right)^{-1} \cong 1.04 \times 10^{-6}$$

The one-ball outcome is associated with the configurations possible using a single object from a set of 23 objects:

$$P_{\text{oneball}} = [C(23,1)]^{-1} = \left(\frac{23!}{1!22!}\right)^{-1} \cong 4.35 \times 10^{-2}$$

The total probability is the product of the above probabilities:

$$P_{\text{total}} = P_{\text{fiveball}} \times P_{\text{oneball}} \cong 4.52 \times 10^{-8}$$

- b) The probability is that for the five-ball case determined above.

- c) This case corresponds to a specific permutation of all permutations possible using five objects from a set of 43 objects:

$$P = [P(43, 5)]^{-1} = \left(\frac{43!}{38!} \right)^{-1} \cong 8.66 \times 10^{-9}$$

P30.12) Fermions and bosons demonstrate different distribution statistics over a set of quantum states. However, in Chapter 31 we will encounter the Boltzmann distribution in which we essentially ignore the differentiation between fermions and bosons. This is appropriate only in the “dilute limit” where the number of available states far outnumbers the number of particles. To illustrate this convergence:

- a) Determine the number of arrangement permutations possible for 3 bosons and 10 states, and repeat this calculation for fermions.
 b) Repeat the calculations from part (a) for 3 particles, but now 100 states. What do you notice about the difference between the two results?

- a) For 3 bosons ($n = 3$) and 10 states ($x = 10$):

$$P_{BE} = \frac{(n+x-1)!}{n!(x-n)!} = \frac{12!}{3!9!} = 220$$

and if the particles are fermions:

$$P_{BE} = \frac{x!}{n!(x-n)!} = \frac{10!}{3!7!} = 45$$

- b) Repeating the above calculations for $n = 3, x = 100$:

$$P_{BE} = \frac{(n+x-1)!}{n!(x-n)!} = \frac{102!}{3!99!} \cong 1.72 \times 10^5$$

$$P_{BE} = \frac{x!}{n!(x-n)!} = \frac{100!}{3!97!} \cong 1.62 \times 10^5$$

Note that the number of permutations is converging for the two cases as the number of available states increases.

P30.13) Consider the 25 players on a professional baseball team. At any point, 9 players are on the field.

- a) How many 9-player batting orders are possible given that the order of batting is important?
 b) How many 9-player batting orders are possible given that the all-star designated hitter must be in the order batting in the fourth spot?
 c) How many 9-player fielding teams are possible, under the assumption that the location of the players on the field is not important?

a) $P(n, j) = P(25, 9) = \binom{n!}{(n-j)!} = \frac{25!}{16!} \approx 7.41 \times 10^{11}$

b) With one of the players hitting in the fourth spot, the number of permutations is reduced to those possible using 8 players from the remaining 24:

$$P(n, j) = P(24, 8) = \binom{n!}{(n-j)!} = \frac{24!}{16!} \approx 2.97 \times 10^{10}$$

c) If location is not important, then we are interested in the number of configurations possible using 9 players from the total of 25 players available:

$$C(n, j) = C(25, 9) = \binom{n!}{n!(n-j)!} = \frac{25!}{9!16!} \approx 2.04 \times 10^6$$

P30.14) Imagine an experiment in which you flip a coin four times. Furthermore, the coin is balanced fairly such that the probability of landing heads or tails is equivalent. After tossing the coin 10 times, what is the probability of observing

- a) no heads?
- b) two heads?
- c) five heads?
- d) eight heads?

a) The quantity of interest is the probability of observing a given number of successful trials (j) in a series of n trials in which the probability of observing a successful trial, P_E , is equal to 1/2:

$$P(j) = C(n, j)(P_E)^j (1 - P_E)^{n-j} = C(n, j) \left(\frac{1}{2}\right)^n$$

Substituting in for the specific case of $j = 0$ and $n = 10$ yields:

$$P(0) = C(10, 0) \left(\frac{1}{2}\right)^{10} \approx 9.77 \times 10^{-4}$$

b) In this case, $j = 2$ and $n = 10$:

$$P(2) = C(10, 2) \left(\frac{1}{2}\right)^{10} = \binom{10!}{2!8!} \left(\frac{1}{2}\right)^{10} \approx 0.044$$

c) In this case, $j = 5$ and $n = 10$:

$$P(5) = C(10, 5) \left(\frac{1}{2}\right)^{10} = \binom{10!}{5!5!} \left(\frac{1}{2}\right)^{10} \approx 0.246$$

d) In this case, $j = 8$ and $n = 10$:

$$P(8) = C(10, 8) \left(\frac{1}{2}\right)^{10} = \binom{10!}{8!2!} \left(\frac{1}{2}\right)^{10} \approx 0.044$$

P30.15) Imagine performing the coin-flip experiment of Problem P30.14, but instead of using a fair coin, a weighted coin is employed for which the probability of landing heads is twofold greater than landing tails. After tossing the coin 10 times, what is the probability of observing

- a) no heads?
- b) two heads?
- c) five heads?
- d) eight heads?

a) The quantity of interest is the probability of observing a given number of successful trials (j) in a series of n trials in which the probability of observing a successful trial, P_E , is equal to $2/3$:

$$P(j) = C(n, j)(P_E)^j(1 - P_E)^{n-j} = C(n, j)\left(\frac{2}{3}\right)^j\left(\frac{1}{3}\right)^{n-j}$$

Substituting in for the specific case of $j = 0$ and $n = 10$ yields:

$$P(0) = C(10, 0)\left(\frac{2}{3}\right)^0\left(\frac{1}{3}\right)^{10} \cong 1.69 \times 10^{-5}$$

b) In this case, $j = 2$ and $n = 10$:

$$P(2) = C(10, 2)\left(\frac{2}{3}\right)^2\left(\frac{1}{3}\right)^8 \cong 3.05 \times 10^{-3}$$

c) In this case, $j = 5$ and $n = 10$:

$$P(5) = C(10, 5)\left(\frac{2}{3}\right)^5\left(\frac{1}{3}\right)^5 \cong 0.137$$

d) In this case, $j = 8$ and $n = 10$:

$$P(8) = C(10, 8)\left(\frac{2}{3}\right)^8\left(\frac{1}{3}\right)^2 \cong 0.195$$

Notice that $P(8) \neq P(2)$, which differs from the case explored in Problem P30.14 where $P_E = 0.5$.

P30.16) In Chapter 35, we will model particle diffusion as a random walk in one dimension. In such processes, the probability of moving an individual step in the $+x$ or $-x$ direction is equal to zero. Imagine starting at $x = 0$ and performing a random walk in which 20 steps are taken.

- a) What is the farthest distance the particle can possibly move in the $+x$ direction? What is the probability of this occurring?
- b) What is the probability the particle will not move at all?
- c) What is the probability of the particle moving half the maximum distance in the x direction?
- d) Plot the probability of the particle moving a given distance versus distance. What does the probability distribution look like? Is the probability normalized?

- a) The problem of a random walk is just like the coin-toss example discussed in the text and which served as the basis for Problem P30.14. Specifically, we will define each step

in the $+x$ direction as a successful trial. Furthermore, the likelihood of taking a step in the positive or negative direction is equivalent such that $P_E = 0.5$. Therefore, the probability of being at $+20x$ after 20 steps is equal to the probability of 20 successful trials out of 20 total trials:

$$P(j) = C(n, j)(P_E)^j(1-P_E)^{n-j} = C(n, j)\left(\frac{1}{2}\right)^j\left(\frac{1}{2}\right)^{n-j} = C(n, j)\left(\frac{1}{2}\right)^n$$

$$P(20) = C(20, 0)\left(\frac{1}{2}\right)^{20} = \left(\frac{1}{2}\right)^{20} \approx 9.57 \times 10^{-7}$$

a) Proceeding as in part (a), but with $j = 10$:

$$P(10) = C(20, 10)\left(\frac{1}{2}\right)^{20} = \left(\frac{20!}{10!10!}\right)\left(\frac{1}{2}\right)^{20} \approx 0.176$$

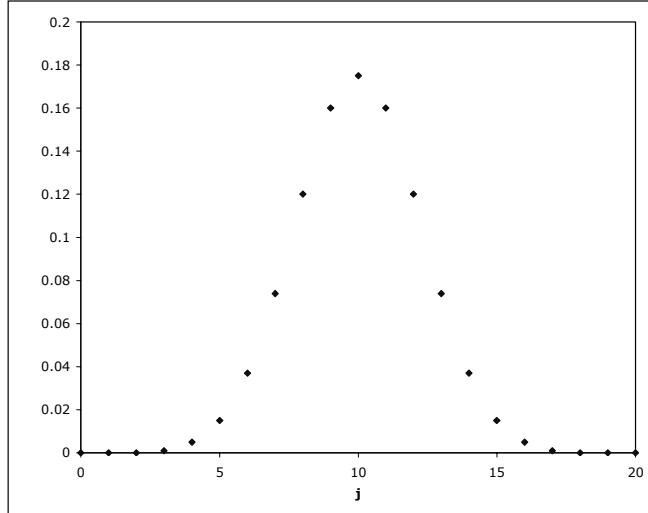
b) Proceeding as in part (a), but with $j = 15$:

$$P(15) = C(20, 15)\left(\frac{1}{2}\right)^{20} = \left(\frac{20!}{15!5!}\right)\left(\frac{1}{2}\right)^{20} \approx 0.015$$

c) Since a step in the $+x$ direction can occur with equal probability to a step in the $-x$ direction, the probability distribution will be symmetric about $x = 0$ corresponding to $j = 10$. Since the probability of taking a step in the $+x$ or $-x$ direction is equivalent, $P(11) = P(9)$, $P(12) = P(8)$, and so forth. Therefore, we only need to calculate the probabilities for $0 \leq j \leq 10$:

j	$P(j)$
0	0.000
1	0.000
2	0.000
3	0.001
4	0.005
5	0.015
6	0.037
7	0.074
8	0.120
9	0.160
10	0.175

A plot of the probability versus j is as follows:



P30.17) Simplify the following expressions:

$$a) \frac{n!}{(n-2)!}$$

$$b) \frac{n!}{\left[\left(\frac{n}{2}\right)!\right]^2}$$

$$a) \frac{n!}{(n-2)!} = \frac{(n)(n-1)(n-2)(n-3)\dots(2)(1)}{(n-2)!} = \frac{(n)(n-1)(n-2)!}{(n-2)!} = (n)(n-1)$$

$$b) \frac{n!}{\left[\left(\frac{n}{2}\right)!\right]^2} = \frac{(n)(n-1)(n-2)\left(\frac{n}{2}+1\right)\left(\frac{n}{2}\right)\dots(2)(1)}{\left[\left(\frac{n}{2}\right)!\right]^2} = \frac{(n)(n-1)(n-2)\left(\frac{n}{2}+1\right)\left(\frac{n}{2}\right)!}{\left[\left(\frac{n}{2}\right)!\right]^2}$$

$$= \frac{(n)(n-1)(n-2)\left(\frac{n}{2}+1\right)}{\left(\frac{n}{2}\right)!}$$

Note: n must be even.

P30.18) You are at a carnival and are considering playing the dart game described in Example Problem 30.12; however, you are confident of your dart-throwing skills such that the probability of hitting the center area of the target is three times greater than the probability determined by area. Assuming the confidence in your skills is warranted, is it a good idea to play?

With improved aim, f_i increases from 1/9 to 3/9. However, the probability is not normalized so that renormalization is required to evaluate the average return per toss ($n_{\$}$):

$$\langle n_{\$} \rangle = \frac{\sum_{i=1}^3 n_{i\$} f_i}{\sum_{i=1}^3 f_i} = \frac{(\$5)\left(\frac{3}{9}\right) + (\$2)\left(\frac{3}{9}\right) + (\$0)\left(\frac{5}{9}\right)}{\left(\frac{3}{9}\right) + \left(\frac{3}{9}\right) + \left(\frac{5}{9}\right)} = \$1.91$$

Since the average return is greater than the cost per toss (\$1.50), it is a good idea to play.

P30.19) Radioactive decay can be thought of as an exercise in probability theory. Imagine that you have a collection of radioactive nuclei at some initial time (N_0) and are interested in how many nuclei will still remain at a later time (N). For first-order radioactive decay, $N/N_0 = e^{-kt}$. In this expression, k is known as the decay constant and t is time.

- a) What is the variable of interest in describing the probability distribution?
- b) At what time will the probability of nuclei undergoing radioactive decay be 0.50

a) The variable (k) defines the width of the distribution of population versus time.

b)

$$\begin{aligned} \frac{N}{N_0} &= 0.5 = e^{-kt} \\ \ln(0.5) &= -kt \\ \frac{-\ln(0.5)}{t} &= \frac{\ln(2)}{t} = k \end{aligned}$$

P30.20) In Chapter 31, we will encounter the energy distribution $P(\varepsilon) = Ae^{-\varepsilon/kT}$, where $P(\varepsilon)$ is the probability of a molecule occupying a given energy state, ε is the energy of the state, k is a constant equal to $1.38 \times 10^{-23} \text{ J K}^{-1}$, and T is temperature. Imagine that there are three energy states at 0, 100, and 500 J mol^{-1} .

- a) Determine the normalization constant for this distribution.
 - b) What is the probability of occupying the highest energy state at 298 K?
 - c) What is the average energy at 298 K?
 - d) Which state makes the largest contribution to the average energy?
- a) Since the energies are given in units of J mol^{-1} , dividing by Avogadro's number will convert this energy to a per particle unit. Alternatively, Avogadro's number can be

included with Boltzmann's constant resulting in $k \times N_a = R$, where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. Using this relationship:

$$P_{500} = e^{-500 \text{ J mol}^{-1}/(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 0.817$$

$$P_{100} = e^{-100 \text{ J mol}^{-1}/(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 0.960$$

$$P_0 = e^{-0 \text{ J mol}^{-1}/(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 1$$

Using these probabilities, the normalization constant becomes:

$$A = \frac{1}{\sum_{i=1}^3 P_i} = \frac{1}{P_0 + P_{100} + P_{500}} \cong 0.360$$

b) With normalization, the normalized probabilities are given by the product of the probabilities determined in part (a) of this question and the normalization constant:

$$P_{500,norm} = A \times P_{500} = 0.360 \times 0.817 = 0.294$$

$$P_{100,norm} = A \times P_{100} = 0.360 \times 0.960 = 0.345$$

$$P_{0,norm} = A \times P_0 = 0.360$$

c) The average energy is given by:

$$\langle E \rangle = \sum_{i=1}^3 E_i P_{i,norm} = (0 \text{ J mol}^{-1})(0.360) + (100 \text{ J mol}^{-1})(0.345) + (500 \text{ J mol}^{-1})(0.294) = 182 \text{ J mol}^{-1}$$

d) Inspection of part (c) of this question illustrates that the highest-energy state makes the largest contribution to the average energy.

P30.21) Assume that the probability of occupying a given energy state is given by the relationship provided in Problem P30.20.

- a) Consider a collection of three total states with the first state beginning at $\varepsilon = 0$ and others at kT and $2kT$, respectively, relative to this first state. What is the normalization constant for the probability distribution?
- b) How would your answer change if there are five states with $\varepsilon = kT$, in addition to the single states at $\varepsilon = 0$ and $\varepsilon = 2kT$?
- c) Determine the probability of occupying the energy level $\varepsilon = kT$ for the cases in which one and five states exist at this energy.

a) $P_{total} = e^{-0/kT} + e^{-kT/kT} + e^{-2kT/kT} = 1 + e^{-1} + e^{-2} = 1.5$

$$C = \frac{1}{P_{total}} = 0.665$$

b) $P_{total} = e^{-0/kT} + 5e^{-kT/kT} + e^{-2kT/kT} = 1 + e^{-1} + e^{-2} = 2.97$

$$C = \frac{1}{P_{total}} = 0.336$$

c) case 1 : $P_{kT} = Ce^{-kT/kT} = (0.665)(e^{-1}) \cong 0.245$
 case 2 : $P_{kT} = C(5e^{-kT/kT}) = (0.336)(5e^{-1}) \cong 0.618$

P30.22) Consider the following probability distribution corresponding to a particle located between point $x = 0$ and $x = a$:

$$P(x)dx = C \sin^2\left[\frac{\pi x}{a}\right]dx$$

- a) Determine the normalization constant, C .
- b) Determine $\langle x \rangle$.
- c) Determine $\langle x^2 \rangle$.
- d) Determine the variance.

a)

$$1 = C \int_0^a \sin^2\left(\frac{\pi x}{a}\right) dx = C \left(\frac{a}{2}\right)$$

$$C = \frac{2}{a}$$

b)

$$\begin{aligned} \langle x \rangle &= \int_0^a (x) \left(\frac{2}{a} \sin^2\left(\frac{\pi x}{a}\right) \right) dx = \frac{2}{a} \int_0^a x \sin^2\left(\frac{\pi x}{a}\right) dx \\ &= \frac{2}{a} \left(\frac{a^2}{4} \right) = \frac{a}{2} \end{aligned}$$

c)

$$\begin{aligned} \langle x^2 \rangle &= \int_0^a (x^2) \left(\frac{2}{a} \sin^2\left(\frac{\pi x}{a}\right) \right) dx = \frac{2}{a} \int_0^a x^2 \sin^2\left(\frac{\pi x}{a}\right) dx \\ &= \left(\frac{2}{a} \right) \left[\left(\frac{a^3}{6} \right) - \left(\frac{a^3}{4\pi^2} \right) \right] = a^2 \left(\frac{1}{3} - \frac{1}{2\pi^2} \right) \end{aligned}$$

d)

$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2 = a^2 \left(\frac{1}{12} - \frac{1}{2\pi^2} \right)$$

P30.23) Consider the probability distribution for molecular velocities in one dimension (v_x) given by $P(v_x)dv_x = Ce^{-mv_x^2/2kT}dv_x$.

- Determine the normalization constant, C .
- Determine $\langle v_x \rangle$.
- Determine $\langle v_x^2 \rangle$.
- Determine the variance.

a) Since the velocity distribution is symmetric about $v_x = 0$:

$$1 = C \int_{-\infty}^{\infty} e^{-mv_x^2/2kT} dv_x = 2C \int_0^{\infty} e^{-mv_x^2/2kT} dv_x$$

The resulting integral is readily evaluated using the integral tables in the math supplement:

$$\begin{aligned} 1 &= 2C \int_0^{\infty} e^{-mv_x^2/2kT} dv_x = 2C \left(\frac{1}{2} \sqrt{\frac{2\pi kT}{m}} \right) \\ C &= \sqrt{\frac{m}{2\pi kT}} \end{aligned}$$

b)

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x \left(\sqrt{\frac{m}{2\pi kT}} e^{-mv_x^2/2kT} \right) dv_x = 0$$

The above result is determined by realizing that v_x is an odd function where the distribution is even. Therefore, integration of the product over all v_x space is equal to zero.

c) Using the integrals provided in the math appendix:

$$\begin{aligned} \langle v_x^2 \rangle &= \int_{-\infty}^{\infty} v_x^2 \left(\sqrt{\frac{m}{2\pi kT}} e^{-mv_x^2/2kT} \right) dv_x = \sqrt{\frac{m}{2\pi kT}} \int_{-\infty}^{\infty} v_x^2 e^{-mv_x^2/2kT} dv_x \\ &= \sqrt{\frac{m}{2\pi kT}} \frac{\sqrt{\pi}}{2 \left(\frac{m}{2kT} \right)^{3/2}} = \frac{kT}{m} \end{aligned}$$

d)
$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2 = \langle x^2 \rangle = \frac{kT}{m}$$

P30.24) In nonlinear optical switching devices based on dye-doped polymer systems, the spatial orientation of the dye molecules in the polymer is an important parameter. These devices are generally constructed by orienting dye molecules with a large dipole moment using an oriented electric field. Imagine placing a vector along the molecular

dipole moment such that the molecular orientation can be described by the orientation of this vector in space relative to the applied field (z direction) as illustrated in the text. For random molecular orientation about the z axis, the probability distribution describing molecular orientation along the z axis is given by:

$$P(\theta) = \frac{\sin \theta d\theta}{\int_0^\pi \sin \theta d\theta}$$

Orientation is quantified using moments of $\cos \theta$.

- a) Determine $\langle \cos \theta \rangle$ for this probability distribution.
- b) Determine $\langle \cos^2 \theta \rangle$ for this probability distribution.

a)

$$\langle \cos \theta \rangle = \frac{\int_0^\pi \cos \theta \sin \theta d\theta}{\int_0^\pi \sin \theta d\theta} = 0$$

b)

$$\langle \cos^2 \theta \rangle = \frac{\int_0^\pi \cos^2 \theta \sin \theta d\theta}{\int_0^\pi \sin \theta d\theta} = \frac{-\cos^3 \theta / 3 \Big|_0^\pi}{-\cos \theta \Big|_0^\pi} = \frac{1}{3}$$

Chapter 31: The Boltzmann Distribution

Problem numbers in italics indicate that the solution is included in the *Student's Solutions Manual*.

Questions on Concepts

Q31.1) What is the difference between a configuration and a microstate?

A configuration is a general arrangement of total energy available to the system.

A microstate is a specific arrangement of energy in which the energy content of specific oscillators is described.

Q31.2) How does one calculate the number of microstates associated with a given configuration?

The number of microstates associated with a given configuration is known as the weight of the configuration (W), and is given by:

$$W = \frac{N!}{\prod_n a_n!}$$

where N is the number of units or oscillators, and a_n is the number of units or oscillators with a certain amount of energy (the occupation number).

Q31.3) What is an occupation number? How is this number used to describe energy distributions?

The occupation number represents the number of units occupying a given energy level. The distribution of energy over a collection of units can be specified as the number of units occupying a given energy level.

Q31.4) Explain the significance of the Boltzmann distribution. What does this distribution describe?

The Boltzmann distribution is the energy distribution associated with the dominant configuration of energy. It provides a quantitative description of the probability of a given unit occupying a certain energy level. The Boltzmann distribution also represents the energy distribution associated with a chemical system at equilibrium.

Q31.5) What is degeneracy? Can you conceptually relate the expression for the partition function without degeneracy to that with degeneracy?

Degeneracy is the case where more than one state exists at a certain energy level. The expression for the partition function (q) including degeneracy is:

$$q = \sum_n g_n e^{-\beta \epsilon_n}$$

In this expression, g_n is the degeneracy of a given energy level, ϵ_n is the energy of the level, and the sum extends over all energy levels.

Q31.6) How is β related to temperature? What are the units of kT ?

β is inversely proportional to temperature, and equal to $(kT)^{-1}$. The units of the Boltzmann constant are J K^{-1} ; therefore, the product kT has units of joules, or energy.

Problems

P31.1)

- a) What is the possible number of microstates associated with tossing a coin N times and having it come up H times heads and T times tails?
 - b) For a series of 1000 tosses, what is the total number of microstates associated with 50% heads and 50% tails?
 - c) How less probable is the outcome that the coin will land 40% heads and 60% tails?
- a) In this case, the number of coin tosses is equal to the number of units (N), and each unit can exist in one of two states: heads (H) or tails (T). Since the number of microstates is equal to the weight (W):

$$W = \frac{N!}{H!T!}$$

- b) For this case, $N = 1000$, $H = 500$, and $T = 500$. Substituting into the above expression for W :

$$W = \frac{N!}{H!T!} = \frac{1000!}{(500!)^2}$$

The factorials that require evaluation are generally too large to determine on a calculator; therefore, evaluation of W is performed using Sterling's approximation:

$$\begin{aligned}\ln W &= \ln(1000!) - 2\ln(500!) \\ &= 1000\ln(1000) - 1000 - 2[500\ln(500) - 500] \\ &= 1000\ln(1000) - 1000\ln(500) = 1000\ln(2) \\ &= 693\end{aligned}$$

Therefore, $W = \exp(693)$.

- c) Proceeding as in part (b), but with $H = 400$ and $T = 600$:

$$\begin{aligned}\ln W &= \ln(1000!) - \ln(400!) - \ln(600!) \\ &= 1000 \ln(1000) - 1000 - 400 \ln(400) + 400 - 600 \ln(600) + 600 \\ &= 1000 \ln(1000) - 400 \ln(400) - 600 \ln(600) \\ &= 673\end{aligned}$$

Therefore, $W = \exp(673)$. Comparing the answers to parts (b) and (c), the $H = 500, T = 500$ outcome is approximately $\exp(20)$ or 4.85×10^8 times more likely than the $H = 400, T = 600$ outcome.

P31.2)

- a) Realizing that the most probable outcome from a series of N coin tosses is $N/2$ heads and $N/2$ tails, what is the expression for W_{max} corresponding to this outcome?

- b) Given your answer for part (a), derive the following relationship between the weight for an outcome other than the most probable and W_{max} :

$$\log\left(\frac{W}{W_{max}}\right) = -H \log\left(\frac{H}{N/2}\right) - T \log\left(\frac{T}{N/2}\right)$$

- c) We can define the deviation of a given outcome from the most probable outcome using a “deviation index,” $\alpha = \frac{H-T}{N}$. Show that the number of heads or tails can be expressed as $H = \frac{N}{2}(1+\alpha)$ and $T = \frac{N}{2}(1-\alpha)$.

- d) Finally, demonstrate that $\frac{W}{W_{max}} = e^{-N\alpha^2}$.

a)

$$W = \frac{N!}{H!T!} = \frac{N!}{\binom{N}{2}\binom{N}{2}} = \frac{N!}{\left[\binom{N}{2}\right]^2}$$

b)

$$\begin{aligned}
 \ln\left(\frac{W}{W_{\max}}\right) &= \ln W - \ln W_{\max} = \ln\left(\frac{N!}{H!T!}\right) - \ln\left(\frac{N!}{\left[\binom{N}{2}!\right]^2}\right) \\
 &= \ln(N!) - \ln(H!) - \ln(T!) - \ln(N!) + 2\ln\left(\binom{N}{2}!\right) \\
 &= -\ln(H!) - \ln(T!) + 2\ln\left(\binom{N}{2}!\right) \\
 &= -H\ln H + H - T\ln T + T + N\ln\left(\binom{N}{2}\right) - N \\
 &= -H\ln H - T\ln T + N\ln\left(\binom{N}{2}\right) \\
 &= -H\ln H - T\ln T + (H+T)\ln\left(\binom{N}{2}\right) \\
 &= -H\ln\left(\frac{H}{\binom{N}{2}}\right) - T\ln\left(\frac{T}{\binom{N}{2}}\right)
 \end{aligned}$$

c) Substituting the definition of part (a) into the expressions for H and T :

$$\begin{aligned}
 H &= \frac{N}{2}(1+\alpha) = \frac{N}{2}\left(1 + \frac{H-T}{N}\right) = \frac{N}{2} + \frac{H-T}{2} = \frac{H+T}{2} + \frac{H-T}{2} = H \\
 T &= \frac{N}{2}(1-\alpha) = \frac{N}{2}\left(1 - \frac{H-T}{N}\right) = \frac{N}{2} - \frac{H-T}{2} = \frac{H+T}{2} - \frac{H-T}{2} = T
 \end{aligned}$$

d) Substituting in the result of part (c) into the final equation of part (b):

$$\ln\left(\frac{W}{W_{\max}}\right) = -\frac{N}{2}(1+\alpha)\ln(1+\alpha) - \frac{N}{2}(1-\alpha)\ln(1-\alpha)$$

If $|\alpha| \ll 1$, then $\ln(1 \pm \alpha) = \pm \alpha$, therefore:

$$\begin{aligned}
 \ln\left(\frac{W}{W_{\max}}\right) &= -\frac{N}{2}(1+\alpha)\ln(1+\alpha) - \frac{N}{2}(1-\alpha)\ln(1-\alpha) \\
 &= -\frac{N}{2}(1+\alpha)(\alpha) - \frac{N}{2}(1-\alpha)(-\alpha) = -N\alpha^2 \\
 \frac{W}{W_{\max}} &= e^{-N\alpha^2}
 \end{aligned}$$

P31.3) Consider the case of 10 oscillators and eight quanta of energy. Determine the dominant configuration of energy for this system by identifying energy configurations and calculating the corresponding weights. What is the probability of observing the dominant configuration?

The configuration with the maximum weight is $a_3 = 1$, $a_2 = 1$, $a_1 = 3$, $a_0 = 5$, with the corresponding weight:

$$W = \frac{10!}{(1!)(1!)(3!)(5!)} = 5040$$

Writing down all possible configurations and summing the weight results in $W_{total} = 20170$. Therefore, the probability of observing the dominant configuration is:

$$P = \frac{W}{W_{total}} = \frac{5040}{20170} \cong 0.25$$

P31.4) Determine the weight associated with the following card hands:

- a) Having any five cards
- b) Having five cards of the same suit (known as a “flush”)
- a) The problem can be solved by recognizing that there are 52 total cards ($N = 52$), with 5 cards in the hand ($a_1 = 5$), and 47 out of the hand ($a_0 = 47$):

$$W = \frac{N!}{a_1!a_0!} = \frac{52!}{5!47!} \cong 2.60 \times 10^6$$

- b) For an individual suit, there are 13 total cards ($N = 13$), 5 of which must be in the hand ($a_1 = 5$) while the other 8 remain in the deck ($a_0 = 47$). Finally, there are four total suits:

$$W = 4 \left(\frac{N!}{a_1!a_0!} \right) = 4 \left(\frac{13!}{5!8!} \right) = 5148$$

P31.5) For a two-level system, the weight of a given energy distribution can be expressed in terms of the number of systems, N , and the number of systems occupying the excited state, n_1 . What is the expression for weight in terms of these quantities?

In a two-level system, $N = n_0 + n_1$ where n_0 is the number of particles in the lowest energy state, and n_1 is the number of particles in the excited energy state. Using this definition:

$$W = \frac{N!}{n_0! n_1!} = \frac{N!}{(N - n_1)! n_1!}$$

P31.6) The probability of occupying a given excited state, p_i , is given

$$\text{by } p_i = \frac{n_i}{N} = \frac{e^{-\beta \epsilon_i}}{q},$$

where n_i is the occupation number for the state of interest, N is the number of particles, and ϵ_i is the energy of the level of interest. Demonstrate that the preceding expression is independent of the definition of energy for the lowest state.

Let q be the partition function defined relative to the ground-state energy, ϵ_0 , and let Δ be the offset from this energy. The partition function with offset is given by:

$$\begin{aligned} q_\Delta &= \sum_n e^{-\beta \epsilon_n} = e^{-\beta(\epsilon_0 + \Delta)} + e^{-\beta(\epsilon_1 + \Delta)} + e^{-\beta(\epsilon_2 + \Delta)} + \dots \\ &= e^{-\beta \Delta} (e^{-\beta \epsilon_0} + e^{-\beta \epsilon_1} + e^{-\beta \epsilon_2} + \dots) \\ &= e^{-\beta \Delta} (q) \end{aligned}$$

The probability of occupying state “ i ” is given by:

$$p_{i,\Delta} = \frac{e^{-\beta(\epsilon_i + \Delta)}}{q_\Delta} = \frac{e^{-\beta \Delta} e^{-\beta \epsilon_i}}{e^{-\beta \Delta} q} = \frac{e^{-\beta \epsilon_i}}{q} = p_i$$

P31.7) Barometric pressure can be understood using the Boltzmann distribution. The potential energy associated with being a given height above the Earth’s surface is mgh , where m is the mass of the particle of interest, g is the acceleration due to gravity, and h is height. Using this definition of the potential energy, derive the following expression for pressure:

$$P = P_o e^{-mgh/kT}$$

Assuming that the temperature remains at 298 K, what would you expect the relative pressures of N₂ and O₂ to be at the tropopause, the boundary between the troposphere and stratosphere roughly 11 km above the Earth’s surface? At the Earth’s surface, the composition of air is roughly 78% N₂, 21% O₂, and the remaining 1% is other gases.

At the Earth’s surface, $h = 0$ meters and the total pressure is 1 atm. Using the mole fractions of N₂ and O₂, the partial pressures at the Earth’s surface are 0.78

and 0.21 atm, respectively. Given this information, the pressure of N₂ at 11 km is given by:

$$P_{11\text{ km}} = P_{0\text{ km}} e^{-mgh/kT} = (0.78 \text{ atm}) e^{-\frac{(0.028 \text{ kg mol}^{-1} \times N_A^{-1})(9.8 \text{ m s}^{-1})(1.1 \times 10^4 \text{ m})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}} = 0.230$$

Performing the identical calculation for O₂ yields:

$$P_{11\text{ km}} = P_{0\text{ km}} e^{-mgh/kT} = (0.21 \text{ atm}) e^{-\frac{(0.032 \text{ kg mol}^{-1} \times N_A^{-1})(9.8 \text{ m s}^{-1})(1.1 \times 10^4 \text{ m})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}} = 0.052$$

P31.8) Consider the following energy-level diagrams:

a) At what temperature will the probability of occupying the second energy level be 0.15 for the states depicted in part (a) of the figure?

b) Perform the corresponding calculation for the states depicted in part (b) of the figure. Before beginning the calculation, do you expect the temperature to be higher or lower than that determined in part (a) of this problem? Why?

- a) According to the energy-level diagram, there is one state at $\varepsilon = 0$ and one state at $\varepsilon = 300 \text{ cm}^{-1}$. Therefore:

$$\begin{aligned} 0.15 &= p_1 = \frac{e^{-\beta\varepsilon_1}}{q} = \frac{e^{-\beta(300 \text{ cm}^{-1})}}{1 + e^{-\beta(300 \text{ cm}^{-1})}} \\ 0.15 + 0.15(e^{-\beta(300 \text{ cm}^{-1})}) &= e^{-\beta(300 \text{ cm}^{-1})} \\ 0.15 &= 0.85(e^{-\beta(300 \text{ cm}^{-1})}) \\ 0.176 &= e^{-\beta(300 \text{ cm}^{-1})} \\ 1.74 &= \beta(300 \text{ cm}^{-1}) = \left(\frac{1}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(T)} \right)(300 \text{ cm}^{-1}) \\ T &= 248 \text{ K} \end{aligned}$$

- b) According to the energy-level diagram, there is one state at $\varepsilon = 0$ and two states at $\varepsilon = 300 \text{ cm}^{-1}$. Therefore:

$$0.15 = p_1 = \frac{2e^{-\beta\epsilon_1}}{q} = \frac{2e^{-\beta(300 \text{ cm}^{-1})}}{1+2e^{-\beta(300 \text{ cm}^{-1})}}$$

$$0.15 + 0.30(e^{-\beta(300 \text{ cm}^{-1})}) = 2e^{-\beta(300 \text{ cm}^{-1})}$$

$$0.15 = 1.70(e^{-\beta(300 \text{ cm}^{-1})})$$

$$0.088 = e^{-\beta(300 \text{ cm}^{-1})}$$

$$2.43 = \beta(300 \text{ cm}^{-1}) = \left(\frac{1}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(T)} \right) (300 \text{ cm}^{-1})$$

$$T = 178 \text{ K}$$

The temperature at which $p_1 = 0.15$ is lower for case b since the presence of two states at the higher energy provides more opportunity for the system to populate the higher energy state.

P31.9) Consider the following energy-level diagrams, modified from Problem P31.8 by the addition of another excited state with energy of 600 cm^{-1} :

- a) At what temperature will the probability of occupying the second energy level be 0.15 for the states depicted in part (a) of the figure?
- b) Perform the corresponding calculation for the states depicted in part (b) of the figure.

a)

$$0.15 = p_1 = \frac{e^{-\beta\epsilon_1}}{q} = \frac{e^{-\beta(300 \text{ cm}^{-1})}}{1+e^{-\beta(300 \text{ cm}^{-1})} + e^{-\beta(600 \text{ cm}^{-1})}}$$

$$0.15 + 0.15(e^{-\beta(300 \text{ cm}^{-1})}) + 0.15(e^{-\beta(600 \text{ cm}^{-1})}) = e^{-\beta(300 \text{ cm}^{-1})}$$

$$0.15 - 0.85(e^{-\beta(300 \text{ cm}^{-1})}) + 0.15(e^{-\beta(600 \text{ cm}^{-1})}) = 0$$

The last expression is a quadratic equation with $x = \exp(-\beta(300 \text{ cm}^{-1}))$. This equation has two roots equal to 0.183 and 5.48. Only the 0.183 root will provide temperature greater than zero, therefore:

$$0.183 = e^{-\beta(300 \text{ cm}^{-1})}$$

$$1.70 = \frac{300 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(T)}$$

$$T = 254 \text{ K}$$

b)

$$0.15 = p_1 = \frac{2e^{-\beta\varepsilon_1}}{q} = \frac{2e^{-\beta(300 \text{ cm}^{-1})}}{1 + 2e^{-\beta(300 \text{ cm}^{-1})} + e^{-\beta(600 \text{ cm}^{-1})}}$$

$$0.15 + 0.30(e^{-\beta(300 \text{ cm}^{-1})}) + 0.15(e^{-\beta(600 \text{ cm}^{-1})}) = 2e^{-\beta(300 \text{ cm}^{-1})}$$

$$0.15 - 1.70(e^{-\beta(300 \text{ cm}^{-1})}) + 0.15(e^{-\beta(600 \text{ cm}^{-1})}) = 0$$

The last expression is a quadratic equation with $x = \exp(-\beta(300 \text{ cm}^{-1}))$. This equation has two roots equal to 0.090 and 11.24. Only the 0.090 root will provide temperature greater than zero, therefore:

$$0.090 = e^{-\beta(300 \text{ cm}^{-1})}$$

$$2.41 = \frac{300 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(T)}$$

$$T = 179 \text{ K}$$

P31.10) Consider the following sets of populations for four equally spaced energy levels:

$\varepsilon/k \text{ (K)}$	Set A	Set B	Set C
300	5	3	4
200	7	9	8
100	15	17	16
0	33	31	32

- a) Demonstrate that the sets have the same energy.
 - b) Determine which of the sets is the most probable.
 - c) For the most probable set, is the distribution of energy consistent with a Boltzmann distribution?
-
- a) The total energy is equal to the sum of energy associated with a given level times the number of particles in that level. We will leave the energy in units of

e/k when performing the sum, then multiply the result by k after summation to convert the answer to joules. For set A:

$$\begin{aligned} E &= \sum_n \varepsilon_n a_n = \varepsilon_0 a_0 + \varepsilon_1 a_1 + \varepsilon_2 a_2 + \varepsilon_3 a_3 \\ &= (0 \text{ K})(33) + (100 \text{ K})(33) + (200 \text{ K})(33) + (300 \text{ K})(33) \\ &= (4400 \text{ K})\left(1.38 \times 10^{-23} \text{ J K}^{-1}\right) = 6.07 \times 10^{-20} \text{ J} \end{aligned}$$

Repeating this calculation for Sets B and C reveals that all three sets contain the same energy.

- b) The most probable distribution of energy will be that distribution with the greatest weight. Calculating the weight associated with the distributions for each set reveals that set C is the most probable:

$$\begin{aligned} W_A &= \frac{N!}{\prod_n a_n!} = \frac{N!}{a_0! a_1! a_2! a_3!} = \frac{60!}{(33!)(15!)(7!)(5!)} = 1.21 \times 10^{27} \\ W_B &= \frac{N!}{\prod_n a_n!} = \frac{60!}{(31!)(17!)(9!)(3!)} = 1.31 \times 10^{27} \\ W_C &= \frac{N!}{\prod_n a_n!} = \frac{60!}{(32!)(16!)(8!)(4!)} = 1.56 \times 10^{27} \end{aligned}$$

- c) The occupation numbers corresponding to the Boltzmann distribution are given by:

$$a_i = N p_i = \frac{N e^{-\beta \varepsilon_i}}{q}$$

The ratio of any two occupation numbers for a set of non-degenerate energy levels is given by:

$$\frac{a_i}{a_j} = e^{-\beta(\varepsilon_i - \varepsilon_j)} = e^{-\left(\frac{\varepsilon_i - \varepsilon_j}{k}\right)\frac{1}{T}}$$

The above expression suggests that the ratio of occupation numbers can be used to determine the temperature. For set C, comparing the occupation numbers for level 2 and level 0 results in:

$$\frac{a_2}{a_0} = e^{-\left(\frac{\epsilon_2 - \epsilon_0}{k}\right)\frac{1}{T}}$$

$$\frac{8}{32} = e^{-\left(\frac{200 \text{ cm}^{-1} - 0 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}}\right)\frac{1}{T}}$$

$$T = 144 \text{ K}$$

Repeating the same calculation for level 3 and level 0:

$$\frac{a_3}{a_0} = e^{-\left(\frac{\epsilon_3 - \epsilon_0}{k}\right)\frac{1}{T}}$$

$$\frac{4}{32} = e^{-\left(\frac{300 \text{ cm}^{-1} - 0 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}}\right)\frac{1}{T}}$$

$$T = 144 \text{ K}$$

The distribution of energy in set C is in accord with the Boltzmann distribution.

P31.11) A set of 13 particles occupies states with energies of 0, 100, and 200 cm⁻¹. Calculate the total energy and number of microstates for the following configurations of energy:

- a) $a_0 = 8$, $a_1 = 5$, and $a_2 = 0$
- b) $a_0 = 9$, $a_1 = 3$, and $a_2 = 1$
- c) $a_0 = 10$, $a_1 = 1$, and $a_2 = 2$

Do any of these configurations correspond to the Boltzmann distribution?

The total energy is equal to the sum of energy associated with a given level times the number of particles in that level. For the occupation numbers in a:

$$E = \sum_n \epsilon_n a_n = \epsilon_0 a_0 + \epsilon_1 a_1 + \epsilon_2 a_2$$

$$= (0 \text{ cm}^{-1})(8) + (100 \text{ cm}^{-1})(5) + (200 \text{ cm}^{-1})(0) = 500 \text{ cm}^{-1}$$

Repeating the calculation for the occupation numbers in (b) and (c) yields the same energy of 500 cm⁻¹. The number of microstates associated with each distribution is given by the weight:

$$W_a = \frac{N!}{\prod_n a_n!} = \frac{N!}{a_0! a_1! a_2!} = \frac{13!}{(8!)(5!)(0!)} = 1287$$

$$W_b = \frac{13!}{(9!)(3!)(1!)} = 2860$$

$$W_c = \frac{13!}{(10!)(1!)(2!)} = 858$$

The ratio of any two occupation numbers for a set of non-degenerate energy levels is given by:

$$\frac{a_i}{a_j} = e^{-\beta(\epsilon_i - \epsilon_j)} = e^{-\left(\frac{\epsilon_i - \epsilon_j}{k}\right)\frac{1}{T}}$$

The above expression suggests that the ratio of occupation numbers can be used to determine the temperature. For set (b), comparing the occupation numbers for level 2 and level 0 results in:

$$\begin{aligned} \frac{a_2}{a_0} &= e^{-\left(\frac{\epsilon_2 - \epsilon_0}{k}\right)\frac{1}{T}} \\ \frac{1}{9} &= e^{-\left(\frac{200 \text{ cm}^{-1} - 0 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}}\right)\frac{1}{T}} \\ T &= 131 \text{ K} \end{aligned}$$

Repeating the same calculation for level 1 and level 0:

$$\begin{aligned} \frac{a_1}{a_0} &= e^{-\left(\frac{\epsilon_1 - \epsilon_0}{k}\right)\frac{1}{T}} \\ \frac{3}{9} &= e^{-\left(\frac{100 \text{ cm}^{-1} - 0 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}}\right)\frac{1}{T}} \\ T &= 131 \text{ K} \end{aligned}$$

The distribution of energy in (b) is in accord with the Boltzmann distribution.

P31.12) For a set of nondegenerate levels with energy $\epsilon/k = 0, 100$, and 200 K, calculate the probability of occupying each state when $T = 50, 500$, and 5000 K. As the

temperature continues to increase, the probabilities will reach a limiting value. What is this limiting value?

The probability of occupying a specific energy level is given by:

$$p_i = \frac{e^{-\beta\epsilon_i}}{q} = \frac{e^{-\beta\epsilon_i}}{e^{-\beta\epsilon_0} + e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}} = \frac{e^{-\beta\epsilon_i}}{1 + e^{-(100 \text{ K}/T)} + e^{-(200 \text{ K}/T)}}$$

At 50 K, the probability of occupying the ground ($i = 0$), and the first two excited states ($i = 1$ and 2 , respectively) is:

$$\begin{aligned} p_{0,50 \text{ K}} &= \frac{e^{-\beta\epsilon_0}}{q} = \frac{1}{1 + e^{-2} + e^{-4}} = 0.867 \\ p_{1,50 \text{ K}} &= \frac{e^{-\beta\epsilon_1}}{q} = \frac{e^{-2}}{1 + e^{-2} + e^{-4}} = 0.117 \\ p_{2,50 \text{ K}} &= \frac{e^{-\beta\epsilon_2}}{q} = \frac{e^{-4}}{1 + e^{-2} + e^{-4}} = 0.016 \end{aligned}$$

Performing this calculation for 500 K and 5000 K yields the following:

i	p_i (50 K)	p_i (500 K)	p_i (5000 K)
0	0.867	0.402	0.340
1	0.117	0.329	0.333
2	0.016	0.269	0.327

The high-temperature limit for the probability is where each state has an equal probability of being populated, or $1/3$ in this example for three, non-degenerate energy levels.

P31.13) Consider a collection of molecules where each molecule has two nondegenerate energy levels that are separated by 6000 cm^{-1} . Measurement of the level populations demonstrates that there are 8 times more molecules in the ground state than in the upper state. What is the temperature of the collection?

The ratio of any two occupation numbers for a set of non-degenerate energy levels is given by:

$$\frac{a_i}{a_j} = e^{-\beta(\epsilon_i - \epsilon_j)} = e^{-\left(\frac{\epsilon_i - \epsilon_j}{k}\right)\frac{1}{T}}$$

The above expression suggests that the ratio of occupation numbers can be used to determine the temperature. The ratio of a_1 to a_0 is 1/8. Using this information and the separation between energy levels, the temperature is:

$$\frac{a_1}{a_0} = e^{-\left(\frac{\epsilon_2 - \epsilon_0}{k}\right)\frac{1}{T}}$$

$$\frac{1}{8} = e^{-\left(\frac{6000 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}}\right)\frac{1}{T}}$$

$$T = 4150 \text{ K}$$

P31.14) The ^{13}C nucleus is a spin 1/2 particle as is a proton. However, the energy splitting for a given field strength is roughly 1/4 of that for a proton. Using a 1.45-T magnet as in Example Problem 31.6, what is the ratio of populations in the excited and ground spin states for ^{13}C at 298 K?

Using the information provided in the example problem, the separation in energy is given by:

$$\Delta E = \frac{1}{4} (2.82 \times 10^{-26} \text{ J T}^{-1}) B = \frac{1}{4} (2.82 \times 10^{-26} \text{ J T}^{-1})(1.45 \text{ T}) = 1.02 \times 10^{-26} \text{ J}$$

Using this separation in energy, the ratio in spin-state occupation numbers is:

$$\frac{a_+}{a_-} = e^{-\left(\frac{\epsilon_+ - \epsilon_-}{kT}\right)} = e^{-\left(\frac{\Delta E}{kT}\right)}$$

$$\frac{a_+}{a_-} = e^{-\left(\frac{1.02 \times 10^{-26} \text{ J}}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}\right)}$$

$$\frac{a_+}{a_-} = 0.999998$$

P31.15) ^{14}N is a spin 1 particle such that the energy levels are at 0 and $\pm \gamma B \hbar$, where γ is the magnetogyric ratio and B is the strength of the magnetic field. In a 4.8-T field, the energy splitting between any two spin states expressed as the resonance frequency is 14.45 MHz. Determine the occupation numbers for the three spin states at 298 K.

The resonance frequency can be converted to energy as follows:

$$\Delta E = \frac{freq.}{c} = \frac{1.445 \times 10^7 \text{ s}^{-1}}{3.00 \times 10^{10} \text{ cm s}^{-1}} = 4.82 \times 10^{-4} \text{ cm}^{-1}$$

With this energy gap, the partition function becomes:

$$q = \sum_n e^{-\beta \epsilon_n} = e^{-\beta \epsilon_-} + e^{-\beta \epsilon_0} + e^{-\beta \epsilon_+} = e^{-\left(\frac{-4.82 \times 10^{-4} \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K})(298 \text{ K})}\right)} + 1 + e^{-\left(\frac{4.82 \times 10^{-4} \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K})(298 \text{ K})}\right)} \approx 3.00$$

With the partition function, the occupation numbers are readily determined:

$$a_- = \frac{e^{-\beta \epsilon_-}}{q} = \frac{e^{-\left(\frac{-4.82 \times 10^{-4} \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K})(298 \text{ K})}\right)}}{3.00} = \frac{1.00000233}{3.00} = 0.333334$$

$$a_0 = \frac{e^{-\beta \epsilon_0}}{q} = \frac{1}{3.00} = 0.333333$$

$$a_+ = \frac{e^{-\beta \epsilon_+}}{q} = \frac{e^{-\left(\frac{4.82 \times 10^{-4} \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K})(298 \text{ K})}\right)}}{3.00} = \frac{0.999998}{3.00} = 0.333333$$

P31.16) The vibrational frequency of I₂ is 208 cm⁻¹. At what temperature will the population in the first excited state be half that of the ground state?

$$\frac{a_1}{a_0} = \frac{1}{2} = e^{-\beta(\epsilon_1 - \epsilon_0)} = e^{-\beta(208 \text{ cm}^{-1})}$$

$$0.5 = e^{-\left(\frac{-208 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K})(T)}\right)}$$

$$0.693 = \frac{208 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K})(T)}$$

$$T = 432 \text{ K}$$

P31.17) The vibrational frequency of Cl₂ is 525 cm⁻¹. Will the temperature be higher or lower relative to I₂ (see Problem P31.16) at which the population in the first excited vibrational state is half that of the ground state? What is this temperature?

Since the energy level spacings are larger for Cl₂ relative to I₂, we would expect the temperature at which $a_1/a_0 = 0.5$ to be greater for Cl₂.

$$\frac{a_1}{a_0} = \frac{1}{2} = e^{-\beta(\epsilon_1 - \epsilon_0)} = e^{-\beta(525 \text{ cm}^{-1})}$$

$$0.5 = e^{\left(\frac{-525 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K})(T)} \right)}$$

$$0.693 = \frac{525 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K})(T)}$$

$$T = 1090 \text{ K}$$

P31.18) Determine the partition function for the vibrational degrees of freedom of Cl₂ ($\tilde{\nu} = 525 \text{ cm}^{-1}$) and calculate the probability of occupying the first excited vibrational level at 300 and 1000 K. Determine the temperature at which identical probabilities will be observed for F₂ ($\tilde{\nu} = 917 \text{ cm}^{-1}$).

For Cl₂ at 300 K:

$$q = \frac{1}{1 - e^{-\beta h c \tilde{\nu}}} = \frac{1}{1 - e^{\left(\frac{-(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(525 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})} \right)}} = 1.087$$

$$p_1 = \frac{e^{-\beta \epsilon_1}}{q} = \frac{e^{-\beta h c \tilde{\nu}}}{q} = \frac{e^{\left(\frac{-(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(525 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})} \right)}}{1.087} = 0.074$$

For Cl₂ at 1000 K:

$$q = \frac{1}{1 - e^{-\beta h c \tilde{\nu}}} = \frac{1}{1 - e^{\left(\frac{-(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(525 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})} \right)}} = 1.885$$

$$p_1 = \frac{e^{-\beta \epsilon_1}}{q} = \frac{e^{-\beta h c \tilde{\nu}}}{q} = \frac{e^{\left(\frac{-(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(525 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})} \right)}}{1.885} = 0.249$$

To determine the temperatures at which F₂ has equivalent populations in the first vibrational excited state, we first reduce the expression for p_1 as follows:

$$p_1 = \frac{e^{-\beta \epsilon_1}}{q} = \frac{e^{-\beta h c \tilde{\nu}}}{\left(\frac{1}{1 - e^{-\beta h c \tilde{\nu}}} \right)} = e^{-\beta h c \tilde{\nu}} (1 - e^{-\beta h c \tilde{\nu}})$$

Substituting in the values for F_2 and solving as a quadratic equation:

$$\begin{aligned} p_1 = 0.074 &= e^{-\beta hc(917 \text{ cm}^{-1})} - e^{-2\beta hc(917 \text{ cm}^{-1})} = e^{-1319 \text{ K}/T} - e^{-2(1319 \text{ K})/T} \\ 0 &= -0.074 + e^{-1319 \text{ K}/T} - e^{-2(1319 \text{ K})/T} \\ T &= 524 \text{ K} \end{aligned}$$

Repeating this calculation to determine at which temperature p_1 will be equal to the Cl_2 case at 1000 K:

$$\begin{aligned} p_1 = 0.249 &= e^{-\beta hc(917 \text{ cm}^{-1})} - e^{-2\beta hc(917 \text{ cm}^{-1})} = e^{-1319 \text{ K}/T} - e^{-2(1319 \text{ K})/T} \\ 0 &= -0.249 + e^{-1319 \text{ K}/T} - e^{-2(1319 \text{ K})/T} \\ T &= 1742 \text{ K} \end{aligned}$$

P31.19) A two-level system is characterized by an energy separation of $1.3 \times 10^{-18} \text{ J}$. At what temperature will the population of the ground state be 5 times greater than that of the excited state?

$$\begin{aligned} \frac{a_1}{a_0} &= \frac{1}{5} = e^{-\beta \Delta E} \\ 0.2 &= e^{-1.30 \times 10^{-18} \text{ J}/[(1.38 \times 10^{-23} \text{ J K}^{-1})(T)]} \\ T &= 5.85 \times 10^4 \text{ K} \end{aligned}$$

P31.20) The lowest two electronic energy levels of the molecule NO are illustrated here. Determine the probability of occupying one of the higher energy states at 100, 500, and 2000 K.

Both the lower and higher energy states are two-fold degenerate, with an energy spacing of 121.1 cm^{-1} . At 100 K, the partition function is:

$$q = \sum_n e^{-\beta \varepsilon_n} = 2 + e^{-\beta(121.1 \text{ cm}^{-1})} = 2 + e^{-121.1 \text{ cm}^{-1}/(0.695 \text{ cm}^{-1} \text{ K}^{-1})(100 \text{ K})} = 2.35$$

With the partition function evaluated, the probability of occupying the excited energy level is readily determined:

$$p_1 = \frac{g_1 e^{-\beta E_1}}{q} = \frac{2e^{-121.1 \text{ cm}^{-1}/(0.695 \text{ cm}^{-1} \text{ K}^{-1})(100 \text{ K})}}{2.35} = 0.149$$

At 500 K:

$$q = 2 + e^{-121.1 \text{ cm}^{-1}/(0.695 \text{ cm}^{-1} \text{ K}^{-1})(500 \text{ K})} = 3.41$$

$$p_1 = \frac{g_1 e^{-\beta E_1}}{q} = \frac{2e^{-121.1 \text{ cm}^{-1}/(0.695 \text{ cm}^{-1} \text{ K}^{-1})(500 \text{ K})}}{3.41} = 0.414$$

Finally, at 2000 K:

$$q = 2 + e^{-121.1 \text{ cm}^{-1}/(0.695 \text{ cm}^{-1} \text{ K}^{-1})(2000 \text{ K})} = 3.83$$

$$p_1 = \frac{g_1 e^{-\beta E_1}}{q} = \frac{2e^{-121.1 \text{ cm}^{-1}/(0.695 \text{ cm}^{-1} \text{ K}^{-1})(2000 \text{ K})}}{3.83} = 0.479$$

Since there are two states per energy level, the probability of occupying an individual excited state is 1/2 of the above probabilities.

Chapter 32: Ensemble and Molecular Partition Functions

Problem numbers in italics indicate that the solution is included in the *Student's Solutions Manual*.

Questions on Concepts

Q32.1) What is the canonical ensemble? What properties are held constant in this ensemble?

An ensemble is a collection of identical units or replicas of the system of interest. In the canonical ensemble, V , N , and T are held constant.

Q32.2) What is the relationship between Q and q ? How does this relationship differ if the particles of interest are distinguishable versus indistinguishable?

Q is the canonical partition function, while q is the molecular partition function, or the partition function that describes an individual member of the ensemble.

The relationship between Q and q depends on if ensemble members are distinguishable or indistinguishable. For N members or units in the ensemble:

$$Q = q^N \text{ (distinguishable)}$$

$$Q = \frac{q^N}{N!} \text{ (indistinguishable)}$$

Q32.3) List the atomic and/or molecular energetic degrees of freedom discussed in this chapter. For each energetic degree of freedom, briefly summarize the corresponding quantum mechanical model.

Translational: Particle in a box

Vibrational: Harmonic oscillator

Rotational: Rigid rotor

Electronic: Hydrogen-atom model, MO theory

Q32.4) For which energetic degrees of freedom are the spacings between energy levels small relative to kT at room temperature?

At room temperature, the spacings between translational energy levels are extremely small relative to kT . The rotational energy level spacings are also generally small relative to kT , although some species involving light atoms (such as H_2) may have energy level spacings that are comparable to kT . Vibrational and electronic energy levels usually have spacings that are greater than kT .

Q32.5) For the translational and rotational degrees of freedom, evaluation of the partition function involved replacement of the summation by integration. Why could integration be performed? How does this relate back to the discussion of probability distributions of discrete variables treated as continuous?

Integration can be performed in evaluating q for the translational and rotational degrees of freedom because the energy level spacings along these degrees of freedom are small relative to kT . Since there are numerous states within the energy range of interest (given by kT , it is reasonable to treat the variable of interest (i.e., the number of states) as continuous.

Q32.6) When is the high-T approximation for rotations and vibrations? For which degree of freedom do you expect this approximation to be generally valid at room temperature?

The high-temperature approximation is when the product kT is significantly greater than the energy level spacings. This will be true for translations at all but lowest temperatures. For rotations, the high-temperature limit is appropriate with $T \geq 10\Theta_R$ where Θ_R is the rotational temperature, equal to B/k where B is the rotational constant. The high-temperature approximation will generally be valid for rotations at room temperature. For vibrations, the high-temperature limit is appropriate when $T \geq 10\Theta_V$ where Θ_V is the vibrational temperature, equal to $\tilde{\nu}/k$ where $\tilde{\nu}$ is the rotational constant.

Q32.7) State the equipartition theorem. Why is this theorem inherently classical?

Any term in the classical Hamiltonian that is quadratic with respect to momentum or position will contribute $kT/2$ to the average energy. It is inherently classical since for a given energetic degree of freedom, the level spacings must be small relative to kT such that the energy levels can be treated as continuous.

Q32.8) Why is the electronic partition function generally equal to the degeneracy of the ground electronic state?

For electronic energy levels, the spacings between the ground and first excited state is generally much larger than kT ; therefore, only the first term in the expression for the partition function contributes to the value of q . If the ground-state energy is defined as zero, this term reduces to the degeneracy of the ground state.

Q32.9) What is q_{Total} , and how is it constructed using the partition functions for each energetic degree of freedom discussed in this chapter?

q_{total} is the total molecular partition function, and is equal to the product of partition functions for each energetic degree of freedom:

$$q_{total} = q_T q_R q_V q_E$$

Q32.10) Why is it possible to set the energy of the ground vibrational and electronic energy level to zero?

The energy of the ground state can be set to zero since it is the relative energy of the levels that is important in determination of quantities such as occupation probabilities.

Problems

P32.1) Evaluate the translational partition function for H₂ confined to a volume of 100 cm³ at 298 K. Perform the same calculation for N₂ under identical conditions. (*Hint:* Do you need to reevaluate the full expression for q_T ?)

$$q_T(H_2) = \frac{V}{\Lambda^3}$$

$$\Lambda = \left(\frac{h^2}{2\pi mkT} \right)^{1/2} = \left(\frac{(6.626 \times 10^{-34} \text{ J s})^2}{2\pi \left(\frac{0.002 \text{ kg mol}^{-1}}{N_A} \right) (1.38 \times 10^{-23} \text{ J K}^{-1}) (298 \text{ K})} \right)^{1/2} = 7.15 \times 10^{-11} \text{ m}$$

$$q_T(H_2) = \frac{V}{(7.15 \times 10^{-11} \text{ m})^3} = \frac{(100 \text{ cm}^3)(10^{-6} \text{ m}^3 \text{ cm}^{-3})}{(7.15 \times 10^{-11} \text{ m})^3} = 2.74 \times 10^{26}$$

$$\frac{q_T(N_2)}{q_T(H_2)} = \frac{\frac{V}{\Lambda^3(N_2)}}{\frac{V}{\Lambda^3(H_2)}} = \frac{\Lambda^3(H_2)}{\Lambda^3(N_2)} = \left(\frac{m(N_2)}{m(H_2)} \right)^{3/2} = \left(\frac{28.014 \text{ g mol}^{-1}}{2.016 \text{ g mol}^{-1}} \right)^{3/2} = 51.8$$

$$q_T(N_2) = 51.8(q_T(H_2)) = 1.42 \times 10^{28}$$

P32.2) Evaluate the translational partition function for Ar confined to a volume of 1000 cm³ at 298 K. At what temperature will the translational partition function of Ne be identical to that of Ar at 298 K confined to the same volume?

$$q_T(Ar) = \frac{V}{\Lambda^3}$$

$$\Lambda = \left(\frac{h^2}{2\pi mkT} \right)^{1/2} = \left(\frac{(6.626 \times 10^{-34} \text{ J s})^2}{2\pi \left(\frac{0.0399 \text{ kg mol}^{-1}}{N_A} \right) (1.38 \times 10^{-23} \text{ J K}^{-1}) (298 \text{ K})} \right)^{1/2} = 1.60 \times 10^{-11} \text{ m}$$

$$q_T(Ar) = \frac{V}{(1.60 \times 10^{-11} \text{ m})^3} = \frac{(1000 \text{ cm}^3)(10^{-6} \text{ m}^3 \text{ cm}^{-3})}{(1.60 \times 10^{-11} \text{ m})^3} = 2.44 \times 10^{29}$$

If the gases are confined to the same volume, then the partition functions will be equal when the thermal wavelengths are equal:

$$\Lambda(Ne) = \Lambda(Ar) = 1.60 \times 10^{-11} \text{ m}$$

$$\left(\frac{h^2}{2\pi mkT} \right)^{1/2} = 1.60 \times 10^{-11} \text{ m}$$

$$T = \frac{h^2}{2\pi mk(1.60 \times 10^{-11} \text{ m})^2} = \frac{(6.626 \times 10^{-34} \text{ J s})^2}{2\pi \left(\frac{0.0202 \text{ kg mol}^{-1}}{N_A} \right) (1.38 \times 10^{-23} \text{ J K}^{-1}) (1.60 \times 10^{-11} \text{ m})^2}$$

$$T = 590 \text{ K}$$

P32.3) At what temperature are there Avogadro's number of translational states available for O₂ confined to a volume of 1000 cm³?
Since the number of translational states is equal to q_T :

$$q_T = 6.022 \times 10^{23} = \frac{V}{\Lambda^3} = \frac{(1000 \text{ cm}^3)(10^{-6} \text{ m}^3 \text{ cm}^{-3})}{\left(\frac{h^2}{2\pi mkT} \right)^{3/2}}$$

$$\left(\frac{h^2}{2\pi mkT} \right)^{3/2} = 1.66 \times 10^{-27} \text{ m}^3$$

$$T = \frac{h^2}{2\pi mk(1.60 \times 10^{-27} \text{ m}^3)^{2/3}} = \frac{(6.626 \times 10^{-34} \text{ J s})^2}{2\pi \left(\frac{0.0320 \text{ kg mol}^{-1}}{N_A} \right) (1.38 \times 10^{-23} \text{ J K}^{-1}) (1.11 \times 10^{-18} \text{ m}^2)}$$

$$T = 0.086 \text{ K}$$

P32.4) Imagine gaseous Ar at 298 K confined to move in a two-dimensional plane of area 1.00 cm^2 . What is the value of the translational partition function?

$$q_T = \frac{A}{\Lambda^2}$$

$$\Lambda = \left(\frac{h^2}{2\pi mkT} \right)^{\frac{1}{2}} = \left(\frac{(6.626 \times 10^{-34} \text{ J s})^2}{2\pi \left(\frac{0.0399 \text{ kg mol}^{-1}}{N_A} \right) (1.38 \times 10^{-23} \text{ J K}^{-1}) (298 \text{ K})} \right)^{\frac{1}{2}} = 1.60 \times 10^{-11} \text{ m}$$

$$q_T = \frac{(1.00 \text{ cm}^2)(10^{-4} \text{ m}^2 \text{ cm}^{-2})}{(1.60 \times 10^{-11} \text{ m})^2} = 3.91 \times 10^{17}$$

P32.5) For N_2 at 77.3 K, 1 atm, in a 1-cm³ container, calculate the translational partition function and ratio of this partition function to the number of N_2 molecules present under these conditions.

$$q_T(N_2) = \frac{V}{\Lambda^3}$$

$$\Lambda = \left(\frac{h^2}{2\pi mkT} \right)^{\frac{1}{2}} = \left(\frac{(6.626 \times 10^{-34} \text{ J s})^2}{2\pi \left(\frac{0.028 \text{ kg mol}^{-1}}{N_A} \right) (1.38 \times 10^{-23} \text{ J K}^{-1}) (77.3 \text{ K})} \right)^{\frac{1}{2}} = 3.75 \times 10^{-11} \text{ m}$$

$$q_T(N_2) = \frac{V}{(3.75 \times 10^{-11} \text{ m})^3} = \frac{(1 \text{ cm}^3)(10^{-6} \text{ m}^3 \text{ cm}^{-3})}{(3.75 \times 10^{-11} \text{ m})^3} = 1.90 \times 10^{25}$$

Next, the number of molecules (N) present at this temperature is determined using the ideal gas law:

$$n = \frac{PV}{RT} = \frac{(1 \text{ atm})(1.00 \times 10^{-3} \text{ L})}{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(77.3 \text{ K})} = 1.58 \times 10^{-4} \text{ mol}$$

$$N = n \times N_A = 9.49 \times 10^{19} \text{ molecules}$$

With N , the ratio is readily determined:

$$\frac{q_T}{N} = \frac{1.90 \times 10^{25}}{9.49 \times 10^{19}} = 2.00 \times 10^5$$

P32.6) What is the symmetry number for the following molecules?

- a) $^{35}\text{Cl}^{37}\text{Cl}$
 b) $^{35}\text{Cl}^{35}\text{Cl}$
 c) H_2O
 d) C_6H_6
 e) CH_2Cl_2

- a) 1 b) 2 c) 2 d) 12 e) 2

P32.7) Which species will have the largest rotational partition function: H_2 , HD , or D_2 ? Which of these species will have the largest translational partition function assuming that volume and temperature are identical? When evaluating the rotational partition functions, you can assume that the high-temperature limit is valid.

With the high-temperature limit, the rotational partition function (q_R) is equal to:

$$q_R = \frac{1}{\sigma \beta B}$$

Since β will be the same for all three species (the comparison is done at a given temperature), and assuming that the bond length is the same for all species then the ratio of rotational partition functions for any two species can be reduced to:

$$\frac{q_R(1)}{q_R(2)} = \frac{\left(\frac{1}{\sigma_1 \beta B_1}\right)}{\left(\frac{1}{\sigma_2 \beta B_2}\right)} = \frac{\sigma_2 B_2}{\sigma_1 B_1} = \frac{\sigma_2 \left(\frac{h}{8\pi^2 c \mu_2 r^2}\right)}{\sigma_1 \left(\frac{h}{8\pi^2 c \mu_1 r^2}\right)} = \frac{\sigma_2 \mu_1}{\sigma_1 \mu_2}$$

The reduced masses and symmetry number for the three species of interest are:

molecule	σ	μ
H_2	2	$m_{\text{H}}/2$
D_2	2	m_{H}
HD	1	$2 m_{\text{H}}/3$

With these values, the ratio of rotational partition functions is readily calculated:

$$\frac{q_R(D_2)}{q_R(H_2)} = \frac{(\sigma_{D_2})\mu_{D_2}}{(\sigma_{H_2})\mu_{H_2}} = \frac{(2)m_H}{(2)m_H/2} = 2$$

$$\frac{q_R(HD)}{q_R(H_2)} = \frac{(\sigma_{HD})\mu_{HD}}{(\sigma_{H_2})\mu_{H_2}} = \frac{(2)^{2m_H/3}}{(1)m_H/2} = \frac{8}{3}$$

Therefore $q_R(\text{HD})$ is greatest, followed by $q_R(\text{D}_2)$.

Performing the same analysis for the translational partition function, we begin by reducing the ratio of translational partition functions for two species:

$$\frac{q_T(1)}{q_T(2)} = \frac{\frac{V}{\Lambda^3(1)}}{\frac{V}{\Lambda^3(2)}} = \frac{\Lambda^3(2)}{\Lambda^3(1)} = \left[\frac{\left(\frac{h^2}{2\pi m_1 kT} \right)^{3/2}}{\left(\frac{h^2}{2\pi m_2 kT} \right)^{3/2}} \right] = \left(\frac{m_2}{m_1} \right)^{3/2}$$

By inspection, the species with the largest mass will have the largest translational partition function at equivalent temperature and volume. Therefore $q_T(D_2)$ is largest followed by $q_T(HD)$.

P32.8) Consider *para*-H₂ ($B = 60.853 \text{ cm}^{-1}$) for which only even- J levels are available. Evaluate the rotational partition function for this species at 50 K. Perform this same calculation for HD ($B = 45.655 \text{ cm}^{-1}$).

For para-H₂, only even J levels are allowed; therefore, the rotational partition function is:

$$q_R = \sum_{J=0,2,4,6,\dots} (2J+1)e^{-\beta hcBJ(J+1)} = 1 + 5e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ m s}^{-1})(60.853 \text{ cm}^{-1})(6)}{(1.38 \times 10^{-23} \text{ J K}^{-1})(50 \text{ K})}} + 9e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ m s}^{-1})(60.853 \text{ cm}^{-1})(20)}{(1.38 \times 10^{-23} \text{ J K}^{-1})(50 \text{ K})}} + \dots$$

$$= 1 + 1.35 \times 10^{-4} + \dots$$

$$\approx 1.00$$

Performing this same calculation for HD where both even and odd J states are allowed:

$$q_R = \sum_{J=0,1,2,3,\dots} (2J+1)e^{-\beta hcBJ(J+1)} = 1 + 3e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ m s}^{-1})(45.655 \text{ cm}^{-1})(2)}{(1.38 \times 10^{-23} \text{ J K}^{-1})(50 \text{ K})}} + 5e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ m s}^{-1})(45.655 \text{ cm}^{-1})(6)}{(1.38 \times 10^{-23} \text{ J K}^{-1})(50 \text{ K})}} + \dots$$

$$= 1 + 0.216 + 3.74 \times 10^{-4} + \dots$$

$$\approx 1.22$$

P32.9) For which of the following diatomic molecules is the high-temperature expression for the rotational partition function valid if $T = 40 \text{ K}$?

- a) DBr ($B = 4.24 \text{ cm}^{-1}$)
- b) DI ($B = 3.25 \text{ cm}^{-1}$)
- c) CsI ($B = 0.0236 \text{ cm}^{-1}$)
- d) F³⁵Cl ($B = 0.516 \text{ cm}^{-1}$)

The high temperature approximation is valid if $T > 10\Theta_R$. Therefore, we simply need to calculate the rotational temperature and compare to T :

a)

$$\Theta_R = \frac{B}{k} = \frac{4.24 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}} = 6.11 \text{ K} \quad (\text{no})$$

b)

$$\Theta_R = \frac{B}{k} = \frac{3.25 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}} = 4.68 \text{ K} \quad (\text{no})$$

c)

$$\Theta_R = \frac{B}{k} = \frac{0.0236 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}} = 0.034 \text{ K} \quad (\text{yes})$$

d)

$$\Theta_R = \frac{B}{k} = \frac{0.516 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}} = 0.743 \text{ K} \quad (\text{yes})$$

P32.10) Calculate the rotational partition function for SO₂ at 298 K where $B_A = 2.03 \text{ cm}^{-1}$, $B_B = 0.344 \text{ cm}^{-1}$, and $B_C = 0.293 \text{ cm}^{-1}$.

$$\begin{aligned} q_R &= \frac{\sqrt{\pi}}{\sigma} \left(\frac{1}{\beta B_A} \right)^{1/2} \left(\frac{1}{\beta B_B} \right)^{1/2} \left(\frac{1}{\beta B_C} \right)^{1/2} \\ &= \frac{\sqrt{\pi}}{2} \left(\frac{(0.695 \text{ cm}^{-1})(298 \text{ K})}{2.03 \text{ cm}^{-1}} \right)^{1/2} \left(\frac{(0.695 \text{ cm}^{-1})(298 \text{ K})}{0.344 \text{ cm}^{-1}} \right)^{1/2} \left(\frac{(0.695 \text{ cm}^{-1})(298 \text{ K})}{0.293 \text{ cm}^{-1}} \right)^{1/2} \\ &\approx 5832 \end{aligned}$$

P32.11) Calculate the rotational partition function for ClNO at 500 K where $B_A = 2.84 \text{ cm}^{-1}$, $B_B = 0.187 \text{ cm}^{-1}$, and $B_C = 0.175 \text{ cm}^{-1}$.

$$\begin{aligned} q_R &= \frac{\sqrt{\pi}}{\sigma} \left(\frac{1}{\beta B_A} \right)^{1/2} \left(\frac{1}{\beta B_B} \right)^{1/2} \left(\frac{1}{\beta B_C} \right)^{1/2} \\ &= \frac{\sqrt{\pi}}{1} \left(\frac{(0.695 \text{ cm}^{-1})(500 \text{ K})}{2.84 \text{ cm}^{-1}} \right)^{1/2} \left(\frac{(0.695 \text{ cm}^{-1})(500 \text{ K})}{0.187 \text{ cm}^{-1}} \right)^{1/2} \left(\frac{(0.695 \text{ cm}^{-1})(500 \text{ K})}{0.175 \text{ cm}^{-1}} \right)^{1/2} \\ &\approx 3.78 \times 10^4 \end{aligned}$$

P32.12)

- a) In the rotational spectrum of H³⁵Cl ($I = 2.65 \times 10^{-47} \text{ kg m}^2$), the transition corresponding to the $J = 4$ to $J = 5$ transition is the most intense. At what temperature was the spectrum obtained?
- b) At 1000 K, which rotational transition of H³⁵Cl would you expect to demonstrate the greatest intensity?

c) Would you expect the answers for parts (a) and (b) to change if the spectrum were of H³⁷Cl?

a) First, solving for the rotational constant (B):

$$B = \frac{h}{8\pi^2 c I} = \frac{6.626 \times 10^{-34} \text{ J s}}{8\pi^2 (3.00 \times 10^{10} \text{ cm s}^{-1})(2.65 \times 10^{-47} \text{ kg m}^2)} = 10.57 \text{ cm}^{-1}$$

with B, the temperature (T) at which the spectrum was obtained can be determined as follows:

$$T = \frac{(2J+1)^2 hcB}{2k} = \frac{(9)^2 (6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(10.57 \text{ cm}^{-1})}{2(1.38 \times 10^{-23} \text{ J K}^{-1})} = 616 \text{ K}$$

b) Using the first expression provided in part (a) to isolate the rotational level J :

$$\begin{aligned} T &= \frac{(2J+1)^2 hcB}{2k} \\ \left(\frac{2kT}{hcB}\right) &= (2J+1)^2 \\ \frac{\left(\frac{2kT}{hcB}\right)^{1/2} - 1}{2} &= J \\ \frac{\left(\frac{2(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(10.57 \text{ cm}^{-1})}\right)^{1/2} - 1}{2} &\equiv 5 = J \end{aligned}$$

c) For the heavier Cl isotope, the moment of inertia will increase leading to a decrease in the rotational constant. Quantitatively:

$$\frac{B_{37}}{B_{35}} = \frac{\frac{h}{8\pi^2 c \mu_{37} r^2}}{\frac{h}{8\pi^2 c \mu_{35} r^2}} = \frac{\mu_{35}}{\mu_{37}} = \frac{\frac{m_H m_{35}}{m_H + m_{35}}}{\frac{m_H m_{37}}{m_H + m_{37}}} \equiv \frac{\frac{35}{36}}{\frac{37}{38}} = 0.998$$

$$B_{37} = 0.998 B_{35} = 0.998 (10.57 \text{ cm}^{-1}) = 10.55 \text{ cm}^{-1}$$

With this rotational constant, the temperature at which the $J = 4$ state is most populated becomes:

$$T = \frac{(2J+1)^2 hcB}{2k} = \frac{(9)^2 (6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(10.55 \text{ cm}^{-1})}{2(1.38 \times 10^{-23} \text{ J K}^{-1})} = 615 \text{ K}$$

This result is essentially identical to the result for the lighter Cl isotope. Therefore, at 1000 K we expect the $J = 5$ level to also be the most populated.

P32.13) Calculate the rotational partition function for oxygen ($B = 1.44 \text{ cm}^{-1}$) at its boiling point, 20.8 K, using the high-temperature approximation and by discrete summation. Why should only odd values of J be included in this summation?

First, O₂ in the ground state is a triplet such that the spins are parallel. Therefore, to ensure an anti-symmetric wavefunction with rotation, only odd J states are allowed.

In the high-temperature approximation, the rotational partition function is given by:

$$q_R = \left(\frac{1}{\sigma \beta B} \right) = \left(\frac{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(20.8 \text{ K})}{2(1.44 \text{ cm}^{-1})} \right) = 5.02$$

And by discrete summation:

$$q_R = \sum_{J=1,3,5,7,\dots} (2J+1)e^{-\beta hcBJ(J+1)} = 3e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ m s}^{-1})(1.44 \text{ cm}^{-1})(2)}{(1.38 \times 10^{-23} \text{ J K}^{-1})(20.8 \text{ K})}} + 7e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ m s}^{-1})(1.44 \text{ cm}^{-1})(12)}{(1.38 \times 10^{-23} \text{ J K}^{-1})(20.8 \text{ K})}} + 11e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ m s}^{-1})(1.44 \text{ cm}^{-1})(30)}{(1.38 \times 10^{-23} \text{ J K}^{-1})(50 \text{ K})}} + \dots$$

$$\cong 5.18$$

P32.14)

a) Calculate the percent population of the first 10 rotational energy levels for HBr ($B = 8.46 \text{ cm}^{-1}$) at 298 K.

b) Repeat this calculation for HF assuming that the bond length of this molecule is identical to that of HBr.

Since $T \gg \Theta_R$, the high-temperature limit is valid. In this limit, the probability of occupying a specific rotational state (p_J) is:

$$p_J = \frac{(2J+1)e^{-\beta hcBJ(J+1)}}{q} = \frac{(2J+1)e^{-\beta hcBJ(J+1)}}{\left(\frac{1}{\sigma \beta hcB} \right)}$$

Evaluating the above expression for $J = 0$:

$$p_J = \frac{(2J+1)e^{-\beta hcBJ(J+1)}}{\left(\frac{1}{\sigma \beta hcB} \right)} = \frac{1}{\left(\frac{1}{\sigma \beta hcB} \right)}$$

$$= \frac{\sigma hcB}{kT} = \frac{(1)(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(8.46 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})} = 0.041$$

Performing similar calculations for $J = 1$ to 9:

J	p_J	J	p_J
0	0.041	5	0.132
1	0.113	6	0.095
2	0.160	7	0.062
3	0.175	8	0.037
4	0.167	9	0.019

- b) The rotational constant of HF must be determined before the corresponding level probabilities can be evaluated. The ratio of rotational constants for HBr versus HF yields:

$$\frac{B_{HBr}}{B_{HF}} = \frac{\left(\frac{h}{8\pi^2 c I_{HBr}}\right)}{\left(\frac{h}{8\pi^2 c I_{HF}}\right)} = \frac{I_{HF}}{I_{HBr}} = \frac{\mu_{HF} r^2}{\mu_{HBr} r^2} = \frac{\mu_{HF}}{\mu_{HBr}} = \frac{\frac{m_H m_F}{m_H + m_F}}{\frac{m_H m_{Br}}{m_H + m_{Br}}} = 0.962$$

$$B_{HF} = \frac{B_{HBr}}{0.962} = 8.80 \text{ cm}^{-1}$$

With this rotational constant, the p_J values for $J = 0$ to 9 are:

J	p_J	J	p_J
0	0.043	5	0.131
1	0.117	6	0.093
2	0.165	7	0.059
3	0.179	8	0.034
4	0.163	9	0.018

P32.15) In general, the high-temperature limit for the rotational partition function is appropriate for almost all molecules at temperatures above their boiling point. Hydrogen is an exception to this generality because the moment of inertia is small due to the small mass of H. Given this, other molecules with H may also represent exceptions to this general rule. For example, methane (CH_4) has relatively modest moments of inertia ($I_A = I_B = I_C = 5.31 \times 10^{-40} \text{ g cm}^2$), and has a relatively low boiling point of $T = 112 \text{ K}$.

- a) Determine B_A , B_B , and B_C for this molecule.
b) Use the answer from part (a) to determine the rotational partition function. Is the high-temperature limit valid?

- a) Using the moment of inertia, the rotational constants can be determined. Since all three moments of inertia are equal, the rotational constants will be equal as well. Paying careful attention to units, the rotational constants are:

$$B_a = B_b = B_c = \frac{h}{8\pi^2 c I} = \frac{6.626 \times 10^{-34} \text{ J s}}{8\pi^2 (3.00 \times 10^8 \text{ m s}^{-1})(5.31 \times 10^{-47} \text{ kg m}^2)} = 5.27 \text{ cm}^{-1}$$

- b) If the high-temperature limit is valid $T > \Theta_R$. Determining Θ_R :

$$\Theta_R = \frac{B}{k} = \frac{5.27 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}} = 7.58 \text{ K}$$

The boiling temperature of CH₄ (112 K) is much greater than the rotational temperature; therefore, the high-temperature limit is appropriate.

P32.16) Calculate the vibrational partition function for H³⁵Cl at 300 and 3000 K. What fraction of molecules will be in the ground vibrational state at these temperatures?

At 300 K:

$$q = \frac{1}{1 - e^{-\beta hc\tilde{\nu}}} = \frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm}^{-1} \text{ s})(2990 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}} \cong 1.00$$

$$p_n = \frac{e^{-\beta hc\tilde{\nu}}}{q}$$

$$p_0 = \frac{1}{q} \cong 1.00$$

and at 3000 K:

$$q = \frac{1}{1 - e^{-\beta hc\tilde{\nu}}} = \frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm}^{-1} \text{ s})(2990 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(3000 \text{ K})}} = 1.32$$

$$p_n = \frac{e^{-\beta hc\tilde{\nu}}}{q}$$

$$p_0 = \frac{1}{q} = 0.762$$

P32.17) For IF ($\tilde{\nu} = 610 \text{ cm}^{-1}$) calculate the vibrational partition function and populations in the first three vibrational energy levels for $T = 300$ and 3000 K . Repeat this calculation for IBr ($\tilde{\nu} = 269 \text{ cm}^{-1}$). Compare the probabilities for IF and IBr. Can you explain the differences between the probabilities of these molecules?

At 300 K for IF:

$$q = \frac{1}{1 - e^{-\beta hc\tilde{\nu}}} = \frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm}^{-1} \text{ s})(610 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}} \cong 1.06$$

$$p_n = \frac{e^{-\beta h c n \bar{v}}}{q}$$

$$p_0 = \frac{1}{q} = 0.943$$

$$p_1 = \frac{e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(610 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}}}{q} = 0.051$$

$$p_2 = \frac{e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(2)(610 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}}}{q} = 0.003$$

Repeating the above calculations for $T = 3000 \text{ K}$:

$$q = 3.94$$

$$p_0 = 0.254$$

$$p_1 = 0.189$$

$$p_2 = 0.141$$

Repeating the above calculations for IBr at 300 and 3000 K:

300 K		3000 K	
q	1.38	q	8.26
p_0	0.725	p_0	0.121
p_1	0.199	p_1	0.106
p_2	0.054	p_2	0.094

The probability of occupying a specific energy level is greater for IBr relative to IF for a given temperature since the energy-level spacings are smaller for IBr.

P32.18) Evaluate the vibrational partition function for H₂O at 2000 K where the vibrational frequencies are 1615, 3694, and 3802 cm⁻¹.

The total vibrational partition function is the product of partition functions for each vibrational degree of freedom:

$$\begin{aligned}
 q_{V,\text{total}} &= (q_{V,1})(q_{V,2})(q_{V,3}) \\
 &= \left(\frac{1}{1-e^{\beta hc\tilde{\nu}_1}} \right) \left(\frac{1}{1-e^{\beta hc\tilde{\nu}_2}} \right) \left(\frac{1}{1-e^{\beta hc\tilde{\nu}_3}} \right) \\
 &= \left(\frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(1615 \text{ cm}^{-1})}{1-e^{\frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(2000 \text{ K})}{}}}} \right) \left(\frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(3694 \text{ cm}^{-1})}{1-e^{\frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(2000 \text{ K})}{}}}} \right) \\
 &\quad \times \left(\frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(3802 \text{ cm}^{-1})}{1-e^{\frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(2000 \text{ K})}{}}}} \right) \\
 &= 1.67
 \end{aligned}$$

P32.19) Evaluate the vibrational partition function for SO₂ at 298 K where the vibrational frequencies are 519, 1151, and 1361 cm⁻¹.

The total vibrational partition function is the product of partition functions for each vibrational degree of freedom:

$$\begin{aligned}
 q_{V,\text{total}} &= (q_{V,1})(q_{V,2})(q_{V,3}) \\
 &= \left(\frac{1}{1-e^{\beta hc\tilde{\nu}_1}} \right) \left(\frac{1}{1-e^{\beta hc\tilde{\nu}_2}} \right) \left(\frac{1}{1-e^{\beta hc\tilde{\nu}_3}} \right) \\
 &= \left(\frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(519 \text{ cm}^{-1})}{1-e^{\frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}{}}}} \right) \left(\frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(1151 \text{ cm}^{-1})}{1-e^{\frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}{}}}} \right) \\
 &\quad \times \left(\frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(1361 \text{ cm}^{-1})}{1-e^{\frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}{}}}} \right) \\
 &= 1.09
 \end{aligned}$$

P32.20) Evaluate the vibrational partition function for NH₃ at 1000 K for which the vibrational frequencies are 950, 1627.5 (doubly degenerate), 3335, and 3414 cm⁻¹ (doubly degenerate). Are there any modes that you can disregard in this calculation? Why or why not?

The total vibrational partition function is the product of partition functions for each vibrational degree of freedom, with the partition function for the mode with degeneracy raised to the power equal to the degeneracy:

$$\begin{aligned}
 q_{V,\text{total}} &= (q_{V,1})(q_{V,2})^2 (q_{V,3})(q_{V,4})^2 \\
 &= \left(\frac{1}{1-e^{\beta hc\tilde{v}_1}} \right) \left(\frac{1}{1-e^{\beta hc\tilde{v}_2}} \right)^2 \left(\frac{1}{1-e^{\beta hc\tilde{v}_3}} \right) \left(\frac{1}{1-e^{\beta hc\tilde{v}_4}} \right)^2 \\
 &= \left(\frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(950 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}} \right) \left(\frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(1627.5 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}} \right)^2 \\
 &\quad \times \left(\frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(3335 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}} \right) \left(\frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(3414 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}} \right)^2 \\
 &= (1.34)(1.11)^2 (1.01)(1.01)^2 \\
 &= 1.70
 \end{aligned}$$

Notice that the two highest-frequency vibrational degrees of freedom have partition functions that are near unity; therefore, their contribution to the total partition function is modest, and could be ignored to a reasonable approximation in evaluating the total partition function.

P32.21) In deriving the vibrational partition function, a mathematical expression for the series expression for the partition function was employed. However, what if one performed integration instead of summation to evaluate the partition function? Evaluate the following expression for the vibrational partition function:

$$q_v = \sum_{n=0}^{\infty} e^{-\beta hc n \tilde{v}} \approx \int_0^{\infty} e^{-\beta hc n \tilde{v}} dn$$

Under what conditions would you expect the resulting expression for q_V to be applicable?

$$\begin{aligned}
 q_v &\approx \int_0^{\infty} e^{-\beta hc n \tilde{v}} dn = \int_0^{\infty} e^{-\alpha n} dn \quad \{\alpha = \beta hc \tilde{v}\} \\
 &= \frac{-e^{-\alpha n}}{\alpha} \Big|_0^{\infty} = \frac{1}{\alpha} = \frac{1}{\beta hc \tilde{v}}
 \end{aligned}$$

This expression for q_V is expected to be valid in the high-temperature limit where many vibrational states will be populated thereby justifying evaluation of the partition function by integration over n .

P32.22) You have in your possession the first vibrational spectrum of a new diatomic molecule, X_2 , obtained at 1000 K. From the spectrum you determine that the fraction of molecules occupying a given vibrational energy state n is as follows:

n	0	1	2	3	>3
Fraction	0.352	0.184	0.0963	0.050	0.318

What are the vibrational energy spacings for X_2 ?

To answer this question, it is helpful to consider the ratio of populations between any two vibrational levels, denoted as n and n' :

$$\frac{p_n}{p_{n'}} = \frac{\frac{e^{-\beta h c n \tilde{\nu}}}{q}}{\frac{e^{-\beta h c n' \tilde{\nu}}}{q}} = e^{-\beta h c \tilde{\nu} (n - n')}$$

Therefore, the ratio of populations between any two states can be used to determine $\tilde{\nu}$ through evaluation of the above expression. Performing this evaluation for $n = 1$ and $n' = 3$:

$$\begin{aligned} \frac{p_1}{p_3} &= \frac{0.184}{0.050} = 3.68 = e^{-\beta h c \tilde{\nu} (1-3)} = e^{2\beta h c \tilde{\nu}} \\ 1.30 &= 2\beta h c \tilde{\nu} \\ \frac{1.30(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}{2(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})} &= \tilde{\nu} \\ 451 \text{ cm}^{-1} &= \tilde{\nu} \end{aligned}$$

P32.23)

a) In this chapter, the assumption was made that the harmonic oscillator model is valid such that anharmonicity can be neglected. However, anharmonicity can be included in the expression for vibrational energies. The energy levels for an anharmonic oscillator are given by

$$E_n = hc\tilde{\nu}\left(n + \frac{1}{2}\right) - hc\tilde{\chi}\tilde{\nu}\left(n + \frac{1}{2}\right)^2 + \dots$$

Neglecting zero point energy, the energy levels become $E_n = hc\tilde{\nu}n - hc\tilde{\chi}\tilde{\nu}n^2 + \dots$.

Using the preceding expression, demonstrate that the vibrational partition function for the anharmonic oscillator is

$$q_{V,anharmonic} = q_{V,harm}\left(1 + \beta hc\tilde{\chi}\tilde{\nu}q_{V,harm}^2 \left(e^{-2\beta\tilde{\nu}n} + e^{-\beta\tilde{\nu}n}\right)\right)$$

In deriving the preceding result, the following series relationship will prove useful:

$$\sum_{n=0}^{\infty} n^2 x^n = \frac{x^2 + x}{(1-x)^3}$$

b) For H₂, $\tilde{\nu} = 4401.2 \text{ cm}^{-1}$ and $\tilde{\chi}\tilde{\nu} = 121.3 \text{ cm}^{-1}$. Use the result from part (a) to determine the percent error in q_V if anharmonicity is ignored.

a)

$$q = \sum_n e^{-\beta E_n} = \sum_n e^{-\beta(hc\tilde{\nu}n - hc\tilde{\chi}\tilde{\nu}n^2)} = \sum_n e^{-\beta hc\tilde{\nu}n} e^{\beta hc\tilde{\chi}\tilde{\nu}n^2}$$

Performing a series expansion for the second exponential term, and keeping only the first two terms since the exponent will be small for limited anharmonicity:

$$\begin{aligned} q &= \sum_n e^{-\beta hc\tilde{\nu}n} e^{\beta hc\tilde{\chi}\tilde{\nu}n^2} = \sum_n e^{-\beta hc\tilde{\nu}n} (1 + \beta hc\tilde{\chi}\tilde{\nu}n^2) \\ &= \sum_n e^{-\beta hc\tilde{\nu}n} + \sum_n (\beta hc\tilde{\chi}\tilde{\nu}n^2) e^{-\beta hc\tilde{\nu}n} \\ &= q_{harm} + \beta hc\tilde{\chi}\tilde{\nu} \sum_n n^2 e^{-\beta hc\tilde{\nu}n} \\ &= q_{harm} + \beta hc\tilde{\chi}\tilde{\nu} \sum_n n^2 (e^{-\beta hc\tilde{\nu}})^n \end{aligned}$$

Using series expression provided in the problem to evaluate the second term in the preceding expression:

$$\begin{aligned} q &= q_{harm} + \beta hc\tilde{\chi}\tilde{\nu} \sum_n n^2 (e^{-\beta hc\tilde{\nu}})^n = q_{harm} + (\beta hc\tilde{\chi}\tilde{\nu}) \left[\frac{e^{-2\beta hc\tilde{\nu}} + e^{-\beta hc\tilde{\nu}}}{(1 - e^{-\beta hc\tilde{\nu}})^3} \right] \\ &= q_{harm} + (\beta hc\tilde{\chi}\tilde{\nu}) (q_{harm}^3) (e^{-2\beta hc\tilde{\nu}} + e^{-\beta hc\tilde{\nu}}) \\ &= q_{harm} (1 + (\beta hc\tilde{\chi}\tilde{\nu}) (q_{harm}^2) (e^{-2\beta hc\tilde{\nu}} + e^{-\beta hc\tilde{\nu}})) \end{aligned}$$

b) First, the partition function in the harmonic-oscillator limit is:

$$q_{harm} = \frac{1}{1 - e^{-\beta hc\tilde{\nu}}} = \frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(4401.2 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}} = 1.0018$$

Next, evaluating the expression for the anharmonic oscillator:

$$\begin{aligned} q_{anhar} &= q_{harm} (1 + (\beta hc\tilde{\chi}\tilde{\nu}) (q_{harm}^2) (e^{-2\beta hc\tilde{\nu}} + e^{-\beta hc\tilde{\nu}})) \\ &= (1.0018) \left(1 + \left(\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(121.3 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})} \right) \right. \\ &\quad \left. \times \left(e^{\frac{2(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(4401.2 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}} + e^{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(4401.2 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}} \right) \right) \\ &= (1.0018) (1 + (0.175) (3.12 \times 10^{-6} + 1.76 \times 10^{-3})) \\ &= 1.0021 \end{aligned}$$

The percent error is :

$$\%error = \frac{q_{anharm} - q_{harm}}{q_{anharm}} \times 100\% = 0.03\%$$

P32.24) Consider a particle free to translate in one dimension. The classical Hamiltonian is $H = \frac{p^2}{2m}$.

a) Determine $q_{classical}$ for this system. To what quantum system should you compare it in order to determine the equivalence of the classical and quantum statistical mechanical treatments?

b) Derive $q_{classical}$ for a system with translational motion in three dimensions for which:

$$H = (p_x^2 + p_y^2 + p_z^2)/2m.$$

a) The particle in a one-dimensional box model is the appropriate quantum-mechanical model for comparison. Integrating

$$q_{class} = \frac{1}{h} \int_{-\infty}^{\infty} \int_0^L e^{-\beta p^2/2m} dx dp = \frac{2L}{h} \int_0^{\infty} e^{-\beta p^2/2m} dp = \frac{2L}{h} \left(\frac{1}{2} \sqrt{\frac{\pi}{\beta/2m}} \right) = L \left(\frac{h^2}{2\pi mkT} \right)^{-1/2} = \frac{L}{\Lambda}$$

b)

$$\begin{aligned} q_{class} &= \frac{1}{h^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^L \int_0^{L_x} \int_0^{L_z} e^{-\beta(p_x^2 + p_y^2 + p_z^2)/2m} dx dy dz dp_x dp_y dp_z \\ &= \frac{8(L_x L_y L_z)}{h^3} \int_0^{\infty} \int_0^{\infty} \int_0^{\infty} e^{-\beta(p_x^2 + p_y^2 + p_z^2)/2m} dp_x dp_y dp_z \\ &= \frac{8V}{h} \left(\frac{1}{2} \sqrt{\frac{\pi}{\beta/2m}} \right)^3 = V \left(\frac{h^2}{2\pi mkT} \right)^{-3/2} = \frac{L}{\Lambda^3} \end{aligned}$$

P32.25) Evaluate the electronic partition function for atomic Fe at 298 K given the following energy levels. Terms in parentheses are divided by $2m$.

Level (n)	Energy (cm $^{-1}$)	Degeneracy
0	0	9
1	415.9	7
2	704.0	5
3	888.1	3
4	978.1	1

$$\begin{aligned}
 q_E &= \sum_n g_n e^{-\beta \epsilon_n} = 9e^{-0} + 7e^{-\beta(415.9 \text{ cm}^{-1})} + 5e^{-\beta(704.0 \text{ cm}^{-1})} + 3e^{-\beta(881.1 \text{ cm}^{-1})} + e^{-\beta(978.1 \text{ cm}^{-1})} \\
 &= 9 + 7e^{-\frac{415.9 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} + 5e^{-\frac{704.0 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} + 3e^{-\frac{881.1 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} + e^{-\frac{978.1 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} \\
 &= 9 + 7(0.134) + 5(0.033) + 3(0.014) + 0.009 \\
 q_E &= 10.2
 \end{aligned}$$

P32.26)

- a) Evaluate the electronic partition function for atomic Si at 298 K given the following energy levels:

Level (n)	Energy (cm^{-1})	Degeneracy
0	0	1
1	77.1	3
2	223.2	5
3	6298	5

- b) At what temperature will the $n = 3$ energy level contribute 0.1 to the electronic partition function?

a)

$$\begin{aligned}
 q_E &= \sum_n g_n e^{-\beta \epsilon_n} = 1e^{-0} + 3e^{-\beta(77.1 \text{ cm}^{-1})} + 5e^{-\beta(223.2 \text{ cm}^{-1})} + 5e^{-\beta(6298 \text{ cm}^{-1})} \\
 &= 1 + 3e^{-\frac{77.1 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} + 5e^{-\frac{223.2 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} + 3e^{-\frac{6298 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} \\
 &= 1 + 3(0.689) + 5(0.340) + 5(6.22 \times 10^{-14}) \\
 q_E &= 4.77
 \end{aligned}$$

- b) Focusing on the contribution to q_E from the $n = 3$ level:

$$\begin{aligned}
 0.1 &= g_3 e^{-\beta \epsilon_3} = 5e^{-\frac{6298 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(T)}} \\
 3.91 &= \frac{6298 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(T)} \\
 T &= \frac{6298 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(3.91)} \\
 T &= 2318 \text{ K}
 \end{aligned}$$

P32.27) NO is a well-known example of a molecular system in which excited electronic energy levels are readily accessible at room temperature. Both the ground and excited electronic states are doubly degenerate, and separated by $\sim 121 \text{ cm}^{-1}$.

- a) Evaluate the electronic partition function for this molecule at 298 K.

- b) Determine the temperature at which $q_E = 3$.

a)

$$\begin{aligned} q_E &= \sum_n g_n e^{-\beta \epsilon_n} = 2e^{-\beta 0} + 2e^{-\beta(121 \text{ cm}^{-1})} \\ &= 2 + 2e^{-\frac{121 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} \\ &= 3.12 \end{aligned}$$

b)

$$\begin{aligned} q_E &= 3 = 2e^{-\beta 0} + 2e^{-\beta(121 \text{ cm}^{-1})} \\ 3 &= 2 + 2e^{-\frac{121 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})T}} \\ 0.5 &= e^{-\frac{121 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})T}} \\ 0.693 &= \frac{121 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})T} \\ T &= \frac{121 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(0.693)} \\ T &= 251 \text{ K} \end{aligned}$$

P32.28) Determine the total molecular partition function for I₂, confined to a volume of 1000 cm³ at 298 K. Other information you will find useful: $B = 0.0374 \text{ cm}^{-1}$, $\tilde{\nu} = 208 \text{ cm}^{-1}$, and the ground electronic state is nondegenerate.

Since q_{Total} is the product of partition functions for each energetic degree of freedom (translational, rotational, vibrational, and electronic), it is more straightforward to calculate the partition function for each of these degrees of freedom separately, then take the product of these functions:

$$\begin{aligned} q_T &= \frac{V}{\Lambda^3} \\ \Lambda &= \left(\frac{h^2}{2\pi mkT} \right)^{1/2} = \left(\frac{(6.626 \times 10^{-34} \text{ J s})^2}{2\pi \left(\frac{0.254 \text{ kg mol}^{-1}}{N_A} \right) (1.38 \times 10^{-23} \text{ J K}^{-1}) (298 \text{ K})} \right)^{1/2} = 6.35 \times 10^{-12} \text{ m} \\ q_T &= \frac{V}{(6.35 \times 10^{-12} \text{ m})^3} = \frac{(1000 \text{ cm}^3)(10^{-6} \text{ m}^3 \text{ cm}^{-3})}{(6.35 \times 10^{-12} \text{ m})^3} = 3.91 \times 10^{30} \end{aligned}$$

$$q_R = \left(\frac{1}{\sigma \beta h c B} \right) = \left(\frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}{(2)(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(0.0374 \text{ cm}^{-1})} \right) \\ = 2.77 \times 10^3$$

$$q_V = \frac{1}{1 - e^{-\beta hc \bar{v}}} = \frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(208 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}} \\ = 1.58$$

$$q_E = 1$$

$$q_{total} = q_T q_R q_V q_E = (3.91 \times 10^{30})(2.77 \times 10^3)(1.58)(1) = 1.71 \times 10^{34}$$

P32.29) Determine the total molecular partition function for gaseous H₂O at 1000 K confined to a volume of 1 cm³. The rotational constants for water are $B_A = 27.8 \text{ cm}^{-1}$, $B_B = 14.5 \text{ cm}^{-1}$, and $B_C = 9.95 \text{ cm}^{-1}$. The vibrational frequencies are 1615, 3694, and 3802 cm⁻¹. The ground electronic state is nondegenerate.

Since q_{Total} is the product of partition functions for each energetic degree of freedom (translational, rotational, vibrational, and electronic), it is more straightforward to calculate the partition function for each of these degrees of freedom separately, then take the product of these functions:

$$q_T = \frac{V}{\Lambda^3}$$

$$\Lambda = \left(\frac{h^2}{2\pi mkT} \right)^{\frac{1}{2}} = \left(\frac{(6.626 \times 10^{-34} \text{ J s})^2}{2\pi \left(\frac{0.018 \text{ kg mol}^{-1}}{N_A} \right) (1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})} \right)^{\frac{1}{2}} = 1.30 \times 10^{-11} \text{ m}$$

$$q_T = \frac{V}{(1.30 \times 10^{-11} \text{ m})^3} = \frac{(1 \text{ cm}^3)(10^{-6} \text{ m}^3 \text{ cm}^{-3})}{(1.30 \times 10^{-11} \text{ m})^3} = 4.53 \times 10^{26}$$

$$\begin{aligned}
 q_R &= \frac{\sqrt{\pi}}{\sigma} \left(\frac{1}{\beta h c B_A} \right)^{1/2} \left(\frac{1}{\beta h c B_B} \right)^{1/2} \left(\frac{1}{\beta h c B_C} \right)^{1/2} = \\
 &= \frac{\sqrt{\pi}}{2} \left(\frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(27.8 \text{ cm}^{-1})} \right)^{1/2} \\
 &\quad \times \left(\frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(14.5 \text{ cm}^{-1})} \right)^{1/2} \\
 &\quad \times \left(\frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(9.95 \text{ cm}^{-1})} \right)^{1/2} \\
 &= 256
 \end{aligned}$$

$$\begin{aligned}
 q_V &= \left(\frac{1}{1 - e^{-\beta h c \tilde{V}_1}} \right) \left(\frac{1}{1 - e^{-\beta h c \tilde{V}_2}} \right) \left(\frac{1}{1 - e^{-\beta h c \tilde{V}_3}} \right) \\
 &= \left(\frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(1615 \text{ cm}^{-1})}{1 - e^{-(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}}} \right) \\
 &\quad \times \left(\frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(3694 \text{ cm}^{-1})}{1 - e^{-(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}}} \right) \\
 &\quad \times \left(\frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(3802 \text{ cm}^{-1})}{1 - e^{-(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}}} \right) \\
 &= (1.11)(1.01)(1.00) \\
 &= 1.12
 \end{aligned}$$

$$q_E = 1$$

$$q_{total} = q_T q_R q_V q_E = (4.53 \times 10^{26})(256)(1.12)(1) = 1.30 \times 10^{29}$$

P32.30) The effect of symmetry on the rotational partition function for H₂ was evaluated by recognizing that each hydrogen is a spin 1/2 particle and is, therefore, a fermion. However, this development is not limited to fermions, but is also applicable to bosons. Consider CO₂ in which rotation by 180° results in the interchange of two spin 0 particles.

- a) Because the overall wave function describing the interchange of two bosons must be symmetric with respect to exchange, to what J levels is the summation limited to in evaluating q_R for CO₂?
- b) The rotational constant for CO₂ is 0.390 cm⁻¹. Calculate q_R at 298 K. Do you have to evaluate q_R by summation of the allowed rotational energy levels? Why or why not?
- a) To ensure that the wavefunction remain symmetric with exchange, the rotational part of the wavefunction must be even; therefore, only even J states (0, 2, 4, 6, ...) are allowed.

- b) Since T >> Θ_R (i.e., 298 K >> 0.56 K) the high-temperature approximation can be applied in evaluating the rotational partition function:

$$\begin{aligned} q_R &= \frac{1}{\sigma \beta h c B} = \frac{kT}{\sigma h c B} \\ &= \frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}{2(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm}^{-1} \text{ s}^{-1})(0.390 \text{ cm}^{-1})} \\ &= 265 \end{aligned}$$

This calculation illustrates that there are roughly 265 rotational states available to CO₂ at 298 K; therefore, the high-temperature expression for the rotational partition function is more than reasonable.

Chapter 33: Statistical Thermodynamics

Problem numbers in italics indicate that the solution is included in the *Student's Solutions Manual*.

Questions on Concepts

Q33.1) What is the relationship between ensemble energy and the thermodynamic concept of internal energy?

The ensemble energy is equal to the difference in internal energy at some finite temperature to that present at 0 K.

Q33.2) List the energetic degrees of freedom expected to contribute to the internal energy at 298 K for a diatomic molecule. Given this list, what spectroscopic information do you need to numerically determine the internal energy?

Translational, rotational, and vibrational energetic degrees of freedom are expected to contribute to the internal energy at 298 K. Translational degrees of freedom will be in the high-temperature limit; therefore, a molar contribution of $1/2RT$ per degree of freedom is expected. Rotations are also expected to be in the high-temperature limit. Since a diatomic has two non-vanishing moments of inertia, a molar contribution of RT is expected. Finally, one needs to know the vibrational frequency to determine if the high-temperature limit is appropriate, and if not to determine the vibrational contribution to the internal energy.

Q33.3) List the energetic degrees of freedom for which the contribution to the internal energy determined by statistical mechanics is equal to the prediction of the equipartition theorem at 298 K.

The high-temperature approximation will generally be applicable to translations and rotations at 298 K; therefore, these degrees of freedom will make contributions to the internal energy in accord with the equipartition theorem.

Q33.4) Write down the contribution to the constant volume heat capacity from translations and rotations for an ideal monatomic, diatomic, and nonlinear polyatomic gas, assuming that the high-temperature limit is appropriate for the rotational degrees of freedom.

	monatomic	diatomic	Non-linear polyatomic
translations	$3/2 R$	$3/2 R$	$3/2 R$
rotations	0	R	$3/2 R$

Q33.5) When are rotational degrees of freedom expected to contribute R or $3/2R$ (linear and nonlinear, respectively) to the molar constant volume heat capacity? When will a vibrational degree of freedom contribute R to the molar heat capacity?

The rotational degrees of freedom will contribute R or $3/2R$ to the molar constant-volume heat capacity when the high-temperature limit is valid, defined as when $T > 10\Theta_R$ where Θ_R is the rotational temperature, defined as B/k . A vibrational degree of freedom will contribute R to the molar heat capacity when the high-temperature limit is applicable, defined as when $T > 10\Theta_V$ where Θ_V is the vibrational temperature, defined as \tilde{v}/k .

Q33.6) Why do electronic degrees of freedom generally not contribute to the constant volume heat capacity?

The electronic degrees of freedom do not generally contribute to the constant volume heat capacity since the electronic-energy level spacings are generally quite large compared to kT . Therefore, the higher electronic energy levels are not readily accessible so that the contribution to the heat capacity is minimal.

Q33.7) What is the Boltzmann formula, and how can it be used to predict residual entropy?

$S = k \ln(W)$ where S is entropy, W is weight, and k is Boltzmann's constant. This equation can be used to determine the residual entropy in a crystal at 0 K associated with the number of spatial arrangements available to the system.

Q33.8) How does the Boltzmann formula provide an understanding of the third law of thermodynamics?

For a perfect crystal at low temperature, only one spatial arrangement of the atoms or molecules will be present so that $W = 1$ and $S = 0$.

Q33.9) Which thermodynamic quantity is used to derive the ideal gas law for a monatomic gas? What molecular partition function is employed in this derivation? Why?

The Helmholtz energy can be used to derive the ideal gas law for a monatomic gas. The translational partition function is employed in the derivation since one is dealing with a monatomic gas for which rotations and vibrations are not present. It should be noted that the derivation can be performed for a molecular system, and will also result in the ideal gas law (see Problem P33.24 of this chapter).

Q33.10) What is the definition of "zero" energy employed in constructing the statistical mechanical expression for the equilibrium constant? Why was this definition necessary?

The zero of energy is the dissociation energy for each molecule. It is employed to establish a common energetic reference state for all species involved in the reaction of interest.

Q33.11) Assume you have an equilibrium expression that involves monatomic species only. What difference in energy between reactants and products would you use in the expression for K_P ?

The difference in energy would be zero; therefore, only the ratio of translational and electronic partition functions would be relevant when calculating the equilibrium constant.

Problems

P33.1) Consider two separate ensembles of particles characterized by the energy-level diagram provided in the text. Derive expressions for the internal energy for each ensemble. At 298 K, which ensemble is expected to have the greatest internal energy?

$$U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V = -N\left(\frac{\partial \ln q}{\partial \beta}\right)_V = \frac{-N}{q} \left(\frac{\partial q}{\partial \beta}\right)_V$$

$$\begin{aligned} q_A &= \sum_n g_n e^{-\beta E_n} = 1 + e^{-\beta(300 \text{ cm}^{-1})} + e^{-\beta(600 \text{ cm}^{-1})} \\ U_A &= \frac{-N}{1 + e^{-\beta(300 \text{ cm}^{-1})} + e^{-\beta(600 \text{ cm}^{-1})}} \left(\frac{\partial}{\partial \beta} (1 + e^{-\beta(300 \text{ cm}^{-1})} + e^{-\beta(600 \text{ cm}^{-1})}) \right) \\ &= \frac{-N}{1 + e^{-\beta(300 \text{ cm}^{-1})} + e^{-\beta(600 \text{ cm}^{-1})}} \left(-((300 \text{ cm}^{-1})e^{-\beta(300 \text{ cm}^{-1})} + (600 \text{ cm}^{-1})e^{-\beta(600 \text{ cm}^{-1})}) \right) \\ &= \frac{N((300 \text{ cm}^{-1})e^{-\beta(300 \text{ cm}^{-1})} + (600 \text{ cm}^{-1})e^{-\beta(600 \text{ cm}^{-1})})}{1 + e^{-\beta(300 \text{ cm}^{-1})} + e^{-\beta(600 \text{ cm}^{-1})}} \end{aligned}$$

$$\begin{aligned} q_B &= \sum_n g_n e^{-\beta E_n} = 1 + 2e^{-\beta(300 \text{ cm}^{-1})} + e^{-\beta(600 \text{ cm}^{-1})} \\ U_B &= \frac{-N}{1 + 2e^{-\beta(300 \text{ cm}^{-1})} + e^{-\beta(600 \text{ cm}^{-1})}} \left(\frac{\partial}{\partial \beta} (1 + 2e^{-\beta(300 \text{ cm}^{-1})} + e^{-\beta(600 \text{ cm}^{-1})}) \right) \\ &= \frac{-N}{1 + 2e^{-\beta(300 \text{ cm}^{-1})} + e^{-\beta(600 \text{ cm}^{-1})}} \left(-((600 \text{ cm}^{-1})e^{-\beta(300 \text{ cm}^{-1})} + (600 \text{ cm}^{-1})e^{-\beta(600 \text{ cm}^{-1})}) \right) \\ &= \frac{N(600 \text{ cm}^{-1})(e^{-\beta(300 \text{ cm}^{-1})} + e^{-\beta(600 \text{ cm}^{-1})})}{1 + 2e^{-\beta(300 \text{ cm}^{-1})} + e^{-\beta(600 \text{ cm}^{-1})}} \end{aligned}$$

Evaluating the expressions for U_A and U_B at 298 K:

$$U_A = \frac{N \left((300 \text{ cm}^{-1}) e^{-\frac{(300 \text{ cm}^{-1})}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} + (600 \text{ cm}^{-1}) e^{-\frac{(600 \text{ cm}^{-1})}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} \right)}{1 + e^{-\frac{(300 \text{ cm}^{-1})}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} + e^{-\frac{(600 \text{ cm}^{-1})}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}}}$$

$$= N(80.3 \text{ cm}^{-1})$$

$$U_B = \frac{N(600 \text{ cm}^{-1}) \left(e^{-\frac{(300 \text{ cm}^{-1})}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} + e^{-\frac{(600 \text{ cm}^{-1})}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} \right)}{1 + 2e^{-\frac{(300 \text{ cm}^{-1})}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} + e^{-\frac{(600 \text{ cm}^{-1})}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}}}$$

$$= N(114 \text{ cm}^{-1})$$

Ensemble B will have the larger internal energy.

P33.2) What is the contribution to the internal energy from translations for an ideal monatomic gas confined to move on a surface? What is the expected contribution from the equipartition theorem?

Motion on a surface is equivalent to translation in two dimensions. From the equipartition theorem, $1/2 RT$ per translational degree of freedom is expected, or RT in total for two-dimensional translation. In evaluating the internal energy for this system, the translational partition function in two dimensions is required:

$$q_{T,2D} = \frac{A}{\Lambda^2} \quad \text{where } A = \text{area}$$

$$U = \frac{-N}{q_{T,2D}} \left(\frac{\partial q_{T,2D}}{\partial \beta} \right)_V$$

$$U = \frac{-N}{q_{T,2D}} \left(\frac{\partial}{\partial \beta} \left(\frac{A}{\Lambda^2} \right) \right)_V = \frac{-N(A)}{q_{T,2D}} \left(\frac{\partial}{\partial \beta} \left(\frac{2\pi m}{h^2 \beta} \right) \right)_V = \frac{-N(A) \left(\frac{2\pi m}{h^2} \right)}{q_{T,2D}} \left(\frac{\partial}{\partial \beta} \beta^{-1} \right)_V$$

$$U = \frac{-N(A) \left(\frac{2\pi m}{h^2} \right)}{q_{T,2D}} (-\beta^{-2}) = \frac{N \left(\frac{A}{\Lambda^2} \right) (\beta^{-1})}{q_{T,2D}}$$

$$U = N(\beta^{-1}) = NkT = nRT$$

P33.3) For a system of energy levels, $\epsilon_m = m^2\alpha$, where α is a constant with units of energy and $m = 0, 1, 2, \dots, \infty$. What is the internal energy and heat capacity of this system in the high-temperature limit?

Writing out the expression for the partition function, and recognizing that in the high-temperature limit the partition function can be evaluated by integration:

$$\begin{aligned} q &= \sum_m e^{-\beta\epsilon_m} = \sum_m e^{-\beta\alpha m^2} \cong \int_0^\infty e^{-\beta\alpha m^2} dm = \frac{1}{2} \sqrt{\frac{\pi}{\alpha\beta}} \\ U &= \frac{-N}{q} \left(\frac{\partial q}{\partial \beta} \right)_V = \frac{-N}{q} \left(\frac{1}{2} \sqrt{\frac{\pi}{\alpha}} \right) \left(\frac{\partial}{\partial \beta} \beta^{-\frac{1}{2}} \right)_V \\ &= \frac{-N}{q} \left(\frac{1}{2} \sqrt{\frac{\pi}{\alpha}} \right) \left(-\frac{1}{2} \beta^{-\frac{3}{2}} \right) = \frac{1}{2} N \beta^{-1} = \frac{1}{2} N k T \\ C_V &= \left(\frac{\partial U}{\partial T} \right)_V = \frac{1}{2} N k \end{aligned}$$

P33.4) Consider the following table of diatomic molecules and associated rotational constants:

Molecule	B (cm $^{-1}$)	$\tilde{\nu}$ (cm $^{-1}$)
H 35 Cl	10.59	2886
12 C 16 O	1.93	2170
39 KI	0.061	200
CsI	0.024	120

- a) Calculate the rotational temperature for each molecule.
- b) Assuming that these species remain gaseous at 100 K, for which species is the equipartition theorem prediction for the rotational contribution to the internal energy appropriate?
- c) Calculate the vibrational temperature for each molecule.
- d) If these species were to remain gaseous at 1000 K, for which species is the equipartition theorem prediction for the vibrational contribution to the internal energy appropriate?

The rotational and vibrational temperatures are given by:

$$\theta_R = \frac{B}{k} \quad \theta_V = \frac{\tilde{\nu}}{k}$$

The high-temperature approximation will be valid for rotations or vibrations when the temperature is at least 10-fold greater than the rotational or vibrational temperature, respectively. Using the spectroscopic information provided in the table:

Molecule	θ_R (K)	High-T for R?	θ_V (K)	High-T for V?
H ³⁵ Cl	15.3	no	4153	no
¹² C ¹⁶ O	2.78	yes	3123	no
³⁹ KI	0.088	yes	288	no
CsI	0.035	yes	173	no

P33.5) The lowest four energy levels for atomic vanadium (V) have the following energies and degeneracies:

Level (n)	Energy (cm ⁻¹)	Degeneracy
0	0	4
1	137.38	6
2	323.46	8
3	552.96	10

What is the contribution to the average energy from electronic degrees of freedom for V when $T = 298$ K?

$$q = \sum_n g_n e^{-\beta E_n} = 4 + 6e^{-\beta(137.38 \text{ cm}^{-1})} + 8e^{-\beta(323.46 \text{ cm}^{-1})} + 10e^{-\beta(552.96 \text{ cm}^{-1})}$$

$$\left(\frac{\partial q}{\partial \beta}\right)_V = -\left((824 \text{ cm}^{-1})e^{-\beta(137.38 \text{ cm}^{-1})} + (2588 \text{ cm}^{-1})e^{-\beta(323.46 \text{ cm}^{-1})} + (5530 \text{ cm}^{-1})e^{-\beta(552.96 \text{ cm}^{-1})}\right)$$

$$U = \frac{-N}{q} \left(\frac{\partial q}{\partial \beta}\right)_V = N \frac{(824 \text{ cm}^{-1})e^{-\beta(137.38 \text{ cm}^{-1})} + (2588 \text{ cm}^{-1})e^{-\beta(323.46 \text{ cm}^{-1})} + (5530 \text{ cm}^{-1})e^{-\beta(552.96 \text{ cm}^{-1})}}{4 + 6e^{-\beta(137.38 \text{ cm}^{-1})} + 8e^{-\beta(323.46 \text{ cm}^{-1})} + 10e^{-\beta(552.96 \text{ cm}^{-1})}}$$

$$= N(143 \text{ cm}^{-1})$$

converting to J:

$$U = N(143 \text{ cm}^{-1})hc = nN_A(143 \text{ cm}^{-1})(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1}) = n(1.71 \text{ kJ mol}^{-1})$$

$$U_m = 1.71 \text{ kJ mol}^{-1}$$

P33.6) Consider an ensemble of units in which the first excited electronic state at energy ε_1 is m_1 -fold degenerate, and the energy of the ground state is m_o -fold degenerate with energy ε_0 .

a) Demonstrate that if $\varepsilon_0 = 0$, the expression for the electronic partition function is

$$q_E = m_o \left(1 + \frac{m_1}{m_o} e^{-\varepsilon_1/kT} \right)$$

b) Determine the expression for the internal energy U of an ensemble of N such units. What is the limiting value of U as the temperature approaches zero and infinity?

a)

$$\begin{aligned} q &= m_0 e^{-\beta \epsilon_0} + m_1 e^{-\beta \epsilon_1} = m_0 + m_1 e^{-\beta \epsilon_1} \\ &= m_0 + m_0 \left(\frac{m_1}{m_0} \right) e^{-\beta \epsilon_1} \\ &= m_0 \left(1 + \left(\frac{m_1}{m_0} \right) e^{-\beta \epsilon_1} \right) \\ &= m_0 \left(1 + \left(\frac{m_1}{m_0} \right) e^{-\frac{\epsilon_1}{kT}} \right) \end{aligned}$$

b)

$$\begin{aligned} U &= \frac{-N}{q} \left(\frac{\partial q}{\partial \beta} \right)_V = \frac{-N}{q} \left(\frac{\partial}{\partial \beta} \left(m_0 \left(1 + \left(\frac{m_1}{m_0} \right) e^{-\beta \epsilon_1} \right) \right) \right)_V \\ &= \frac{-N}{q} (-m_1 \epsilon_1 e^{-\beta \epsilon_1}) \\ &= \frac{Nm_1 \epsilon_1 e^{-\beta \epsilon_1}}{m_0 \left(1 + \left(\frac{m_1}{m_0} \right) e^{-\beta \epsilon_1} \right)} = \frac{Nm_1 \epsilon_1 e^{-\frac{\epsilon_1}{kT}}}{m_0 \left(1 + \left(\frac{m_1}{m_0} \right) e^{-\frac{\epsilon_1}{kT}} \right)} \end{aligned}$$

Looking at the limiting behavior with temperature:

$$\begin{aligned} \lim_{T \rightarrow 0} U &= \lim_{T \rightarrow 0} \frac{Nm_1 \epsilon_1 e^{-\frac{\epsilon_1}{kT}}}{m_0 \left(1 + \left(\frac{m_1}{m_0} \right) e^{-\frac{\epsilon_1}{kT}} \right)} = \lim_{T \rightarrow 0} \frac{Nm_1 \epsilon_1}{m_0 \left(e^{\frac{\epsilon_1}{kT}} + \left(\frac{m_1}{m_0} \right) \right)} = 0 \\ \lim_{T \rightarrow \infty} U &= \lim_{T \rightarrow \infty} \frac{Nm_1 \epsilon_1 e^{-\frac{\epsilon_1}{kT}}}{m_0 \left(1 + \left(\frac{m_1}{m_0} \right) e^{-\frac{\epsilon_1}{kT}} \right)} = \frac{Nm_1 \epsilon_1}{m_0 + m_1} \end{aligned}$$

P33.7) Calculate the molar internal energy of He, Ne, and Ar under standard thermodynamic conditions. Do you need to redo the entire calculation for each species?

Since the high-temperature limit is applicable at $T = 298$ K for translational degrees of freedom, all three gases will have a contribution of $3/2 RT$ to the total energy from translations. Since all three species are monatomic, there are no rotational or vibrational contributions to the total internal energy. Finally, under the assumption that excited electronic energy levels are not accessible at this temperature, electronic degrees of

freedom will also not make a contribution to the total internal energy. Therefore, for all three species;

$$\begin{aligned} U_{total,m} &= U_{trans,m} + U_{rot,m} + U_{vib,m} + U_{elec,m} \\ &= U_{trans,m} = \frac{3}{2}RT = \frac{3}{2}(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \\ &= 3.72 \text{ kJ mol}^{-1} \end{aligned}$$

P33.8) Determine the internal energy of HCl ($B = 10.59 \text{ cm}^{-1}$ and $\tilde{\nu} = 2886 \text{ cm}^{-1}$) under standard thermodynamic conditions.

The translational and rotational energetic degrees of freedom will be in the high temperature limit; therefore, their contribution to the molar internal energy will be $3/2 RT$ and RT , respectively, with $n = 1 \text{ mol}$. The vibrational contribution still remains, and is calculated as follows:

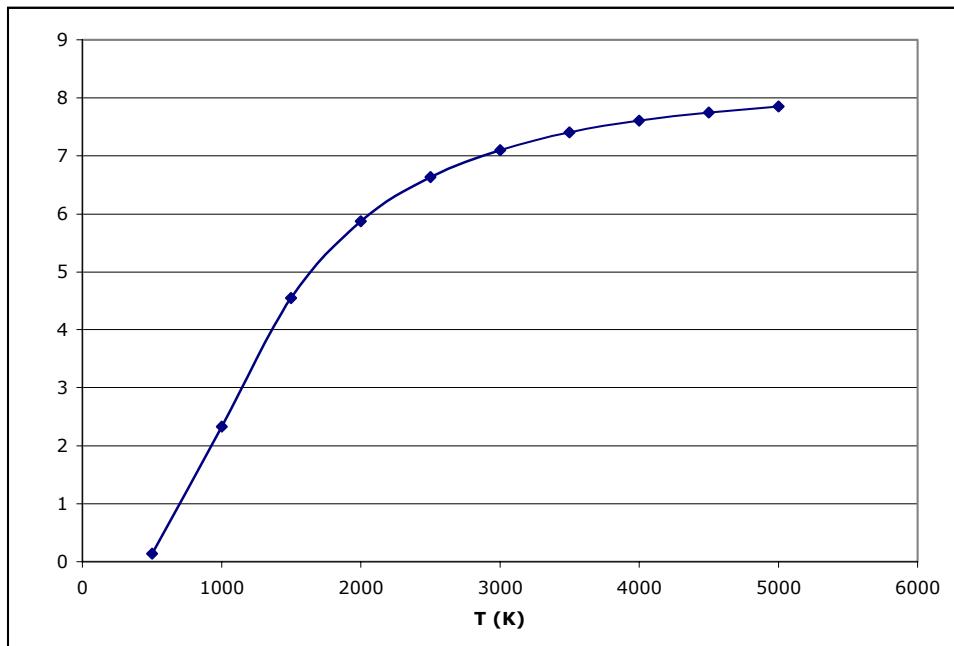
$$\begin{aligned} q_V &= \frac{1}{1 - e^{-\beta hc\tilde{\nu}}} \\ U_V &= \frac{-N}{q_V} \left(\frac{\partial q_V}{\partial \beta} \right)_V = \frac{-nN_A}{q_V} \left(\frac{\partial}{\partial \beta} (1 - e^{-\beta hc\tilde{\nu}})^{-1} \right)_V \\ &= \frac{-nN_A}{q_V} \left(- (hc\tilde{\nu} e^{-\beta hc\tilde{\nu}}) (1 - e^{-\beta hc\tilde{\nu}})^{-2} \right) \\ &= \frac{nN_A hc\tilde{\nu} e^{-\beta hc\tilde{\nu}}}{1 - e^{-\beta hc\tilde{\nu}}} = \frac{nN_A hc\tilde{\nu}}{e^{\beta hc\tilde{\nu}} - 1} \\ &= \frac{nN_A (6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(2886 \text{ cm}^{-1})}{e^{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(2886 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298.15 \text{ K})}} - 1 \\ &= n(0.03 \text{ J mol}^{-1}) \\ U_{V,m} &= 0.03 \text{ J mol}^{-1} \\ U_{total,m} &= U_{T,m} + U_{R,m} + U_{V,m} = \frac{3}{2}RT + RT + 0.03 \text{ J mol}^{-1} = 6.19 \text{ kJ mol}^{-1} \end{aligned}$$

P33.9) Determine the vibrational contribution to C_V for a mole of HCl ($\tilde{\nu} = 2886 \text{ cm}^{-1}$) over a temperature range from 500 to 5000 K in 500-K intervals and plot your result. At what temperature do you expect to reach the high-temperature limit for the vibrational contribution to C_V ?

The problem requires evaluation of the following expression versus temperature:

$$C_V = \frac{N}{kT^2} (hc\tilde{\nu})^2 \frac{e^{\frac{hc\tilde{\nu}}{kT}}}{\left(e^{\frac{hc\tilde{\nu}}{kT}} - 1\right)^2}$$

Using Excel or a similar program, the following plot of the molar heat capacity versus temperature can be constructed.



The high-temperature limit value for the molar heat capacity is $(1 \text{ mol}) \times R = 8.314 \text{ J K}^{-1}$. Comparison of this value to the graph illustrates that the high-temperature limit will be value for temperatures well above 6000. Specifically, the high-temperature limit is applicable when $T > 10\Theta_V$ or $\sim 40,000 \text{ K}$ for HCl.

P33.10) Determine the vibrational contribution to C_V for HCN where $\tilde{\nu}_1 = 2041 \text{ cm}^{-1}$, $\tilde{\nu}_2 = 712 \text{ cm}^{-1}$ (doubly degenerate), and $\tilde{\nu}_3 = 3369 \text{ cm}^{-1}$ at $T = 298, 500$, and 1000 K .

The total vibrational heat capacity will be equal to the sum of heat capacity contributions from each vibrational degree of freedom. Keeping track of the degeneracy of the 712 cm^{-1} mode, the total heat capacity can be written as:

$$C_{V,\text{total}} = C_{V,\tilde{\nu}_1} + 2C_{V,\tilde{\nu}_2} + C_{V,\tilde{\nu}_3}$$

where the heat capacity for a specific mode is determined using:

$$C_V = \frac{N}{kT^2} (hc\tilde{\nu})^2 \frac{e^{\frac{hc\tilde{\nu}}{kT}}}{\left(e^{\frac{hc\tilde{\nu}}{kT}} - 1\right)^2}$$

Evaluating this expression for the 2041 cm^{-1} mode at 500 K yields:

$$\begin{aligned}
 C_V &= \frac{N}{kT^2} (hc\tilde{\nu})^2 \frac{e^{\frac{hc\tilde{\nu}}{kT}}}{\left(e^{\frac{hc\tilde{\nu}}{kT}} - 1\right)^2} \\
 &= \frac{N}{(1.38 \times 10^{-23}\text{ J K}^{-1})(500\text{ K})^2} \left((6.626 \times 10^{-34}\text{ J s})(3.00 \times 10^{10}\text{ cm s}^{-1})(2041\text{ cm}^{-1}) \right)^2 \\
 &\quad \times \frac{e^{\frac{(6.626 \times 10^{-34}\text{ J s})(3.00 \times 10^{10}\text{ cm s}^{-1})(2041\text{ cm}^{-1})}{(1.38 \times 10^{-23}\text{ J K}^{-1})(500\text{ K})}}}{e^{\frac{(6.626 \times 10^{-34}\text{ J s})(3.00 \times 10^{10}\text{ cm s}^{-1})(2041\text{ cm}^{-1})}{(1.38 \times 10^{-23}\text{ J K}^{-1})(500\text{ K})}} - 1}^2 \\
 &= N(4.77 \times 10^{-22}\text{ J K}^{-1})(2.81 \times 10^{-3}) \\
 &= nN_A(2.29 \times 10^{-24}\text{ J K}^{-1}) \\
 &= nN_A(2.29 \times 10^{-24}\text{ J K}^{-1}) \\
 &= n(0.811\text{ J mol}^{-1}\text{ K}^{-1})
 \end{aligned}$$

Similar calculations for the other vibrational degrees of freedom and temperatures of interest yields the following table of molar constant volume heat capacities (units of $\text{J mol}^{-1}\text{ K}^{-1}$)

	298 K	500 K	1000 K
2041 cm^{-1}	0.042	0.811	4.24
712 cm^{-1}	3.37	5.93	7.62
3369 cm^{-1}	0.000	0.048	1.56
Total	6.78	12.7	21.0

P33.11) Consider the following energy levels and associated degeneracies for atomic Fe:

Level (n)	Energy (cm^{-1})	Degeneracy
0	0	9
1	415.9	7
2	704.0	5
3	888.1	3
4	978.1	1

- a) Determine the electronic contribution to C_V for atomic Fe at 150 K assuming that only the first two levels contribute to C_V .

b) How does your answer to part (a) change if the $n = 2$ level is included in the calculation of C_V ? Do you need to include the other levels?

$$\begin{aligned}
 q &= 9 + 7e^{-\beta\epsilon_1} \\
 U &= N \left(\frac{7\epsilon_1 e^{-\beta\epsilon_1}}{9 + 7e^{-\beta\epsilon_1}} \right) = N \left(\frac{7\epsilon_1}{9e^{\beta\epsilon_1} + 7} \right) \\
 C_V &= -k\beta^2 \left(\frac{\partial U}{\partial \beta} \right)_V = -Nk\beta^2 \left(\frac{\partial}{\partial \beta} \left(\frac{7\epsilon_1}{9e^{\beta\epsilon_1} + 7} \right) \right)_V \\
 &= Nk\beta^2 \frac{63\epsilon_1^2}{(9e^{\beta\epsilon_1} + 7)^2} = \frac{N}{kT^2} \frac{63\epsilon_1^2 e^{\beta\epsilon_1}}{\left(9e^{\frac{\epsilon_1}{kT}} + 7 \right)^2} \\
 &= \frac{N}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(150 \text{ K})^2} \left(\frac{63(415.9 \text{ cm}^{-1})^2 e^{\frac{415.9 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(150 \text{ K})}}}{\left(9e^{\frac{415.9 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(150 \text{ K})}} + 7 \right)^2} \right) \\
 &= N(0.156 \text{ cm}^{-1} \text{ K}) \\
 &= nN_A(0.156 \text{ cm}^{-1} \text{ K})(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1}) = n(1.86 \text{ J mol}^{-1} \text{ K}^{-1})
 \end{aligned}$$

P33.12) The speed of sound is given by the relationship

$$c_{\text{sound}} = \left(\frac{\frac{C_p}{C_V} RT}{M} \right)^{1/2}$$

where C_p is the constant pressure heat capacity (equal to $C_V + R$), R is the ideal gas constant, T is temperature, and M is molar mass.

- a) What is the expression for the speed of sound for an ideal monatomic gas?
- b) What is the expression for the speed of sound of an ideal diatomic gas?
- c) What is the speed of sound in air at 298 K, assuming that air is mostly made up of nitrogen ($B = 2.00 \text{ cm}^{-1}$ and $\tilde{\nu} = 2359 \text{ cm}^{-1}$)?

- a) For a monatomic gas, only translational degrees of freedom contribute to the C_V :

$$C_V = \frac{3}{2} Nk = \frac{3}{2} nR$$

$$\frac{C_p}{C_V} = \frac{\frac{5}{2}nR}{\frac{3}{2}nR} = \frac{5}{3}$$

$$c_{sound} = \left(\frac{\frac{C_p}{C_V} RT}{M} \right)^{1/2} = \left(\frac{\frac{5}{3} RT}{M} \right)^{1/2}$$

b) In addition to translations, rotational and vibrational degrees of freedom will also contribute to C_V :

$$C_V = C_{V,trans} + C_{V,rot} + C_{V,vib} = \frac{3}{2} nR + nR + nR\beta^2 (hc\tilde{v})^2 \frac{e^{\beta hc\tilde{v}}}{(e^{\beta hc\tilde{v}} + 1)^2}$$

$$= nR \left(\frac{5}{2} + \beta^2 (hc\tilde{v})^2 \frac{e^{\beta hc\tilde{v}}}{(e^{\beta hc\tilde{v}} + 1)^2} \right)$$

$$\frac{C_p}{C_V} = \frac{\left(\frac{7}{2} + \beta^2 (hc\tilde{v})^2 \frac{e^{\beta hc\tilde{v}}}{(e^{\beta hc\tilde{v}} + 1)^2} \right)}{\left(\frac{5}{2} + \beta^2 (hc\tilde{v})^2 \frac{e^{\beta hc\tilde{v}}}{(e^{\beta hc\tilde{v}} + 1)^2} \right)}$$

$$c_{sound} = \left(\frac{\left(\frac{7}{2} + \beta^2 (hc\tilde{v})^2 \frac{e^{\beta hc\tilde{v}}}{(e^{\beta hc\tilde{v}} + 1)^2} \right) RT}{\left(\frac{5}{2} + \beta^2 (hc\tilde{v})^2 \frac{e^{\beta hc\tilde{v}}}{(e^{\beta hc\tilde{v}} + 1)^2} \right) M} \right)^{1/2}$$

c) First, evaluation of the vibrational contribution to C_V demonstrates that this contribution is small relative to the contribution from translational and rotational degrees of freedom, and can be neglected to good approximation:

$$\begin{aligned} \frac{C_{V,vib}}{nR} &= \beta^2 (hc\tilde{\nu})^2 \frac{e^{\beta hc\tilde{\nu}}}{(e^{\beta hc\tilde{\nu}} + 1)^2} \\ &= \left(\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(2359 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})} \right)^2 \\ &\quad \times \frac{e^{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(2359 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}}}{e^{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(2359 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}} + 1}^2 \\ &= 1.47 \times 10^{-3} \ll \frac{5}{2} \end{aligned}$$

Therefore, keeping only the translational and rotational contributions to C_V yields the following value for the speed of sound in N₂:

$$\begin{aligned} c_{sound} &= \left(\frac{C_p}{C_V} RT \right)^{1/2} \equiv \left(\frac{7}{5} RT \right)^{1/2} = \left(\frac{7}{5} \left(8.314 \text{ J mol}^{-1} \text{ K}^{-1} \right) (298 \text{ K}) \right)^{1/2} \\ &= 352 \text{ m s}^{-1} \end{aligned}$$

P33.13) The measured molar heat capacities for crystalline KCl are as follows at the indicated temperatures:

T (K)	50	100	175	250
$C_{V,m}$ (J/mol K)	21.1	39.0	46.1	48.6

- a) Explain why the high-temperature limit for C_V is apparently twofold greater than that predicted by the Dulong–Petit law.
- b) Determine if the Einstein model is applicable to ionic solids. To do this use the value for C_V at 50 K to determine Θ_V , then use this temperature to determine C_V at 175 K.
- a) The Dulong–Petit law is applicable to atomic crystals. KCl is a molecular crystal where vibrational degrees of freedom will also contribute to C_V .

b)

$$C_V = 3Nk \left(\frac{\theta_V}{T} \right)^2 \frac{e^{\frac{\theta_V}{T}}}{\left(e^{\frac{\theta_V}{T}} - 1 \right)^2}$$

$$21.0 \text{ J mol}^{-1} \text{ K}^{-1} = 3 \left(8.314 \text{ J mol}^{-1} \text{ K}^{-1} \right) \left(\frac{\theta_V}{50 \text{ K}} \right)^2 \frac{e^{\frac{\theta_V}{50 \text{ K}}}}{\left(e^{\frac{\theta_V}{50 \text{ K}}} - 1 \right)^2}$$

$$0.841 = \left(\frac{\theta_V}{50 \text{ K}} \right)^2 \frac{e^{\frac{\theta_V}{50 \text{ K}}}}{\left(e^{\frac{\theta_V}{50 \text{ K}}} - 1 \right)^2}$$

$$\theta_V = 71.4 \text{ K} \text{ (determined using Excel)}$$

Using the vibrational temperature, the predicted heat capacity at 175 K can be determined:

$$C_V = 3Nk \left(\frac{\theta_V}{T} \right)^2 \frac{e^{\frac{\theta_V}{T}}}{\left(e^{\frac{\theta_V}{T}} - 1 \right)^2}$$

$$C_{V,m} = 3 \left(8.314 \text{ J mol}^{-1} \text{ K}^{-1} \right) \left(\frac{71.4 \text{ K}}{175 \text{ K}} \right)^2 \frac{e^{\frac{71.4 \text{ K}}{175 \text{ K}}}}{\left(e^{\frac{71.4 \text{ K}}{175 \text{ K}}} - 1 \right)^2}$$

$$= 24.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

P33.14) Inspection of the thermodynamic tables in the back of the text reveals that many molecules have quite similar constant volume heat capacities.

- a) The value of $C_{V,m}$ for Ar(g) at standard temperature and pressure is $12.48 \text{ J mol}^{-1} \text{ K}^{-1}$, identical to gaseous He(g). Using statistical mechanics, demonstrate why this equivalence is expected.
- b) The value of $C_{V,m}$ for N₂(g) is $20.81 \text{ J mol}^{-1} \text{ K}^{-1}$. Is this value expected given your answer to part (a)? For N₂, $\tilde{v} = 2359 \text{ cm}^{-1}$ and $B = 2.00 \text{ cm}^{-1}$.

- a) Assuming excited electronic energy levels are not accessible at 298.15 K (standard thermodynamic temperature), translational degrees of freedom will

make the only contribution to C_V for these monatomic gases. Translational degrees of freedom will be in the high-temperature limit; therefore, the expected contribution is $3/2 R$, or $12.5 \text{ J mol}^{-1} \text{ K}^{-1}$.

- b) For N_2 , both translational and rotational degrees of freedom will be in the high-temperature limit; therefore, a total contribution of $5/2 R$ from these degrees of freedom is expected. The vibrational contribution is determined by evaluating the following:

$$\begin{aligned} C_{V,m} &= R\beta^2 (hc\tilde{\nu})^2 \frac{e^{\beta hc\tilde{\nu}}}{(e^{\beta hc\tilde{\nu}} + 1)^2} \\ &= R \left(\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(2359 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298.15 \text{ K})} \right)^2 \\ &\quad \times \frac{e^{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(2359 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298.15 \text{ K})}}}{\left(e^{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(2359 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298.15 \text{ K})}} + 1 \right)^2} \\ &= R(1.47 \times 10^{-3}) \end{aligned}$$

At 298.15 K, the contribution to C_V from the vibrational degree of freedom is small, and can be neglected to good approximation. Therefore, C_V for N_2 is expected to be $5/2 R$, or $20.8 \text{ J mol}^{-1} \text{ K}^{-1}$.

P33.15) Determine the molar entropy for 1 mol of gaseous Ar at 200, 300, and 500 K and $V = 1000 \text{ cm}^3$ assuming that Ar can be treated as an ideal gas. How does the result of this calculation change if the gas is Kr instead of Ar?

Determining the molar entropy for gaseous Ar at 200 K yields:

$$\begin{aligned}
S &= \frac{U}{T} + k \ln Q = \frac{3}{2} Nk + k \ln \left(\frac{q^N}{N!} \right) = \frac{3}{2} Nk + NK \ln q - k \ln(N!) \\
&= \frac{3}{2} Nk + Nk \ln q - k(N \ln N - N) \\
&= \frac{5}{2} nR + nR \ln q - nR \ln(nN_A) \\
S_m &= \frac{5}{2} R + R \ln \left(\frac{V}{\Lambda^3} \right) - R \ln(6.022 \times 10^{23}) \\
&= 20.79 \text{ J mol}^{-1} \text{ K}^{-1} + R \ln \left(\frac{V}{\left(\frac{h^2}{2\pi mkT} \right)^{3/2}} \right) - 456 \text{ J mol}^{-1} \text{ K}^{-1} \\
&= 20.79 \text{ J mol}^{-1} \text{ K}^{-1} \\
&+ R \ln \left(\frac{0.001 \text{ m}^3}{N_A \left(\frac{(6.626 \times 10^{-34} \text{ J s})^2}{2\pi \left(\frac{0.040 \text{ kg mol}^{-1}}{N_A} \right) (1.38 \times 10^{-23} \text{ J K}^{-1}) (200 \text{ K})} \right)^{3/2}} \right) - 456 \text{ J mol}^{-1} \text{ K}^{-1} \\
&= 123 \text{ J mol}^{-1} \text{ K}^{-1}
\end{aligned}$$

Repeating the calculation for $T = 300$ and 500 K, and the molar entropy is found to be $128 \text{ J mol}^{-1} \text{ K}^{-1}$ and $135 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. Kr is heavier than Ar; therefore, the thermal wavelength will be shorter, and the translational partition function will correspondingly be larger. Since the molar entropy is linearly related to $\ln(q)$, we would expect the molar entropy for Kr to be greater than that of Ar. This expectation can be confirmed by repeating the above calculation for Kr, or by simply looking at the difference in entropy between Kr and Ar:

$$\begin{aligned}
 S_{Kr} - S_{Ar} &= \left(\frac{U}{T} + k \ln Q \right)_{Kr} - \left(\frac{U}{T} + k \ln Q \right)_{Ar} \\
 &= k \ln \left(\frac{Q_{Kr}}{Q_{Ar}} \right) = Nk \ln \left(\frac{q_{Kr}}{q_{Ar}} \right) = Nk \ln \left(\frac{\Lambda_{Ar}^3}{\Lambda_{Kr}^3} \right) = Nk \ln \left(\frac{m_{Kr}}{m_{Ar}} \right)^{3/2} \\
 S_{m,Kr} - S_{m,Ar} &= \frac{3}{2} R \ln \left(\frac{m_{Kr}}{m_{Ar}} \right) = \frac{3}{2} R \ln (2.00) \\
 S_{m,Kr} &= 8.64 \text{ J mol}^{-1} \text{ K}^{-1} + S_{m,Ar}
 \end{aligned}$$

P33.16) The standard molar entropy of O₂ is 205.14 J mol⁻¹ K⁻¹. Using this information, determine the bond length of O₂. For this molecule, $\tilde{\nu} = 1580 \text{ cm}^{-1}$, and the ground electronic state degeneracy is three.

The bond length of O₂ is one component of O₂ the rotational constant, which in turn is part of the rotational partition function. Therefore, we need to isolate the rotational component of the entropy, and use this information to determine q_R . Also, standard thermodynamic conditions are V = 22.48 L and T = 298.15 K. Using this information:

$$S_m = \frac{U_m}{T} + k \ln Q = \frac{U_m}{T} + k \ln \left(\frac{q_{total}^N}{N!} \right) = \frac{U_m}{T} + Nk \ln(q_{total}) - k \ln(N!)$$

$$= \frac{5}{2}R + R \ln(q_T q_R q_V q_E) - R \ln((1 \text{ mol}) N_A) + R$$

$$= \frac{7}{2}R - 54.8R + R \ln(q_T q_R q_V q_E)$$

$$632 \text{ J mol}^{-1} \text{ K}^{-1} = R \ln(q_T q_R q_V q_E)$$

$$76.0 = \ln(q_T q_R q_V q_E) = \ln(q_T) + \ln(q_R) + \ln(q_V) + \ln(q_E)$$

$$= \ln\left(\frac{V}{\Lambda^3}\right) + \ln(q_R) + \ln\left(\frac{1}{1-e^{-\beta hc\bar{v}}}\right) + \ln(g_0)$$

$$= \ln\left(\frac{0.0245 \text{ m}^3}{5.72 \times 10^{-33} \text{ m}^3}\right) + \ln(q_R) + \ln(1) + \ln(3)$$

$$76.0 = 70.5 + \ln(q_R) + 1.10$$

$$4.4 = \ln(q_R)$$

$$81.5 = q_R = \left(\frac{kT}{\sigma B} \right)$$

$$B = \frac{kT}{\sigma(81.5)} = \frac{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{2(81.5)} = 1.27 \text{ cm}^{-1}$$

$$B = \frac{h}{8\pi^2 c I} = \frac{h}{8\pi^2 c \mu r^2} = 1.27 \text{ cm}^{-1}$$

$$r^2 = \frac{h}{8\pi^2 c \mu (1.27 \text{ cm}^{-1})} = \frac{(6.626 \times 10^{-34} \text{ J s})}{8\pi^2 (3.00 \times 10^{10} \text{ cm s}^{-1})(1.33 \times 10^{-26} \text{ kg})(1.27 \text{ cm}^{-1})}$$

$$r^2 = 1.66 \times 10^{-20} \text{ m}^2$$

$$r = 1.28 \times 10^{-10} \text{ m}$$

The experimental value for the bond length is $1.28 \times 10^{-10} \text{ m}$.

P33.17) Determine the standard molar entropy of N_2O , a linear triatomic molecule at 298 K. For this molecule, $B = 0.419 \text{ cm}^{-1}$ and $\tilde{\nu}_1 = 1285 \text{ cm}^{-1}$, $\tilde{\nu}_2 = 589 \text{ cm}^{-1}$ (doubly degenerate), and $\tilde{\nu}_3 = 2224 \text{ cm}^{-1}$.

At 298.15 K, both the translational and rotational degrees of freedom will be in the high-temperature limit, but the vibrational contributions must be calculated. Using the standard volume of 24.5 L and temperature of 298.15 K the entropy is determined as follows:

$$\begin{aligned}
U_m^\circ &= U_{T,m}^\circ + U_{R,m}^\circ + U_{V,m}^\circ + U_{E,m}^\circ \\
&= \frac{3}{2}RT + RT + N_A hc \left[\left(\frac{\tilde{\nu}_1}{e^{\beta hc \tilde{\nu}_1} - 1} \right) + 2 \left(\frac{\tilde{\nu}_2}{e^{\beta hc \tilde{\nu}_2} - 1} \right) + \left(\frac{\tilde{\nu}_3}{e^{\beta hc \tilde{\nu}_3} - 1} \right) \right] \\
&= \frac{5}{2}R(298.15 \text{ K}) + 906 \text{ J mol}^{-1} = 7.10 \text{ kJ mol}^{-1} \\
S_m^\circ &= \frac{U_m^\circ}{T} + k \ln Q = \frac{U_m^\circ}{T} + k \ln \left(\frac{q_{total}^N}{N!} \right) = \frac{U_m^\circ}{T} + Nk \ln(q_{total}) - k \ln(N!) \\
&= \frac{7.10 \text{ kJ mol}^{-1}}{298.15 \text{ K}} + R \ln(q_T q_R q_V q_E) - R \ln((1 \text{ mol}) N_A) + R \\
&= -424 \text{ J mol}^{-1} \text{ K}^{-1} + R \ln(q_T q_R q_V q_E)
\end{aligned}$$

$$\begin{aligned}
q_T &= \left(\frac{V}{\Lambda^3} \right) = \frac{0.0245 \text{ m}^3}{3.55 \times 10^{-33} \text{ m}^3} = 6.91 \times 10^{30} \\
q_R &= \left(\frac{kT}{\sigma B} \right) = \frac{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{0.42 \text{ cm}^{-1}} = 493 \\
q_V &= \left(\frac{1}{1 - e^{-\beta \tilde{\nu}_1}} \right) \left(\frac{1}{1 - e^{-\beta \tilde{\nu}_2}} \right)^2 \left(\frac{1}{1 - e^{-\beta \tilde{\nu}_3}} \right) \\
&= \left(\frac{1}{1 - e^{-\frac{1285 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1})(298.15 \text{ K})}}} \right) \left(\frac{1}{1 - e^{-\frac{589 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1})(298.15 \text{ K})}}} \right)^2 \left(\frac{1}{1 - e^{-\frac{2224 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1})(298.15 \text{ K})}}} \right) \\
&= 1.00 \\
q_E &= 1.00
\end{aligned}$$

$$\begin{aligned}
S_m^\circ &= -424 \text{ J mol}^{-1} \text{ K}^{-1} + R \ln(q_T q_R q_V q_E) = -424 \text{ J mol}^{-1} \text{ K}^{-1} + 643 \text{ J mol}^{-1} \text{ K}^{-1} \\
S_m^\circ &= 219 \text{ J mol}^{-1} \text{ K}^{-1}
\end{aligned}$$

P33.18) Determine the standard molar entropy of OClO, a nonlinear triatomic molecule where $B_A = 1.06 \text{ cm}^{-1}$, $B_B = 0.31 \text{ cm}^{-1}$, $B_C = 0.29 \text{ cm}^{-1}$ and $\tilde{\nu}_1 = 938 \text{ cm}^{-1}$, $\tilde{\nu}_2 = 450 \text{ cm}^{-1}$, and $\tilde{\nu}_3 = 1100 \text{ cm}^{-1}$.

$$\begin{aligned}
 U_m^\circ &= U_{T,m}^\circ + U_{R,m}^\circ + U_{V,m}^\circ + U_{E,m}^\circ \\
 &= \frac{3}{2}RT + \frac{3}{2}RT + N_A hc \left[\left(\frac{\tilde{\nu}_1}{e^{\beta hc\tilde{\nu}_1} - 1} \right) + \left(\frac{\tilde{\nu}_2}{e^{\beta hc\tilde{\nu}_2} - 1} \right) + \left(\frac{\tilde{\nu}_3}{e^{\beta hc\tilde{\nu}_3} - 1} \right) \right] + 0 \\
 &= 3R(298.15 \text{ K}) + 479 \text{ J mol}^{-1} = 7.92 \text{ kJ mol}^{-1} \\
 S_m^\circ &= \frac{U_m^\circ}{T} + k \ln Q = \frac{U_m^\circ}{T} + k \ln \left(\frac{q_{total}^N}{N!} \right) = \frac{U_m^\circ}{T} + Nk \ln(q_{total}) - k \ln(N!) \\
 &= \frac{7.92 \text{ kJ mol}^{-1}}{298.15 \text{ K}} + R \ln(q_T q_R q_V q_E) - R \ln((1 \text{ mol}) N_A) + R \\
 &= -420 \text{ J mol}^{-1} \text{ K}^{-1} + R \ln(q_T q_R q_V q_E) \\
 q_T &= \left(\frac{V}{\Lambda^3} \right) = \frac{0.0245 \text{ m}^3}{1.89 \times 10^{-33} \text{ m}^3} = 1.30 \times 10^{31} \\
 q_R &= \frac{\sqrt{\pi}}{\sigma} \left(\frac{kT}{B_A} \right)^{1/2} \left(\frac{kT}{B_B} \right)^{1/2} \left(\frac{kT}{B_C} \right)^{1/2} \\
 &= \frac{\sqrt{\pi}}{2} \left(\frac{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{1.60 \text{ cm}^{-1}} \right)^{1/2} \left(\frac{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{0.31 \text{ cm}^{-1}} \right)^{1/2} \\
 &\quad \times \left(\frac{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{0.29 \text{ cm}^{-1}} \right)^{1/2} \\
 &= 6.98 \times 10^3 \\
 q_V &= \left(\frac{1}{1 - e^{-\beta \tilde{\nu}_1}} \right) \left(\frac{1}{1 - e^{-\beta \tilde{\nu}_2}} \right) \left(\frac{1}{1 - e^{-\beta \tilde{\nu}_3}} \right) \\
 &= \left(\frac{1}{1 - e^{-\frac{938 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1})(298.15 \text{ K})}}} \right) \left(\frac{1}{1 - e^{-\frac{450 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1})(298.15 \text{ K})}}} \right) \left(\frac{1}{1 - e^{-\frac{1100 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1})(298.15 \text{ K})}}} \right) \\
 &= 1.14 \\
 q_E &= 2 \\
 S_m^\circ &= -420 \text{ J mol}^{-1} \text{ K}^{-1} + R \ln(q_T q_R q_V q_E) = -424 \text{ J mol}^{-1} \text{ K}^{-1} + 676 \text{ J mol}^{-1} \text{ K}^{-1} \\
 S_m^\circ &= 256 \text{ J mol}^{-1} \text{ K}^{-1}
 \end{aligned}$$

P33.19) Determine the standard molar entropy of N₂ ($\tilde{\nu} = 2359 \text{ cm}^{-1}$ and $B = 2.00 \text{ cm}^{-1}$, $g_0 = 1$) and the entropy when $p = 1 \text{ atm}$, but $T = 2500 \text{ K}$.

Since the vibrational frequency is much greater than kT at 298.15 K, vibrational contributions to the internal energy and entropy can be neglected to good

approximation. Furthermore, the translational and rotational degrees of freedom are in the high-temperature limit. Therefore, the standard molar entropy is:

$$\begin{aligned} U_m^\circ &= U_{T,m}^\circ + U_{R,m}^\circ = \frac{5}{2}RT \\ S_m^\circ &= \frac{U_m^\circ}{T} + k \ln Q = \frac{U_m^\circ}{T} + k \ln \left(\frac{q_{total}^N}{N!} \right) = \frac{U_m^\circ}{T} + Nk \ln(q_{total}) - k \ln(N!) \\ &= \frac{5}{2}R + R \ln(q_T q_R q_V q_E) - R \ln((1 \text{ mol}) N_A) + R \\ &= -51.3R + R \ln(q_T q_R q_V q_E) \end{aligned}$$

$$q_T = \left(\frac{V}{\Lambda^3} \right) = \frac{0.0245 \text{ m}^3}{6.99 \times 10^{-33} \text{ m}^3} = 3.51 \times 10^{30}$$

$$q_R = \left(\frac{kT}{\sigma B} \right) = \frac{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{(2)(2.00 \text{ cm}^{-1})} = 51.8$$

$$q_V = 1.00$$

$$q_E = 1.00$$

$$S_m^\circ = -51.3R + R \ln(q_T q_R q_V q_E) = -51.3R + 74.3R$$

$$S_m^\circ = 23.0R = 191 \text{ J mol}^{-1} \text{ K}^{-1}$$

Next, with an increase in temperature the contribution of the vibrational degree of freedom to the internal energy and entropy must also be considered:

$$\begin{aligned}
 U_m &= U_{T,m} + U_{R,m} + U_{V,m} = \frac{5}{2}RT + N_A hc \left(\frac{\tilde{\nu}}{e^{\beta hc\tilde{\nu}} - 1} \right) \\
 &= 61.7 \text{ kJ mol}^{-1} \\
 S_m &= \frac{U_m}{T} + k \ln Q = \frac{U_m}{T} + k \ln \left(\frac{q_{total}^N}{N!} \right) = \frac{U_m}{T} + Nk \ln(q_{total}) - k \ln(N!) \\
 &= 24.7 \text{ J mol}^{-1} \text{ K}^{-1} + R \ln(q_T q_R q_V q_E) - R \ln((1 \text{ mol}) N_A) + R \\
 &= -422 \text{ J mol}^{-1} \text{ K}^{-1} + R \ln(q_T q_R q_V q_E)
 \end{aligned}$$

$$\begin{aligned}
 q_T &= \left(\frac{V}{\Lambda^3} \right) = \frac{0.205 \text{ m}^3}{2.88 \times 10^{-34} \text{ m}^3} = 7.12 \times 10^{32} \\
 &\left\{ \text{note: } V = \frac{nRT}{P} = 205.15 \text{ L @ } T = 2500 \text{ K} \right\} \\
 q_R &= \left(\frac{kT}{\sigma B} \right) = \frac{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(2500 \text{ K})}{(2)(2.00 \text{ cm}^{-1})} = 434 \\
 q_V &= \left(\frac{1}{1 - e^{-\beta hc\tilde{\nu}}} \right) = \frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(2359 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(2500 \text{ K})}} = 1.35 \\
 q_E &= 1.00
 \end{aligned}$$

$$\begin{aligned}
 S_m &= -422 \text{ J mol}^{-1} \text{ K}^{-1} + R \ln(q_T q_R q_V q_E) = -422 \text{ J mol}^{-1} \text{ K}^{-1} + 82.0R \\
 S_m &= 260 \text{ J mol}^{-1} \text{ K}^{-1}
 \end{aligned}$$

P33.20) Determine the standard molar entropy of HCl³⁵ at 298 K where $B = 10.58 \text{ cm}^{-1}$, $\tilde{\nu} = 2886 \text{ cm}^{-1}$, and the ground-state electronic level degeneracy is 1.

$$\begin{aligned}
U_m^\circ &= U_{T,m}^\circ + U_{R,m}^\circ = \frac{5}{2}RT \\
S_m^\circ &= \frac{U_m^\circ}{T} + k \ln Q = \frac{U_m^\circ}{T} + k \ln \left(\frac{q_{total}^N}{N!} \right) = \frac{U_m^\circ}{T} + Nk \ln(q_{total}) - k \ln(N!) \\
&= \frac{5}{2}R + R \ln(q_T q_R q_V q_E) - R \ln((1 \text{ mol}) N_A) + R \\
&= -51.3R + R \ln(q_T q_R q_V q_E)
\end{aligned}$$

$$\begin{aligned}
q_T &= \left(\frac{V}{\Lambda^3} \right) = \frac{0.0245 \text{ m}^3}{4.79 \times 10^{-33} \text{ m}^3} = 5.11 \times 10^{30} \\
q_R &= \left(\frac{kT}{\sigma B} \right) = \frac{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{(1)(10.58 \text{ cm}^{-1})} = 19.6 \\
q_V &= 1.00 \\
q_E &= 1.00
\end{aligned}$$

$$\begin{aligned}
S_m^\circ &= -51.3R + R \ln(q_T q_R q_V q_E) = -51.3R + 73.6R \\
S_m^\circ &= 22.4R = 186 \text{ J mol}^{-1} \text{ K}^{-1}
\end{aligned}$$

P33.21) Derive the expression for the standard molar entropy of a monatomic gas restricted to two-dimensional translational motion. (*Hint:* You are deriving the two-dimensional version of the Sackur–Tetrode equation.)

$$\begin{aligned}
S &= \frac{U}{T} + k \ln Q = \frac{U}{T} + k \ln \left(\frac{q_{total}^N}{N!} \right) = \frac{U_m^\circ}{T} + Nk \ln(q_{total}) - k \ln(N!) \\
&= nR + nR \ln(q_T) - nR \ln(nN_A) + nR \\
&= 2nR + nR \ln(q_T) - nR \ln(nN_A) \\
q_T &= \frac{A}{\Lambda^2} \quad \text{where } \Lambda = \left(\frac{h^2}{2\pi mkT} \right)^{\frac{1}{2}} \quad \text{and } A = \text{area} \\
S &= 2nR + nR \ln \left(\frac{A}{\Lambda^2} \right) - nR \ln(nN_A) \\
&= nR \left[\ln(e^2) + \ln \left(\frac{A}{\Lambda^2} \right) - \ln(nN_A) \right] \\
S_m &= R \ln \left(\frac{e^2 A}{nN_A \Lambda^2} \right)
\end{aligned}$$

P33.22) The molecule NO has a ground electronic level that is doubly degenerate, and a first excited level at 121.1 cm^{-1} that is also twofold degenerate. Determine the contribution of electronic degrees of freedom to the standard molar entropy of NO. Compare your result to $R\ln(4)$. What is the significance of this comparison?

$$\begin{aligned} q_E &= g_0 + g_1 e^{-\beta E_1} = 2 + 2e^{-\beta hc(121.1 \text{ cm}^{-1})} = 3.11 \\ U_E &= \frac{-N}{q_E} \left(\frac{\partial q_E}{\partial \beta} \right)_V = \frac{2Nhc(121.1 \text{ cm}^{-1})e^{-\beta hc(121.1 \text{ cm}^{-1})}}{2 + 2e^{-\beta hc(121.1 \text{ cm}^{-1})}} \\ &= \frac{Nhc(121.1 \text{ cm}^{-1})e^{-\beta hc(121.1 \text{ cm}^{-1})}}{1 + e^{-\beta hc(121.1 \text{ cm}^{-1})}} \\ U_{E,m} &= \frac{N_A hc(121.1 \text{ cm}^{-1})e^{-\beta hc(121.1 \text{ cm}^{-1})}}{1 + e^{-\beta hc(121.1 \text{ cm}^{-1})}} = 518 \text{ J mol}^{-1} \\ S_{E,m} &= \frac{U_{E,m}}{T} + R \ln(q_E) = \frac{518 \text{ J mol}^{-1}}{298.15 \text{ K}} + R \ln(3.11) \\ &= 1.73 \text{ J mol}^{-1} \text{ K}^{-1} + 9.43 \text{ J mol}^{-1} \text{ K}^{-1} \\ &= 11.2 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

$$R \ln(4) = 11.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

At sufficiently high temperatures, $q_E = 4$, and the contribution of the two lowest electronic energy levels to the molar entropy would equal $R\ln(4)$. The similarity between the calculated and limiting values demonstrates that this limiting behavior is being approached at this temperature.

P33.23) Determine the residual molar entropies for molecular crystals of the following:

- a) $^{35}\text{Cl}^{37}\text{Cl}$
- b) CFCl_3
- c) CF_2Cl_2
- d) CO_2

a)

$$S = k \ln W = k \ln(2)^N = Nk \ln 2$$

$$S_m = R \ln 2$$

b)

$$S_m = R \ln 4$$

c)

$$S_m = R \ln 2$$

d)
 $S_m = R \ln 1 = 0$

P33.24) Using the Helmholtz energy, demonstrate that the pressure for an ideal polyatomic gas is identical to that derived for an ideal monatomic gas in the text.

$$A = -kT \ln Q$$

$$\begin{aligned} P &= -\left(\frac{\partial A}{\partial V}\right)_T = kT \left(\frac{\partial \ln Q}{\partial V}\right)_T = kT \left(\frac{\partial \ln \left(\frac{q^N}{N!}\right)}{\partial V}\right)_T = NkT \left(\frac{\partial \ln q}{\partial V}\right)_T \\ &= NkT \left(\frac{\partial \ln (q_T q_R q_V q_E)}{\partial V}\right)_T = NkT \left(\frac{\partial}{\partial V} (\ln q_T + \ln q_R + \ln q_V + \ln q_E)\right)_T \end{aligned}$$

Recall that only the translational partition function (q_T) is a function of volume, the other partition functions have no volume dependence. Therefore, only the derivative of the term involving q_T is non-vanishing:

$$\begin{aligned} P &= NkT \left(\frac{\partial}{\partial V} (\ln q_T)\right)_T \\ P &= \frac{NkT}{q_T} \left(\frac{\partial q_T}{\partial V}\right)_T = \frac{NkT \Lambda^3}{V} \left(\frac{1}{\Lambda^3} \left(\frac{\partial V}{\partial V}\right)_T\right) \\ P &= \frac{NkT}{V} = \frac{nRT}{V} \end{aligned}$$

P33.25) Derive an expression for the standard moles enthalpy of an ideal monatomic gas by evaluation of the statistical mechanical expression for enthalpy as opposed to the thermodynamic argument provided in Example Problem 33.7.

$$\begin{aligned}
H &= T \left[kT \left(\frac{\partial \ln Q}{\partial T} \right)_V + V k \left(\frac{\partial \ln Q}{\partial V} \right)_T \right] \\
&= T \left[kT \left(\frac{\partial \ln \left(\frac{q^N}{N!} \right)}{\partial T} \right)_V + V k \left(\frac{\partial \ln \left(\frac{q^N}{N!} \right)}{\partial V} \right)_T \right] \\
&= T \left[NkT \left(\frac{\partial \ln q}{\partial T} \right)_V + VNk \left(\frac{\partial \ln q}{\partial V} \right)_T \right] \\
&= T \left[NkT \left(\frac{\partial \ln \left(\frac{V}{\Lambda^3} \right)}{\partial T} \right)_V + VNk \left(\frac{\partial \ln \frac{V}{\Lambda^3}}{\partial V} \right)_T \right] \\
&= T \left[\frac{NkT\Lambda^3}{V} \left(\frac{\partial \left(\frac{V}{\Lambda^3} \right)}{\partial T} \right)_V + Nk\Lambda^3 \left(\frac{\partial \frac{V}{\Lambda^3}}{\partial V} \right)_T \right] \\
&= T \left[NkT\Lambda^3 \left(\frac{\partial \Lambda^{-3}}{\partial T} \right)_V + Nk \right] \\
&= T \left[NkT\Lambda^3 \left(\frac{2\pi mk}{h^2} \right)^{3/2} \left(\frac{\partial T^{3/2}}{\partial T} \right)_V + Nk \right] \\
&= T \left[NkT\Lambda^3 \left(\frac{2\pi mk}{h^2} \right)^{3/2} \frac{3}{2} T^{1/2} + Nk \right] \\
&= T \left[\frac{3}{2} Nk + Nk \right] = \frac{5}{2} NkT = \frac{5}{2} nRT
\end{aligned}$$

P33.26) Determine that the molar enthalpy is equal to the molar energy for a collection of one-dimensional harmonic oscillators.

$$\begin{aligned}
H &= T \left[kT \left(\frac{\partial \ln Q}{\partial T} \right)_V + V k \left(\frac{\partial \ln Q}{\partial V} \right)_T \right] \\
&= T \left[kT \left(\frac{\partial \ln (q_V)^N}{\partial T} \right)_V + V k \left(\frac{\partial \ln (q_V)^N}{\partial V} \right)_T \right] \\
&= NkT^2 \left(\frac{\partial \ln (q_V)}{\partial T} \right)_V \\
&= \frac{NkT^2}{q_V} \left(\frac{\partial q_V}{\partial T} \right)_V = -\frac{N}{q_V} \left(\frac{\partial q_V}{\partial \beta} \right)_V \\
&= -N \left(1 - e^{-\beta h c \tilde{v}} \right) \left(\frac{-h c \tilde{v} e^{-\beta h c \tilde{v}}}{(1 - e^{-\beta h c \tilde{v}})^2} \right) \\
&= \frac{N h c \tilde{v} e^{-\beta h c \tilde{v}}}{(1 - e^{-\beta h c \tilde{v}})} = \frac{N h c \tilde{v}}{(e^{\beta h c \tilde{v}} - 1)} \\
H_m &= \frac{N_A h c \tilde{v}}{(e^{\beta h c \tilde{v}} - 1)} = U_m
\end{aligned}$$

P33.27) Calculate the standard Helmholtz energy for molar ensembles of Ne and Kr at 298 K.

First, performing the calculation for Ne ($M = 0.020 \text{ kJ mol}^{-1}$):

$$\begin{aligned}
A &= -kT \ln Q = -kT \ln \left(\frac{q^N}{N!} \right) \\
&= -NkT \ln q + kT \ln(N!) \\
&= -NkT \ln q + kT(N \ln N - N) \\
&= -NkT(\ln q - \ln N + 1) \\
q &= q_T = \frac{V}{\Lambda^3} = \frac{0.0245 \text{ m}^3}{\left(\frac{h^2}{2\pi mkT} \right)^{3/2}} = \frac{0.0245 \text{ m}^3}{1.08 \times 10^{-32} \text{ m}^3} = 2.27 \times 10^{30}
\end{aligned}$$

$$N = n \times N_A = 6.022 \times 10^{23}$$

$$A = -nRT(\ln q - \ln N + 1)$$

$$\overset{\circ}{A}_m = -\left(8.314 \text{ J mol}^{-1} \text{ K}^{-1} \right)(298.15 \text{ K}) \left(\ln(2.27 \times 10^{30}) - \ln(6.022 \times 10^{23}) + 1 \right)$$

$$\overset{\circ}{A}_m = -40.0 \text{ kJ mol}^{-1}$$

This calculation can be repeated for Kr ($M = 0.083 \text{ kJ mol}^{-1}$), or the difference between the Helmholtz energy of Kr and Ne can be determined:

$$\begin{aligned}
 A_{Kr} - A_{Ar} &= -kT(\ln Q_{Kr} - \ln Q_{Ar}) \\
 &= -kT \ln \left(\frac{Q_{Kr}}{Q_{Ar}} \right) \\
 &= -NkT \ln \left(\frac{q_{Kr}}{q_{Ar}} \right) \\
 &= -NkT \ln \left(\left(\frac{\Lambda_{Ar}}{\Lambda_{Kr}} \right)^3 \right) \\
 &= -NkT \ln \left(\left(\frac{m_{Kr}}{m_{Ar}} \right)^{3/2} \right) \\
 &= -\frac{3}{2} NkT \ln \left(\frac{m_{Kr}}{m_{Ar}} \right) \\
 &= -\frac{3}{2} nRT \ln \left(\frac{0.083}{0.020} \right) \\
 A_{Kr,m}^\circ &= -\frac{3}{2} RT \ln(4.15) + A_{Ar,m}^\circ = -40.3 \text{ kJ mol}^{-1}
 \end{aligned}$$

P33.28) What is the vibrational contribution to the Helmholtz and Gibbs energies from a molar ensemble of one-dimensional harmonic oscillators?

$$\begin{aligned}
 A &= -kT \ln(q_V^N) = -NkT \ln q_V \\
 &= -nRT \ln(1 - e^{-\beta hc\tilde{\nu}})^{-1} \\
 A_m &= RT \ln(1 - e^{-\beta hc\tilde{\nu}}) \\
 G &= -kT \left[\ln(q_V^N) - V \left(\frac{\partial \ln(q_V^N)}{\partial V} \right)_T \right] \\
 G &= -kT \ln(q_V^N) = -NkT \ln q_V \\
 G_m &= RT \ln(1 - e^{-\beta hc\tilde{\nu}})
 \end{aligned}$$

The vibrational contribution to the molar Helmholtz and Gibbs energies are equivalent.

P33.29) Determine the standard Gibbs energy for $^{35}\text{Cl}^{35}\text{Cl}$ where $\tilde{\nu} = 560 \text{ cm}^{-1}$, $B = 0.244 \text{ cm}^{-1}$, and the ground electronic state is nondegenerate.

$$\begin{aligned}
G &= -kT \left[\ln Q - V \left(\frac{\partial \ln Q}{\partial V} \right)_T \right] \\
G &= -kT \left[\ln \left(\frac{q^N}{N!} \right) - V \left(\frac{\partial \ln \left(\frac{q^N}{N!} \right)}{\partial V} \right)_T \right] \\
G &= -NkT \ln q + NkT \ln N - NkT + VNkT \left(\frac{\partial \ln q}{\partial V} \right)_T \\
G_m &= -RT \ln q + RT \ln N - RT + VRT \left(\frac{\partial \ln q}{\partial V} \right)_T \\
&= -RT \ln (q_T q_R q_V q_E) + RT \ln N - RT + VRT \left(\frac{\partial \ln q_T}{\partial V} \right) \\
&= -RT (\ln (q_T q_R q_V q_E) - \ln N + 1) + \frac{VRT}{q_T} \left(\frac{\partial q_T}{\partial V} \right) \\
&= -RT (\ln (q_T q_R q_V q_E) - \ln N + 1) + RT \\
&= -RT \ln \left(\frac{(q_T q_R q_V q_E)}{N} \right) \\
q_T &= \frac{V}{\Lambda^3} = \frac{0.0245 \text{ m}^3}{1.77 \times 10^{-33} \text{ m}^3} = 1.39 \times 10^{31} \\
q_R &= \frac{kT}{\sigma B} = \frac{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{(2)(0.244 \text{ cm}^{-1})} = 425 \\
q_V &= \frac{1}{1 - e^{-\beta hc\tilde{\nu}}} = 1.07 \\
q_E &= 1 \\
G_m^\circ &= - (8.134 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K}) \ln \left(\frac{6.32 \times 10^{33}}{6.022 \times 10^{23}} \right) \\
G_m^\circ &= -57.2 \text{ kJ mol}^{-1}
\end{aligned}$$

P33.30) Determine the rotational and vibrational contributions to the standard Gibbs energy for N₂O (NNO), a linear triatomic molecule where $B = 0.419 \text{ cm}^{-1}$ and $\tilde{\nu}_1 = 1285 \text{ cm}^{-1}$, $\tilde{\nu}_2 = 589 \text{ cm}^{-1}$ (doubly degenerate), and $\tilde{\nu}_3 = 2224 \text{ cm}^{-1}$.

$$G_R = -NkT \ln q_R$$

$$G_{R,m} = -RT \ln q_R$$

$$q_R = \frac{kT}{\sigma B} = \frac{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{(2)(0.42 \text{ cm}^{-1})} = 493$$

$$G_{R,m}^\circ = -(8.134 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K}) \ln(493) = -15.4 \text{ kJ mol}^{-1}$$

$$G_V = -NkT \ln q_V$$

$$G_{V,m} = -RT \ln q_V$$

$$\begin{aligned} q_V &= \left(\frac{1}{1-e^{-\beta\tilde{\nu}_1}} \right) \left(\frac{1}{1-e^{-\beta\tilde{\nu}_2}} \right)^2 \left(\frac{1}{1-e^{-\beta\tilde{\nu}_3}} \right) \\ &= \left(\frac{1}{1-e^{\frac{-1285 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1})(298.15 \text{ K})}}} \right) \left(\frac{1}{1-e^{\frac{-589 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1})(298.15 \text{ K})}}} \right)^2 \left(\frac{1}{1-e^{\frac{-2224 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1})(298.15 \text{ K})}}} \right) \\ &= 1.13 \end{aligned}$$

$$G_{V,m}^\circ = -(8.134 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K}) \ln(1.13) = -0.30 \text{ kJ mol}^{-1}$$

P33.31) Determine the equilibrium constant for the dissociation of sodium at 298 K: $\text{Na}_2(g) \rightleftharpoons 2\text{Na}(g)$.

For Na_2 , $B = 0.155 \text{ cm}^{-1}$, $\tilde{\nu} = 159 \text{ cm}^{-1}$, the dissociation energy is 70.4 kJ/mol, and the ground-state electronic degeneracy for Na is 2.

$$\begin{aligned}
K &= \frac{\left(\frac{q}{N_A}\right)_{Na}^2 e^{-\beta\varepsilon_d}}{\left(\frac{q}{N_A}\right)_{Na_2}} \\
q_{Na} &= q_T q_E = \left(\frac{V}{\Lambda^3}\right)(2) = \left(\frac{0.0245 \text{ m}^3}{9.38 \times 10^{-33} \text{ m}^3}\right)(2) = 5.22 \times 10^{30} \\
q_{Na_2} &= q_T q_R q_V q_E = \left(\frac{V}{\Lambda^3}\right) \left(\frac{kT}{\sigma B}\right) \left(\frac{1}{1 - e^{-\beta hc\nu}}\right)(1) \\
&= \left(\frac{0.0245 \text{ m}^3}{3.32 \times 10^{-33} \text{ m}^3}\right) \left(\frac{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{(2)(0.155 \text{ cm}^{-1})}\right) \\
&\quad \times \left(\frac{1}{\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(159 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298.15 \text{ K})}}\right)(1) \\
&= 9.22 \times 10^{33} \\
K &= \frac{\left(\frac{5.22 \times 10^{30}}{N_A}\right)_{Na}^2 e^{\frac{70,400 \text{ J mol}^{-1}/N_A}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298.15 \text{ K})}}}{\left(\frac{9.22 \times 10^{33}}{N_A}\right)_{Na_2}} \\
&= 2.25 \times 10^{-9}
\end{aligned}$$

P33.32) The isotope exchange reaction for Cl₂ is as



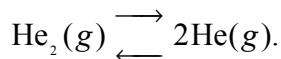
The equilibrium constant for this reaction is ~4. Furthermore, the equilibrium constant for similar isotope-exchange reactions is also close to this value. Demonstrate why this would be so.

The molecular masses are quite similar; therefore, the thermal wavelength and q_T will be essentially identical. Furthermore, the rotational constants will also be essentially identical. Using these approximations, the equilibrium constant reduces to an expression involving the ratio of symmetry numbers (σ) for the species involved?

$$\begin{aligned}
 K &= \frac{\left(\frac{q}{N_A}\right)_{35/37}^2}{\left(\frac{q}{N_A}\right)_{35/35}\left(\frac{q}{N_A}\right)_{37/37}} e^{-\beta\varepsilon_D} = \frac{(q)_{35/37}^2}{(q)_{35/35}(q)_{37/37}} \\
 q_{35/37} &= q_T q_R = \left(\frac{V}{\Lambda_{35/37}^3}\right) \left(\frac{1}{\sigma\beta B_{35/37}}\right) \\
 q_{35/35} &= q_T q_R = \left(\frac{V}{\Lambda_{35/35}^3}\right) \left(\frac{1}{\sigma\beta B_{35/35}}\right) \\
 q_{37/37} &= q_T q_R = \left(\frac{V}{\Lambda_{37/37}^3}\right) \left(\frac{1}{\sigma\beta B_{37/37}}\right) \\
 K &= \frac{(q)_{35/37}^2}{(q)_{35/35}(q)_{37/37}} = \frac{\left(\left(\frac{V}{\Lambda_{35/37}^3}\right)\left(\frac{1}{\sigma_{35/37}\beta B_{35/37}}\right)\right)^2}{\left(\left(\frac{V}{\Lambda_{35/35}^3}\right)\left(\frac{1}{\sigma_{35/35}\beta B_{35/35}}\right)\right)\left(\left(\frac{V}{\Lambda_{37/37}^3}\right)\left(\frac{1}{\sigma_{37/37}\beta B_{37/37}}\right)\right)} \\
 &\approx \frac{\sigma_{37/37}\sigma_{35/35}}{\sigma_{35/37}^2} = \frac{(2)(2)}{(1)^2} = 4
 \end{aligned}$$

P33.33) In “Direct Measurement of the Size of the Helium Dimer” by F. Luo, C. F. Geise, and W. R. Gentry [J. Chemical Physics 104 (1996), 1151], evidence for the helium dimer is presented. As one can imagine, the chemical bond in the dimer is extremely weak, with an estimated value of only 8.3 mJ/mol.

- a) An estimate for the bond length of 65 Å is presented in the paper. Using this information, determine the rotational constant for He₂. Using this value for the rotational constant, determine the location of the first rotational state. If correct, you will determine that the first excited rotational level is well beyond the dissociation energy of He₂.
- b) Consider the following equilibrium between He₂ and its atomic constituents:



If there are no rotational or vibrational states to consider, the equilibrium is determined exclusively by the translational degrees of freedom and the dissociation energy of He₂. Using the dissociation energy provided earlier and $V = 1000 \text{ cm}^3$, determine K_p assuming that $T = 10 \text{ K}$. The experiments were actually performed at 1 mK; why was such a low temperature employed?

a) Since the helium is ^4He , only even J states are allowed; therefore, the first excited rotational state is $J = 2$.

$$I = \mu r^2 = \left(\frac{m_{\text{He}}}{2} \right) (65 \times 10^{-10} \text{ m})^2 = \left(\frac{0.004 \text{ kg mol}^{-1}}{2(N_A)} \right) (4.23 \times 10^{-17} \text{ m}^2)$$

$$= 1.40 \times 10^{-43} \text{ kg m}^2$$

$$B = \frac{h}{8\pi^2 c I} = \frac{6.626 \times 10^{-34} \text{ J s}}{8\pi^2 (3.00 \times 10^{10} \text{ cm s}^{-1})(1.40 \times 10^{-43} \text{ kg m}^2)}$$

$$= 0.002 \text{ cm}^{-1} = 23.9 \text{ mJ mol}^{-1}$$

$$E_{J=2} = BJ(J+1) = 23.9 \text{ mJ mol}^{-1} (6) = 143.4 \text{ mJ mol}^{-1}$$

b)

$$K = \frac{\left(\frac{q}{N_A} \right)_{He}^2}{\left(\frac{q}{N_A} \right)_{He_2}} e^{-\beta \epsilon_D} = \frac{\left(\frac{q_T}{N_A} \right)_{He}^2}{\left(\frac{q_T}{N_A} \right)_{He_2}} e^{-\beta \left(\frac{0.083 \text{ J mol}^{-1}}{N_A} \right)}$$

$$q_{T,He} = \frac{V}{\Lambda_{He}^3} = \left(\frac{0.001 \text{ m}^3}{2.11 \times 10^{-29} \text{ m}^3} \right) = 4.75 \times 10^{25}$$

$$q_{T,He_2} = \frac{V}{\Lambda_{He_2}^3} = \left(\frac{0.001 \text{ m}^3}{7.45 \times 10^{-30} \text{ m}^3} \right) = 1.34 \times 10^{26}$$

$$K = \frac{\left(\frac{q_T}{N_A} \right)_{He}^2}{\left(\frac{q_T}{N_A} \right)_{He_2}} e^{-\beta \left(\frac{0.083 \text{ J mol}^{-1}}{N_A} \right)} = \frac{\left(\frac{4.75 \times 10^{25}}{N_A} \right)_{He}^2}{\left(\frac{1.34 \times 10^{26}}{N_A} \right)_{He_2}} e^{-\frac{\left(\frac{0.083 \text{ J mol}^{-1}}{N_A} \right)}{(1.38 \times 10^{-23} \text{ J K}^{-1})(10 \text{ K})}}$$

$$K = (28.0)(0.999) \cong 28.0$$

Even at this low temperature, equilibrium favors dissociation.

Chapter 34: Kinetic Theory of Gases

Problem numbers in italics indicate that the solution is included in the *Student's Solutions Manual*.

Questions on Concepts

Q34.1) Why is probability used to describe the velocity and speed of gas molecules?

Velocity is a measure of kinetic energy. As with any large ensemble of particles ($\sim N_A$) not all of the particles will have the same energies. Instead, the particle energies are distributed through a range of values. The fraction of gas particles with a specific energy is defined by a probability.

Q34.2) Describe pressure using gas kinetic theory. Why would one expect pressure to depend on the inverse of volume in this theory?

Pressure arises due to collision of particles with the walls of the container. Since the pressure is dependent upon the number of particles striking the wall of the container per unit area, the pressure is dependent upon the density of the gas (number of particles per volume). As the volume increases, the density decreases, and the pressure will subsequently decrease.

Q34.3) What are the inherent assumptions about gas particle interactions in gas kinetic theory?

The assumptions made are that the particles do not interact at long distances (i.e., the intermolecular potential is zero when particles are separated) and) particles interact only through elastic collisions (total conservation of kinetic energy).

Q34.4) Provide a physical explanation as to why the Maxwell speed distribution approaches zero at high speeds. Why is $f(v) = 0$ at $v = 0$?

Since kinetic energy content is related to temperature, higher particle speeds corresponds to a high inherent particle temperature. The ensemble of particles demonstrates an average temperature, and we can think of the inherent particle temperatures as distributed around this value. We would expect this number of particles demonstrating temperatures higher than the average temperature to decrease as the inherent temperature increases. Also, a non-zero distribution at infinite inherent temperature implies that the ensemble consists of an infinite number of particles. The distribution must reach zero as $T \rightarrow 0$ and $T \rightarrow \infty$ in order to preserve unit probability. Conversely, there can be no distribution at $v = 0$, due to the Uncertainty Principle since zero velocity would allow one to know both the position and velocity to arbitrary precision.

Q34.5) How would the Maxwell speed distributions for He versus Kr compare if the gases were at the same temperature?

The two distributions differ because of the mass difference between He and Kr. The Kr distribution will have a most probable speed that is smaller than He, the width of the Kr distribution will be smaller in comparison to He, and the Kr distribution will have a larger maximum amplitude.

Q34.6) How does the average speed of a collection of gas particles vary with particle mass and temperature?

The average speed of a particle in a gas is directly proportional to the square root of the temperature, and inversely proportional to the square root of the mass. Thus, as the temperature increases, the average speed increases (as the square root) and as the mass increases, the average speed decreases (as the square root).

Q34.7) Does the average kinetic energy of a particle depend on particle mass?

The average kinetic energy is defined as

$$\bar{E}_k = \frac{1}{2} m v_{ave}^2,$$

where

$$v_{ave}^2 = \left(\frac{8kT}{\pi m} \right)^{1/2}$$

In the preceding expression, k = Boltzmann constant, T = temperature, and m = mass. Thus combining the two equations,

$$\bar{E}_k = \frac{1}{2} m \left[\left(\frac{8kT}{\pi m} \right)^{1/2} \right]^2 = \frac{4kT}{\pi}$$

Thus the average kinetic energy is not dependent upon the mass of the particle.

Q34.8) Why does the mean free path depend on σ^2 ? Would an increase in \tilde{N} increase or decrease the mean free path?

The cross section is an effective area related to the size of the particles. The larger this area for collision is, the more probable a collision resulting in a corresponding decrease in the mean free path. Collisional frequencies are directly proportional to \tilde{N} ; therefore, the mean free path will be inversely proportional to \tilde{N} .

Q34.9) What is the typical length scale for a molecular diameter?

The typical atomic diameter is on the order of 0.2 nm or about 2 Å.

Q34.10) What is the difference between z_{11} and z_{12} ?

The term z_{11} is the single-particle collision frequency. The term z_{12} is the two-particle collision frequency. Term z_{11} corresponds to homogenous gas with only one particle type. Term z_{12} corresponds to a gas mixture in which two types of particles occur. This principle difference between the two are a) z_{11} depends on the number density of particle 1, whereas z_{12} depends on the number density of particle 2 and b) z_{11} depends on the single particle reduced mass (mass = $m_1/2$), where z_{12} depends on the two particle reduced mass ($m = (m_1 m_2) / (m_1 + m_2)$).

Q34.11) Define the mean free path. How does this quantity vary with number density, particle diameter, and average particle speed?

The mean free path is the average distance traveled by a gas particle between successive collisions.

Problems

P34.1) Consider a collection of gas particles confined to translate in two dimensions (for example, a gas molecule on a surface). Derive the Maxwell speed distribution for such a gas.

Beginning with the Maxwell-Boltzmann velocity distribution in one-dimension

$$f(v_j) = \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-\frac{m}{2kT}v_j^2}$$

and the definition of speed in 2 dimensions

$$v = (v_x^2 + v_y^2)^{1/2}$$

The speed distribution in 2 dimensions is given by:

$$Fd\nu = f(v_x)f(v_y)dv_xdv_y$$

where dv_j is the differential of velocity in the jth direction. Thus

$$\begin{aligned}
 Fd\nu &= \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-\frac{m}{2kT}v_x^2} \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-\frac{m}{2kT}v_y^2} dv_x dv_y \\
 &= \left(\frac{m}{2\pi kT} \right) e^{-\frac{m}{2kT}(v_x^2 + v_y^2)} dv_x dv_y \\
 Fd\nu &= \left(\frac{m}{2\pi kT} \right) e^{-\frac{m}{2kT}v^2} dv_x dv_y
 \end{aligned}$$

The differential area is defined as:

$$dv_x dv_y = 2\pi v dv$$

Substituting this into the expression for $Fd\nu$:

$$Fd\nu = \left(\frac{m}{2\pi kT} \right) e^{-\frac{m}{2kT}v^2} (2\pi v) dv = \frac{m}{kT} e^{-\frac{m}{2kT}v^2}$$

P34.2) Determine v_{mp} , v_{ave} , and v_{rms} for the following species at 298 K:

- a) Ne
- b) Kr
- c) CH₄
- d) C₆H₆
- e) C₆₀

Note: J kg⁻¹ ≡ m² s⁻²

a) Ne: M = 0.020 mol⁻¹

$$v_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{0.020 \text{ kg mol}^{-1}}} = 495 \text{ m s}^{-1}$$

$$v_{ave} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{\pi(0.020 \text{ kg mol}^{-1})}} = 559 \text{ m s}^{-1}$$

$$v_{rms} = \sqrt{\frac{8RT}{M}} = \sqrt{\frac{3(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{0.020 \text{ kg mol}^{-1}}} = 607 \text{ m s}^{-1}$$

b) Kr: M = 0.084 kg mol⁻¹

$$v_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{0.084 \text{ kg mol}^{-1}}} = 243 \text{ m s}^{-1}$$

$$v_{\text{ave}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{\pi(0.084 \text{ kg mol}^{-1})}} = 274 \text{ m s}^{-1}$$

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{0.084 \text{ kg mol}^{-1}}} = 298 \text{ m s}^{-1}$$

c) CH₄: M = 0.016 kg mol⁻¹

$$v_{\text{mp}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{0.016 \text{ kg mol}^{-1}}} = 555 \text{ m s}^{-1}$$

$$v_{\text{ave}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{\pi(0.016 \text{ kg mol}^{-1})}} = 626 \text{ m s}^{-1}$$

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{0.016 \text{ kg mol}^{-1}}} = 680 \text{ m s}^{-1}$$

d) C₂H₆: M = 0.030 kg mol⁻¹

$$v_{\text{mp}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{0.030 \text{ kg mol}^{-1}}} = 406 \text{ m s}^{-1}$$

$$v_{\text{ave}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{\pi(0.030 \text{ kg mol}^{-1})}} = 458 \text{ m s}^{-1}$$

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{0.030 \text{ kg mol}^{-1}}} = 497 \text{ m s}^{-1}$$

e) C₆₀: M = 0.721 kg mol⁻¹

$$v_{\text{mp}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{0.721 \text{ kg mol}^{-1}}} = 82.9 \text{ m s}^{-1}$$

$$v_{ave} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{\pi(0.721 \text{ kg mol}^{-1})}} = 93.6 \text{ m s}^{-1}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{0.721 \text{ kg mol}^{-1}}} = 102 \text{ m s}^{-1}$$

P34.3) Compute v_{mp} , v_{ave} , and v_{rms} for O₂ at 300 and 500 K. How would your answers change for H₂?

$$\text{O}_2: M = 0.032 \text{ kg mol}^{-1} \quad \text{H}_2: M = 0.002 \text{ kg mol}^{-1}$$

O₂ @ 300 K:

$$v_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(300 \text{ K})}{0.032 \text{ kg mol}^{-1}}} = 395 \text{ m s}^{-1}$$

$$v_{ave} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(300 \text{ K})}{\pi(0.032 \text{ kg mol}^{-1})}} = 446 \text{ m s}^{-1}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(300 \text{ K})}{0.032 \text{ kg mol}^{-1}}} = 484 \text{ m s}^{-1}$$

O₂ @ 500 K

$$v_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(500 \text{ K})}{0.032 \text{ kg mol}^{-1}}} = 510 \text{ m s}^{-1}$$

$$v_{ave} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(500 \text{ K})}{\pi(0.032 \text{ kg mol}^{-1})}} = 575 \text{ m s}^{-1}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(500 \text{ K})}{0.032 \text{ kg mol}^{-1}}} = 624 \text{ m s}^{-1}$$

All of these values depend on the square root of the mass of the particle, so that:

$$\nu_{H_2} = \left(\frac{M_{O_2}}{M_{H_2}} \right)^{1/2} \nu_{O_2}$$

$$\nu_{H_2} = \left(\frac{0.032 \text{ kg mol}^{-1}}{0.002 \text{ kg mol}^{-1}} \right)^{1/2} \nu_{O_2}$$

$$\nu_{H_2} = (3.98) \nu_{O_2} \text{ for each velocity and T.}$$

P34.4) Compare the average speed and average kinetic energy of O₂ with that of CCl₄ at 298 K.

$$M_{O_2} = 0.032 \text{ kg mol}^{-1} \quad M_{CCl_4} = 0.154 \text{ kg mol}^{-1}$$

At the same temperature, the speed for two particles of different mass is related by the square root of the mass ratios. For this case of O₂ and CCl₄:

$$\nu_{CCl_4} = \left(\frac{M_{O_2}}{M_{CCl_4}} \right)^{1/2} \nu_{O_2}$$

$$\nu_{CCl_4} = \left(\frac{0.0320 \text{ kg mol}^{-1}}{0.154 \text{ kg mol}^{-1}} \right)^{1/2} \nu_{O_2} = (0.456) \nu_{O_2}$$

The average speed for O₂ at 298 K is:

$$\nu_{ave} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{\pi \cdot 0.032 \text{ kg mol}^{-1}}} = 444 \text{ m s}^{-1}$$

Using this result, the average speed for CCl₄ at this same temperature is:

$$\nu_{ave,CCl_4} = 0.456 \times \nu_{ave, O_2}$$

$$\nu_{ave,CCl_4} = (0.456)(444 \text{ m s}^{-1})$$

$$\nu_{ave,CCl_4} = 203 \text{ m s}^{-1}$$

The average kinetic energy is mass independent, thus for a given temperature, all gases have the same kinetic energy. The average kinetic energy per gas particle is therefore:

$$\langle KE \rangle = \frac{3}{2} kT = \frac{3}{2} (1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})$$

$$\langle KE \rangle = 6.17 \times 10^{-21} \text{ J}$$

P34.5)

- What is the average time required for H₂ to travel 1 meter at 298 K and 1 atm?
- How much longer does it take N₂ to travel 1 m on average relative to H₂ under these same conditions?

c) (Challenging) What fraction of N₂ particles will require more than this average time to travel 1 m? Answering this question will require evaluating a definite integral of the speed distribution, which requires using numerical methods such as Simpson's rule.

- a) The inverse of the average speed is the time required to travel a certain distance. For 1 meter of travel and M_{H₂} = 0.002 kg mol⁻¹:

$$\frac{1}{v_{\text{ave}}} = \sqrt{\frac{\pi M}{8RT}} = \sqrt{\frac{\pi(0.002 \text{ kg mol}^{-1})}{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}} = 5.66 \times 10^{-4} \text{ s m}^{-1}$$

- b) Here, M_{N₂} = 0.028 kg mol⁻¹, and the mass ratio relative to H₂ is:

$$\sqrt{\frac{M_{N_2}}{M_{H_2}}} = \sqrt{\frac{0.028 \text{ kg mol}^{-1}}{0.002 \text{ kg mol}^{-1}}} = 3.72$$

$$\frac{1}{v_{\text{ave}, N_2}} = 3.72 \cdot \frac{1}{v_{\text{ave}, H_2}} = 2.11 \times 10^{-3} \text{ s m}^{-1}$$

- c) The average velocity for N₂ @ 298 K can be found from part (b):

$$v_{\text{ave}, N_2} = 475 \text{ m s}^{-1}$$

The fraction of particles with speed less than the average velocity can be found by integrating the Maxwell speed distribution from v = 0 to v = v_{ave}.

$$\begin{aligned} f &= \int_0^{v_{\text{ave}}} 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-\frac{Mv^2}{2RT}} dv \\ &= (3.03 \times 10^{-8}) \int_0^{475} v^2 e^{-(5.66 \times 10^{-4})v^2} dv \end{aligned}$$

Numerical integration of the above expression demonstrates that f = 0.534.

P34.6) As mentioned in Section 34.3, the only differences between the quantities v_{mp}, v_{ave}, and v_{rms} involve constants.

- a) Derive the expressions for v_{ave} and v_{rms} relative to v_{mp}.
 b) Your result from part (a) will involve quantities that are independent of gas-specific quantities such as mass or temperature. Given this, it is possible to construct a “generic” speed distribution curve for speed in reduced units of v/v_{mp}. Transform the Maxwell speed distribution into a corresponding expression involving reduced speed.

a)

$$\nu_{mp} = \sqrt{\frac{2RT}{M}}$$

$$\frac{\nu_{avg}}{\nu_{mp}} = \frac{\sqrt{\frac{8RT}{\pi M}}}{\sqrt{\frac{2RT}{M}}} = \frac{2}{\sqrt{\pi}}$$

$$\frac{\nu_{rms}}{\nu_{mp}} = \frac{\sqrt{\frac{3RT}{M}}}{\sqrt{\frac{2RT}{M}}} = \sqrt{\frac{3}{2}}$$

b) Defining the reduced velocity, ν_{red} , as follows:

$$\nu_{red} = \frac{\nu}{\nu_{mp}}$$

and relating the differentials for reduced and actual speed:

$$\frac{d\nu_{red}}{d\nu} = \frac{1}{\nu_{mp}} = \left(\frac{M}{2RT} \right)^{1/2}$$

We can use the above relationship to express the speed distribution in terms of a relative speed:

$$f(\nu_{red}) d\nu_{red} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \left(\nu_{red} \sqrt{\frac{2RT}{M}} \right)^2 e^{-\frac{M}{2RT} \left(\nu_{red} \sqrt{\frac{2RT}{M}} \right)^2} \left(\frac{2RT}{M} \right)^{1/2} d\nu_{red}$$

$$= \frac{4}{\sqrt{\pi}} \nu_{red}^2 e^{-\nu_{red}^2} d\nu_{red}$$

P34.7) At what temperature is the ν_{rms} of Ar equal to that of SF₆ at 298 K? Perform the same calculation for ν_{mp} .

$$M_{Av} = 0.040 \text{ kg mol}^{-1} \text{ and } M_{SF_6} = 0.146 \text{ kg mol}^{-1}$$

Setting the rms speeds equal and reducing yields:

$$\sqrt{\frac{3RT_{Ar}}{M_{Ar}}} = \sqrt{\frac{3RT_{SF_6}}{M_{SF_6}}}$$

$$T_{Ar} = \frac{M_{Ar}}{M_{SF_6}} \cdot T_{SF_6}$$

Therefore:

$$T_{\text{Ar}} = \left(\frac{0.040 \text{ kg mol}^{-1}}{0.146 \text{ kg mol}^{-1}} \right) 298 \text{ K}$$

$$T_{\text{Ar}} = 81.5 \text{ K}$$

Since v_{rms} and v_{mp} are related by non-gas-dependent factors, the temperature relation for v_{mp} is the same as the temperature relation for v_{rms} .

P34.8) The probability that a particle will have a velocity in the x direction in the range of $-v_{x_0}$ and v_{x_0} is given by

$$f(-v_{x_0} \leq v_x \leq v_{x_0}) = \left(\frac{m}{2\pi kT} \right)^{1/2} \int_{-v_{x_0}}^{v_{x_0}} e^{\frac{-mv_x^2}{2kT}} dv_x = \left(\frac{2m}{\pi kT} \right)^{1/2} \int_0^{v_{x_0}} e^{\frac{-mv_x^2}{2kT}} dv_x$$

The preceding integral can be rewritten using the following substitution: $\xi^2 = \frac{mv_x^2}{2kT}$,

resulting in $f(-v_{x_0} \leq v_x \leq v_{x_0}) = \frac{2}{\sqrt{\pi}} \int_0^{\xi_0} e^{-\xi^2} d\xi$, which can be evaluated using the error

function defined as $\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-x^2} dx$. The complementary error function is defined

as $\text{erfc}(z) = 1 - \text{erf}(z)$. Finally, a plot of both $\text{erf}(z)$ and $\text{erfc}(z)$ as a function of z is shown in the text (tabulated values are available in the Math Supplement, Appendix A): Using this graph of $\text{erf}(z)$, determine the probability that $|v_x| \leq (2kT/m)^{1/2}$. What is the probability that $|v_x| > (2kT/m)^{1/2}$?

$$\text{If } |v_x| \leq \left(\frac{2 \text{ kT}}{m} \right)^{1/2}, \text{ then}$$

$$\xi^2 \leq \frac{m}{2 \text{ kT}} \left(\frac{2 \text{ kT}}{m} \right) = 1$$

and

$$\xi_0 \leq \sqrt{1} \leq 1$$

The probability that the particle has $|v_x| \leq \left(\frac{2 \text{ kT}}{m} \right)^{1/2}$ is given by:

$$f_{\leq} = \frac{2}{\sqrt{\pi}} \int_0^1 e^{-\xi^2} d\xi$$

$$f_{\leq} = \text{erf}(1)$$

$$f_{\leq} = 0.8427$$

The probability that the particle would have a velocity $|v_x| > \left(\frac{2 kT}{m}\right)^{1/2}$ is found

from the previous part, since the total probability must be 1:

$$f_s = 1 - 0.8427$$

$$f_s = 0.1573$$

P34.9) The speed of sound is given by $v_{\text{sound}} = \sqrt{\frac{\gamma kT}{m}} = \sqrt{\frac{\gamma RT}{M}}$, where $\gamma = C_p/C_v$.

- a) What is the speed of sound in Ne, Kr, and Ar at 1000 K?
 b) At what temperature will the speed of sound in Kr equal the speed of sound in Ar at 1000 K?

a) $M_{\text{Ne}} = 0.020 \text{ kg mol}^{-1}$ $M_{\text{Kr}} = 0.084 \text{ kg mol}^{-1}$ $M_{\text{Ar}} = 0.040 \text{ kg mol}^{-1}$

The heat capacities for the three gases are the same:

$$C_v = 12.5 \text{ J K}^{-1} \text{ mol}^{-1} \text{ and } C_p = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

Thus, $\gamma = 1.6666$.

a) Ne:

$$v_{\text{sound}} = \sqrt{\frac{1.67(8.314 \text{ J mol}^{-1} \text{ K})(1000 \text{ K})}{0.020 \text{ kg mol}^{-1}}} = 829 \text{ m s}^{-1}$$

Kr:

$$v_{\text{sound}} = \sqrt{\frac{1.67(8.314 \text{ J mol}^{-1} \text{ K})(1000 \text{ K})}{0.084 \text{ kg mol}^{-1}}} = 407 \text{ m s}^{-1}$$

Ar:

$$v_{\text{sound}} = \sqrt{\frac{1.67(8.314 \text{ J mol}^{-1} \text{ K})(1000 \text{ K})}{0.040 \text{ kg mol}}} = 589 \text{ m s}^{-1}$$

b) Setting the speed of sound equal for Kr and Ar:

$$\sqrt{\frac{\gamma R T_{\text{Kr}}}{M_{\text{Kr}}}} = \sqrt{\frac{\gamma R T_{\text{Ar}}}{M_{\text{Ar}}}}$$

$$T_{\text{Kr}} = \frac{M_{\text{Kr}}}{M_{\text{Ar}}} \cdot T_{\text{Ar}}$$

Therefore:

$$T_{\text{Kr}} = \left(\frac{0.084 \text{ kg mol}^{-1}}{0.040 \text{ kg mol}^{-1}} \right) 1000 \text{ K}$$

$$T_{\text{Kr}} = (2.10) 1000 \text{ K}$$

$$T_{\text{Kr}} = 2100 \text{ K}$$

P34.10) For O₂ at 1 atm and 298 K, what fraction of molecules has a speed that is greater than v_{rms}?

For O₂ @ 1 atm and 298 K

$$v_{\text{rms}} = \sqrt{\frac{3(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{0.032 \text{ kg mol}^{-1}}} = 482 \text{ m s}^{-1}$$

The fraction of O₂ particles with a speed greater than v_{rms} = 482 m s⁻¹ is found by integration of the speed distribution.

$$\begin{aligned} f &= \int_{482 \text{ m s}^{-1}}^{\infty} 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-\frac{M}{2RT}v^2} dv \\ f &= 3.70 \times 10^{-8} \int_{482}^{\infty} v^2 e^{-6.46 \times 10^{-6} v^2} dv \end{aligned}$$

Evaluating the above expression numerically, the fraction of molecules with a speed greater than v_{rms} yields f = 0.392.

P34.11) The escape velocity from the Earth's surface is given by v_E = (2gR)^{1/2} where g is gravitational acceleration (9.80 m s⁻²) and R is the radius of the Earth (6.37 × 10⁶ m).

- a) At what temperature will v_{mp} for N₂ be equal to the escape velocity?
- b) How does the answer for part (a) change if the gas of interest is He?

- a) The escape velocity of earth is given as

$$\begin{aligned} v_E &= \sqrt{2(9.80 \text{ m s}^{-2})(6.37 \times 10^6 \text{ m})} \\ v_E &= 1.11 \times 10^4 \text{ m s}^{-1} \end{aligned}$$

For N₂:

$$\begin{aligned} v_{\text{mp}} &= \sqrt{\frac{2RT}{M}} = v_E \\ 1.12 \times 10^4 \text{ m s}^{-1} &= \sqrt{\frac{2(8.314 \text{ J mol}^{-1} \text{ K}^{-1})T}{0.028 \text{ kg mol}^{-1}}} \\ T &= \frac{(1.12 \times 10^4 \text{ m s}^{-1})^2 \cdot 0.028 \text{ kg mol}^{-1}}{2(8.314 \text{ J mol}^{-1} \text{ K}^{-1})} = 2.10 \times 10^5 \text{ K} \end{aligned}$$

- b) The temperature should decrease as the mass decreases; therefore, we would expect the corresponding temperature for He to be lower than that of N₂:

$$\sqrt{\frac{2RT_{N_2}}{M_{N_2}}} = \sqrt{\frac{2RT_{He}}{M_{He}}}$$

$$T_{He} = \frac{M_{He}}{M_{N_2}} T_{N_2}$$

$$T_{He} = \left(\frac{0.004 \text{ kg mol}^{-1}}{0.028 \text{ kg mol}^{-1}} \right) 2.10 \times 10^5 \text{ K}$$

$$T_{He} = 3.00 \times 10^4 \text{ K}$$

P34.12) For N₂ at 298 K, what fraction of molecules has a speed between 200 and 300 m s⁻¹? What is this fraction if the gas temperature is 500 K?

The fraction of N₂ particles can be found by integrating the speed distribution between the speeds 200 and 300 m/s.

$$\begin{aligned} @ 298 \text{ K} \quad \frac{M}{2RT} &= \frac{0.028 \text{ kg mol}^{-1}}{2(8.314 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})} = 5.65 \times 10^{-6} \text{ m}^{-2}\text{s}^2 \\ f &= \int_{200}^{300} 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-\frac{M}{2RT}v^2} dv \\ f &= 3.03 \times 10^{-8} \int_{200}^{300} v^2 e^{-5.65 \times 10^{-6} v^2} dv \end{aligned}$$

Using numerical integration the above expression can be evaluated to yield $f = 0.132$. With an increase in temperature to 500 K, the fraction becomes:

$$\begin{aligned} @ 500 \text{ K} \quad \frac{M}{2RT} &= \frac{0.028 \text{ kg mol}^{-1}}{2(8.314 \text{ J mol}^{-1}\text{K}^{-1})(500 \text{ K})} = 3.37 \times 10^{-6} \text{ m}^{-2}\text{s}^2 \\ f &= \int_{200}^{300} 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-\frac{M}{2RT}v^2} dv \\ f &= 1.39 \times 10^{-8} \int_{200}^{300} v^2 e^{-3.37 \times 10^{-6} v^2} dv \\ f &= 0.071 \end{aligned}$$

P34.13) Demonstrate that the Maxwell–Boltzmann speed distribution is normalized.

If the Maxwell speed distribution is normalized, then the integral of the distribution function over the range of possible speeds (zero to infinity) should equal unity. Using the integral tables provided in the Math Supplement, this is accomplished shown as follows:

$$\begin{aligned}
 \int_0^\infty F v dv &= \int_0^\infty 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-\frac{M}{2RT}v^2} dv \\
 &= 4\beta \sqrt{\frac{\beta}{\pi}} \int_0^\infty v^2 e^{-\beta v^2} dv \quad \left\{ \text{where } \beta = \frac{M}{2RT} \right\} \\
 &= 4\beta \sqrt{\frac{\beta}{\pi}} \cdot \frac{1}{4\beta} \sqrt{\frac{\pi}{\beta}} \\
 &= 1
 \end{aligned}$$

P34.14) (Challenging) Derive the Maxwell–Boltzmann distribution using the Boltzmann distribution introduced in statistical mechanics. Begin by developing the expression for the distribution in translational energy in one dimension and then extend it to three dimensions.

The Boltzmann distribution states that the probability of residing in an energy level $P(\epsilon)$ is given by the following:

$$P(\epsilon) = Ce^{-\frac{\epsilon}{kT}}$$

The translational energy is related to the velocity in one dimension by:

$$\epsilon_x = \frac{1}{2}mv_x^2$$

Using the above expressions and normalizing the probability distribution results in the following expression for the velocity distribution in one dimension:

$$\begin{aligned}
 P(\epsilon_x) d\epsilon_x &= Ce^{-\frac{\epsilon_x}{kT}} \\
 P(v_x) dv_x &= Ce^{-\frac{mv_x^2}{2kT}} dv_x \\
 \int_{-\infty}^{\infty} P(v_x) dv_x &= 1 = \int_{-\infty}^{\infty} Ce^{-\frac{mv_x^2}{2kT}} dv_x \\
 1 &= 2C \int_0^{\infty} e^{-\frac{mv_x^2}{2kT}} dv_x \\
 1 &= 2C \left(\frac{1}{2} \sqrt{\frac{2\pi kT}{m}} \right) \\
 \left(\frac{m}{2\pi kT} \right)^{1/2} &= C \\
 P(v_x) dv_x &= \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-\frac{mv_x^2}{2kT}} dv_x
 \end{aligned}$$

The speed distribution is then related to the product of velocity distributions in one dimension as described in the text:

$$\begin{aligned}
 P(v)dv &= P(v_x)P(v_y)P(v_z)dv_xdv_ydv_z \\
 &= \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2kT}} dv_x dv_y dv_z \\
 &= \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} (4\pi v^2 dv) \\
 &= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} dv
 \end{aligned}$$

P34.15) Starting with the Maxwell speed distribution, demonstrate that the probability distribution for translational energy for $\epsilon_{Tr} \gg kT$ is given by:

$$f(\epsilon_{Tr})d\epsilon_{Tr} = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} e^{-\epsilon_{Tr}/kT} \epsilon_{Tr}^{1/2} d\epsilon_{Tr}$$

The translational energy of a particle can be related to the velocity of the particle by the expressions

$$\begin{aligned}
 \epsilon_{Tr} &= \frac{1}{2}mv^2 \\
 v &= \sqrt{\frac{2\epsilon_T}{m}} \\
 dv &= \sqrt{\frac{2}{m}} \cdot \frac{1}{2} \sqrt{\frac{1}{\epsilon_{Tr}}} d\epsilon_{Tr} = \frac{1}{2} \sqrt{\frac{2}{m\epsilon_{Tr}}} d\epsilon_{Tr}
 \end{aligned}$$

Substituting this result into the Maxwell speed distribution:

$$\begin{aligned}
 f(\epsilon_{Tr})d\epsilon_{Tr} &= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \left(\frac{2\epsilon_{Tr}}{m}\right) e^{-\frac{m(2\epsilon_{Tr})}{2kT}} \left(\frac{1}{2} \sqrt{\frac{2}{m\epsilon_{Tr}}} d\epsilon_{Tr}\right) \\
 &= 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} e^{-\frac{\epsilon_{Tr}}{kT}} \epsilon_{Tr}^{1/2} d\epsilon_{Tr}
 \end{aligned}$$

P34.16) Using the distribution of particle translational energy provided in Problem P34.15, derive expressions for the average and most probable translational energies for a collection of gaseous particles.

The average energy is given by:

$$\begin{aligned}
 \langle \epsilon_{T_v} \rangle &= \int_0^{\infty} \epsilon_{T_r} \left(2\pi \left(\frac{1}{\pi kT} \right)^{3/2} \epsilon_{T_r}^{1/2} e^{-\frac{\epsilon_{T_r}}{kT}} d\epsilon_{T_r} \right) \\
 &= 2\pi \left(\frac{1}{\pi kT} \right)^{3/2} \int_0^{\infty} \epsilon_{T_r}^{3/2} e^{-\frac{\epsilon_{T_r}}{kT}} d\epsilon_{T_r} \\
 &= 2\pi \left(\frac{1}{\pi kT} \right)^{3/2} \cdot \frac{3\sqrt{\pi}}{4} \left(\frac{1}{kT} \right)^{-5/2} \\
 &= \frac{3}{2} kT
 \end{aligned}$$

The most probable energy is determined by taking the derivative of the probability distribution function, setting the derivative equal to zero, then solving for energy:

$$\begin{aligned}
 \frac{\partial}{\partial \epsilon_{T_r}} f(\epsilon_{T_r}) &= 0 = 2\pi \left(\frac{1}{\pi kT} \right)^{3/2} \frac{\partial}{\partial \epsilon_{T_r}} \left[\epsilon_{T_r}^{1/2} e^{-\frac{\epsilon_{T_r}}{kT}} \right] \\
 0 &= 2\pi \left(\frac{1}{\pi kT} \right)^{3/2} \left[\frac{1}{2} \epsilon_{T_r}^{-1/2} e^{-\frac{\epsilon_{T_r}}{kT}} - \frac{\epsilon_{T_r}^{1/2}}{kT} e^{-\frac{\epsilon_{T_r}}{kT}} \right] \\
 0 &= 2\pi \left(\frac{1}{\pi kT} \right)^{3/2} e^{-\frac{\epsilon_{T_r}}{kT}} \left[\frac{1}{2} \epsilon_{T_r}^{-1/2} - \frac{\epsilon_{T_r}^{1/2}}{kT} \right]
 \end{aligned}$$

The equality will be true when the term in square brackets equals zero:

$$0 = \frac{1}{2} \epsilon_{mp}^{-1/2} - \frac{\epsilon_{mp}^{1/2}}{kT}$$

$$\frac{1}{2} \epsilon_{mp}^{-1/2} = \frac{1}{kT} \epsilon_{mp}^{1/2}$$

$$\epsilon_{mp} = \frac{1}{2} kT$$

P34.17) (Challenging) Using the distribution of particle translational energy provided in Problem P34.15, derive an expression for the fraction of molecules that have energy greater than some energy ϵ^* . The rate of many chemical reactions is dependent on the thermal energy available, kT , versus some threshold energy. Your answer to this question will provide insight into why one might expect the rate of such chemical reactions to vary with temperature.

The fraction of particles with kinetic energy greater than ϵ^* is given by integration of the kinetic-energy distribution over the appropriate limits:

$$f = \frac{2\pi}{(\pi kT)^{3/2}} \int_{\epsilon^*}^{\infty} \epsilon_{T_v}^{1/2} e^{-\epsilon_{T_v}/kT} d\epsilon_{T_v}$$

Using the following substitutions:

$$\begin{aligned}\varepsilon &= kTx^2 \\ d\varepsilon &= 2kTdx(x^2)\end{aligned}$$

the integral becomes:

$$f = \frac{2}{\sqrt{\pi}} \int_{(\varepsilon^*/kT)^{1/2}}^{\infty} xe^{-x^2} dx = -\frac{2}{\sqrt{\pi}} \int_{(\varepsilon^*/kT)^{1/2}}^{\infty} x d(e^{-x^2})$$

Evaluating the above integral using integration by parts yields:

$$\begin{aligned}f &= -\frac{2}{\sqrt{\pi}} \int_{(\varepsilon^*/kT)^{1/2}}^{\infty} x d(e^{-x^2}) = -\frac{2}{\sqrt{\pi}} \left[xe^{-x^2} \Big|_{(\varepsilon^*/kT)^{1/2}}^{\infty} - \int_{(\varepsilon^*/kT)^{1/2}}^{\infty} e^{-x^2} dx \right] \\ &= 2 \left(\frac{\varepsilon^*}{\pi kT} \right)^{1/2} e^{-\varepsilon^*/kT} + \frac{2}{\sqrt{\pi}} \int_{(\varepsilon^*/kT)^{1/2}}^{\infty} e^{-x^2} dx \\ &= 2 \left(\frac{\varepsilon^*}{\pi kT} \right)^{1/2} e^{-\varepsilon^*/kT} + erfc \left(\left(\frac{\varepsilon^*}{kT} \right)^{1/2} \right)\end{aligned}$$

When $\varepsilon^* \gg kT$, the co-error function will be negligible, and the fraction of particles with energy sufficient to react becomes:

$$f = 2 \left(\frac{\varepsilon^*}{\pi kT} \right)^{1/2} e^{-\varepsilon^*/kT}$$

P34.18) As discussed in Chapter 30, the n th moment of a distribution can be determined as follows: $\langle x^n \rangle = \int x^n f(x) dx$, where integration is over the entire domain of the distribution. Derive expressions for the n th moment of the gas speed distribution.

$$\begin{aligned}\langle v^n \rangle &= \int_0^{\infty} v^n F(v) dv \quad \text{for } n = 1, 2, \dots \\ &= \int_0^{\infty} v^n 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-\frac{M}{2RT}v^2} dv \\ &= 4\pi \left(\frac{\beta}{\pi} \right)^{3/2} \int_0^{\infty} v^{n+2} e^{-\beta v^2} dv \quad \text{for } \beta = \frac{M}{2RT}\end{aligned}$$

This integral has 2 possible forms, depending on the parity of the integrand. If n is even (for $n = 2, 4, 6, \dots$) then $2m = n + 2$ for $m = 1, 2, 3, \dots$. And the integral becomes

$$\begin{aligned}\langle v^n \rangle &= 4\pi \left(\frac{\beta}{\pi}\right)^{3/2} \int_0^{\infty} v^{2m} e^{-\beta v^2} dv \quad \text{for } m = 2, 3, 4, \dots \\ &= 4\pi \left(\frac{\beta}{\pi}\right)^{3/2} \cdot \frac{(2m-1)!}{2(2\beta)^m} \left(\frac{\pi}{\beta}\right)^{1/2} \\ &= \frac{4\beta(2m-1)!}{2(2\beta)^m} \\ \langle v^n \rangle &= \frac{2\beta(n+1)!}{(2\beta)^{\frac{n+2}{2}}} \quad \text{for } n = 2, 4, 6, \dots\end{aligned}$$

If n is odd ($n = 1, 3, 5, \dots$) then $2m + 1 = n + 2$ for $m = 1, 2, 3, \dots$. The integral becomes

$$\begin{aligned}\langle v^n \rangle &= 4\pi \left(\frac{\beta}{\pi}\right)^{3/2} \int_0^{\infty} v^{2m+1} e^{-\beta v^2} dv \quad \text{for } m = 1, 2, 3, 4, \dots \\ &= 4\pi \left(\frac{\beta}{\pi}\right)^{3/2} \frac{m!}{2\beta^{m+1}} \\ &= 2\sqrt{\frac{\beta}{\pi}} \cdot \frac{m!}{\beta^m} \\ \langle v^n \rangle &= 2\sqrt{\frac{\beta}{\pi}} \frac{\left(\frac{n+1}{2}\right)!}{\beta^{\frac{n+1}{2}}} \quad \text{for } n = 1, 3, 5, \dots\end{aligned}$$

P34.19) Imagine a cubic container with sides 1 cm in length that contains 1 atm of Ar at 298 K. How many gas–wall collisions are there per second?

The collisional rate is given by:

$$\frac{dN_c}{dt} = \frac{PAV_{ave}}{4kT} = \frac{PA N_A V_{avg,e}}{4RT}$$

With $M_{Ar} = 0.040 \text{ kg mol}^{-1}$ and $T = 298 \text{ K}$ the average speed is:

$$\begin{aligned}V_{avg} &= \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{\pi(0.040 \text{ kg mol}^{-1})}} \\ V_{avg} &= 459 \text{ m s}^{-1}\end{aligned}$$

Substituting into the expression for the collisional rate:

$$\frac{dN_c}{dt} = \frac{\left(1 \text{ atm} \cdot \frac{101.325 \times 10^3 \text{ N m}^{-2}}{1 \text{ atm}}\right) \left(1 \text{ cm}^2 \left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^2\right) (6.022 \times 10^{23} \text{ mol}^{-1}) (459 \text{ m s}^{-1})}{4(8.314 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}$$

$$\frac{dN_c}{dt} = 2.823 \times 10^{23} \text{ coll. per sec. per wall}$$

Taking into account the six walls that comprise the container, the total collisional rate is:

$$\frac{dN_c}{dt} = 6 \text{ walls} \cdot 2.823 \times 10^{23} \text{ coll. s}^{-1} \text{ wall}^{-1}$$

$$\frac{dN_c}{dt} = 1.70 \times 10^{24} \text{ coll. s}^{-1}$$

P34.20) The vapor pressure of various substances can be determined using effusion. In this process, the material of interest is placed in an oven (referred to as a Knudsen cell) and the mass of material lost through effusion is determined. The mass loss (Δm) is given by $\Delta m = Z_c A m \Delta t$, where Z_c is the collisional flux, A is the area of the aperture through which effusion occurs, m is the mass of one atom, and Δt is the time interval over which the mass loss occurs. This technique is quite useful for determining the vapor pressure of nonvolatile materials. A 1.00-g sample of UF_6 is placed in a Knudsen cell equipped with a $100\text{-}\mu\text{m}$ -radius hole and heated to 18.2°C where the vapor pressure is 100 Torr.

- The best scale in your lab has an accuracy of $\pm 0.01\text{g}$. What is the minimum amount of time must you wait until the mass change of the cell can be determined by your balance?
- How much UF_6 will remain in the Knudsen cell after 5 min of effusion?

Calculation of the collisional flux proceeds as follows:

$$r = 100 \text{ }\mu\text{m} \left(\frac{1\text{m}}{10^6 \mu\text{m}}\right) = 1.00 \times 10^{-4} \text{ m}$$

$$A = \pi r^2 = \pi (1.00 \times 10^{-4} \text{ m})^2 = 3.14 \times 10^{-8} \text{ m}^2$$

$$m = \frac{0.352 \text{ kg mol}^{-1}}{N_A} = 5.85 \times 10^{-25} \text{ kg}$$

$$Z_c = \frac{P}{(2\pi mkT)^{1/2}} = \frac{100 \text{ torr} \left(\frac{133.3 \text{ Pa}}{1 \text{ torr}}\right)}{\left(2\pi (5.85 \times 10^{-25} \text{ kg})(1.38 \times 10^{-23} \text{ J K}^{-1})(291.4 \text{ K})\right)^{1/2}}$$

$$Z_c = \frac{1.33 \times 10^4 \text{ Pa}}{1.22 \times 10^{-22} \text{ kg m s}^{-1}} = 1.10 \times 10^{26} \text{ m}^{-2} \text{ s}^{-1}$$

$$\text{a) } \Delta t = \frac{\Delta m}{Z_c A m} = \frac{0.01 \text{ g} \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right)}{(1.10 \times 10^{26} \text{ m}^{-2} \text{s}^{-1})(3.14 \times 10^{-8} \text{ m}^2)(5.85 \times 10^{-25} \text{ kg})} \\ = 4.97 \text{ s}$$

b)

$$\Delta m = Z_c A m \Delta t \\ = (1.10 \times 10^{26} \text{ m}^{-2} \text{s}^{-1})(3.14 \times 10^{-8} \text{ m}^2)(5.85 \times 10^{-25} \text{ kg})(5 \text{ min}) \left(\frac{60 \text{ sec}}{1 \text{ min}} \right) \\ = 6.03 \times 10^{-4} \text{ kg}$$

Therefore 0.940 g of UF₆ remains in the cell.

P34.21)

- a) How many molecules strike a 1-cm² surface during 1 min if the surface is exposed to O₂ at 1 atm and 298 K?
- b) Ultrahigh vacuum studies typically employ pressures on the order of 10⁻¹⁰ Torr. How many collisions will occur at this pressure at 298 K?

$$\text{For O}_2, M = 0.032 \text{ kg mol}^{-1} \text{ and } Z_c = \frac{PN_A}{(2\pi MRT)^{1/2}}$$

$$\text{a) } @ 1 \text{ atm: } Z_c = \frac{(1 \text{ atm}) \left(\frac{101.325 \times 10^3 \text{ Pa}}{1 \text{ atm}} \right) (6.022 \times 10^{23} \text{ mol}^{-1})}{(2\pi(0.032 \text{ kg mol}^{-1})(8.314 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K}))^{1/2}}$$

$$Z_c = 2.73 \times 10^{27} \text{ m}^{-2} \text{s}^{-1}$$

$$\frac{dN_c}{dt} = Z_c \times A = (2.73 \times 10^{27} \text{ m}^{-2} \text{s}^{-1})(1 \text{ cm}^2) \left(\frac{1 \text{ m}}{100 \text{ cm}} \right)^2$$

$$\frac{dN_c}{dt} = 2.73 \times 10^{23} \text{ coll. s}^{-1}$$

$$\text{b) } @ 10^{-10} \text{ torr: } Z_c = \frac{(10^{-10} \text{ torr})(\frac{133.32 \text{ Pa}}{1 \text{ torr}})(6.022 \times 10^{23} \text{ mol}^{-1})}{(2\pi(0.032 \text{ kg mol}^{-1})(8.314 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K}))^{1/2}}$$

$$Z_c = 3.60 \times 10^{14} \text{ m}^{-2}\text{s}^{-1}$$

$$\frac{dN_c}{dt} = Z_c \times A = (3.60 \times 10^{14} \text{ m}^{-2}\text{s}^{-1})(1 \text{ cm}^2)\left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^2$$

$$\frac{dN_c}{dt} = 3.60 \times 10^{14} \text{ coll s}^{-1}$$

P34.22) You are a NASA engineer faced with the task of ensuring that the material on the hull of a spacecraft can withstand puncturing by space debris. The initial cabin air pressure in the craft of 1 atm can drop to 0.7 atm before the safety of the crew is jeopardized. The volume of the cabin is 100 m³, and the temperature in the cabin is 285 K. Assuming it takes the space shuttle about 8 hours from entry into orbit until landing, what is the largest circular aperture created by a hull puncture that can be safely tolerated assuming that the flow of gas out of the spaceship is effusive? Can the escaping gas from the spaceship be considered as an effusive process? (You can assume that the air is adequately represented by N₂.)

$$\frac{dP}{dt} = \frac{-PA}{V} \left(\frac{kT}{2\pi m}\right)^{1/2}$$

$$P = P_0 e^{\frac{-At}{V} \left(\frac{kT}{2\pi m}\right)^{1/2}}$$

$$0.7 \text{ atm} = (1 \text{ atm}) e^{\frac{-At}{V} \left(\frac{kT}{2\pi m}\right)^{1/2}}$$

$$0.7 = e^{\frac{-At}{V} \left(\frac{kT}{2\pi m}\right)^{1/2}}$$

$$0.357 = \frac{At}{V} \left(\frac{kT}{2\pi m}\right)^{1/2} = \frac{A(2.88 \times 10^4 \text{ s})}{100 \text{ m}^3} \left(\frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(285 \text{ K})}{2\pi \left(\frac{0.028 \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \right)} \right)^{1/2}$$

$$0.357 = A(3.34 \times 10^4 \text{ m}^{-2})$$

$$1.07 \times 10^{-5} \text{ m}^2 = A$$

If the process can be considered effusive, then the diameter of the hole should be smaller than the mean free path. The mean free path (λ) for N₂ at 1 atm and 285 K is:

$$\begin{aligned}\lambda_{N_2} &= \left(\frac{RT}{P_{N_2} N_A} \right) \frac{1}{\sqrt{2\sigma_{N_2}}} \\ &= \left(\frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{(101,325 \text{ Pa})(6.022 \times 10^{23} \text{ mol}^{-1})} \right) \frac{1}{\sqrt{2}(4.3 \times 10^{-19} \text{ m}^2)} \\ &= 6.39 \times 10^{-8} \text{ m}\end{aligned}$$

Comparison of this length scale to the aperture dimensions demonstrates that this process is not effusive.

P34.23) Many of the concepts developed in this chapter can be applied to understanding the atmosphere. Because atmospheric air is comprised primarily of N₂ (roughly 78% by volume), approximate the atmosphere as consisting only of N₂ in answering the following questions:

- a) What is the single-particle collisional frequency at sea level, with T = 298 K and P = 1 atm? The corresponding single-particle collisional frequency is reported as 10¹⁰ s⁻¹ in the *CRC Handbook of Chemistry and Physics* (62nd ed., p. F-171).
- b) At the tropopause (11 km in altitude), the collisional frequency decreases to 3.16 × 10⁹ s⁻¹, primarily due to a reduction in temperature and barometric pressure (i.e., fewer particles). The temperature at the tropopause is ~220 K. What is the pressure of N₂ at this altitude?
- c) At the tropopause, what is the mean free path for N₂?

The collisional cross section of N₂ is $\sigma = 4.3 \times 10^{-19} \text{ m}^2$, and M = 0.028 kg mol⁻¹.

$$\begin{aligned}\text{a) } z_{11} &= \sqrt{2}\sigma \frac{PN_A}{RT} \left(\frac{8RT}{\pi M} \right)^{1/2} \\ &= \sqrt{2}(4.3 \times 10^{-19} \text{ m}^2) \frac{(1 \text{ atm})(6.022 \times 10^{23} \text{ mol}^{-1})}{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})} \left(\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{\pi(0.028 \text{ kg mol}^{-1})} \right)^{1/2} \\ &= \sqrt{2}(2.46 \times 10^{22} \text{ L}^{-1})(4.3 \times 10^{-19} \text{ m}^2)(475 \text{ m s}^{-1}) \left(\frac{1000 \text{ L}}{\text{m}^3} \right) \\ z_{11} &= 7.11 \times 10^9 \text{ s}^{-1}\end{aligned}$$

$$\text{b) } 3.16 \times 10^9 \text{ s}^{-1} = \frac{\sqrt{2}(P)(6.022 \times 10^{23} \text{ mol}^{-1})}{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1})(220 \text{ K})} (4.3 \times 10^{-19} \text{ m}^2) \left(\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(220 \text{ K})}{\pi(0.028 \text{ kg mol}^{-1})} \right)^{1/2}$$

$$P = \frac{(3.16 \times 10^9 \text{ s}^{-1})}{\sqrt{2}(3.34 \times 10^{22} \text{ L}^{-1} \text{ atm}^{-1})(4.3 \times 10^{-19} \text{ m}^2)(408 \text{ m s}^{-1})} \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right)$$

$$P = 0.382 \text{ atm}$$

$$\text{c) } \lambda = \left(\frac{RT}{PN_A} \right) \frac{1}{\sqrt{2}\sigma} = \left(\frac{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ s}^{-1})(220 \text{ K})}{(0.382 \text{ atm})(6.022 \times 10^{23} \text{ mol}^{-1})} \right) \frac{1}{\sqrt{2}(4.3 \times 10^{-19} \text{ m}^2)}$$

$$\lambda = \left(\frac{18.1 \text{ L atm mol}^{-1}}{1.40 \times 10^5 \text{ atm mol}^{-1} \text{ m}^2} \right) \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right)$$

$$\lambda = 1.29 \times 10^{-7} \text{ m}$$

P34.24)

- a) Determine the total collisional frequency for CO₂ at 1 atm and 298 K.
 b) At what temperature would the collisional frequency be 10% of the value determined in part (a)?

For CO₂, $\sigma = 5.2 \times 10^{-19} \text{ m}^2$ and $M = 0.044 \text{ kg mol}^{-1}$

$$\begin{aligned} \text{a) } Z_{11} &= \frac{1}{\sqrt{2}} \sigma \left(\frac{N_A P}{R T} \right)^2 \left(\frac{8 R T}{\pi M} \right)^{1/2} \\ &= \frac{1}{\sqrt{2}} (5.2 \times 10^{-19} \text{ m}^2) \left(\frac{(6.022 \times 10^{23} \text{ mol}^{-1})(1 \text{ atm})}{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})} \right)^2 \\ &\quad \times \left(\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{\pi(0.044 \text{ kg mol}^{-1})} \right)^{1/2} \left(\frac{1000 \text{ L}}{1 \text{ m}^3} \right)^2 \end{aligned}$$

$$Z_{11} = 8.44 \times 10^{34} \text{ m}^{-3} \text{s}^{-1}$$

$$\begin{aligned}
 \text{b) } 8.44 \times 10^{33} \text{ m}^{-3}\text{s}^{-1} &= \frac{1}{\sqrt{2}} \left(\frac{(6.022 \times 10^{23} \text{ mol}^{-1})(1 \text{ atm})}{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1})(T)} \right)^2 \\
 &\quad \times (5.2 \times 10^{-19} \text{ m}^2) \left(\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(T)}{\pi(0.044 \text{ kg mol}^{-1})} \right)^{1/2} \\
 8.44 \times 10^{33} \text{ m}^{-3}\text{s}^{-1} &= \frac{1}{\sqrt{2}} \left(\frac{5.38 \times 10^{49} \text{ L}^{-2} \text{ K}^2}{T^2} \right) (5.2 \times 10^{-19} \text{ m}^2) (21.9 \text{ m s}^{-1} \text{ K}^{-1/2}) (T)^{1/2} \left(\frac{1000 \text{ L}}{\text{m}^3} \right)^2 \\
 8.44 \times 10^{33} \text{ m}^{-3}\text{s}^{-1} &= \frac{4.34 \times 10^{38} \text{ m}^{-3} \text{ s}^{-1} \text{ K}^{3/2}}{T^{3/2}} \\
 T &= \left(\frac{4.34 \times 10^{38} \text{ m}^{-3} \text{ s}^{-1} \text{ K}^{3/2}}{8.44 \times 10^{33} \text{ m}^{-3} \text{ s}^{-1}} \right)^{2/3} \\
 T &= 227 \text{ K}
 \end{aligned}$$

P34.25)

- a) A standard rotary pump is capable of producing a vacuum on the order of 10^{-3} Torr. What is the single-particle collisional frequency and mean free path for N₂ at this pressure and 298 K?
- b) A cryogenic pump can produce a vacuum on the order of 10^{-10} Torr. What is the collisional frequency and mean free path for N₂ at this pressure and 298 K?

For N₂ $\sigma = 4.3 \times 10^{-19} \text{ m}^2$ and M = 0.028 kg mol⁻¹

$$\begin{aligned}
 \text{a) } z_{11} &= \left(\frac{PN_A}{RT} \right) \sigma \sqrt{2} \left(\frac{8RT}{\pi M} \right)^{1/2} \\
 &= \frac{\left(10^{-3} \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) \right) (6.022 \times 10^{23} \text{ mol}^{-1})}{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})} \\
 &\quad \times \sqrt{2} (4.3 \times 10^{-19} \text{ m}^2) \left(\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{\pi(0.028 \text{ kg mol}^{-1})} \right)^{1/2} \left(\frac{1000 \text{ L}}{1 \text{ m}^3} \right) \\
 &= (3.24 \times 10^{16} \text{ L}^{-1}) (6.08 \times 10^{-19} \text{ m}^2) (475 \text{ m s}^{-1}) (1000 \text{ L m}^{-3}) \\
 z_{11} &= 9.35 \times 10^3 \text{ s}^{-1}
 \end{aligned}$$

$$\lambda = \left(\frac{RT}{PN_A} \right) \frac{1}{\sqrt{2}\sigma} = \left(\frac{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{\left((10^{-3} \text{ torr}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) \right) (6.022 \times 10^{23} \text{ mol}^{-1})} \right) \frac{1}{\sqrt{2}(4.3 \times 10^{-19} \text{ m}^2)} \\ = (50.8 \text{ L m}^{-2}) \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right)$$

$\lambda = 0.051 \text{ m}$

b) $z_{11} = \frac{PN_A}{RT} \sigma \sqrt{2} \left(\frac{8RT}{\pi M} \right)^{1/2}$

$$= \frac{\left((10^{-10} \text{ torr}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) \right) (6.022 \times 10^{23} \text{ mol}^{-1})}{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})} \\ \cdot \sqrt{2}(4.3 \times 10^{-19} \text{ m}^2) \left(\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{\pi(0.028 \text{ kg mol}^{-1})} \right)^{1/2} \left(\frac{1000 \text{ L}}{1 \text{ m}^3} \right)$$

$z_{11} = 9.35 \times 10^{-4} \text{ s}^{-1}$ or a 10^{-7} decrease from (a)

$$\lambda = \left(\frac{RT}{PN_A} \right) \frac{1}{\sqrt{2}\sigma} = \left(\frac{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{\left((10^{-10} \text{ torr}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) \right) (6.022 \times 10^{23} \text{ mol}^{-1})} \right) \frac{1}{\sqrt{2}(4.3 \times 10^{-19} \text{ m}^2)} \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right)$$

$\lambda = 5.08 \times 10^5 \text{ m}$

P34.26) Determine the mean free path for Ar at 298 K at the following pressures:

- a) 0.5 atm
- b) 0.005 atm
- c) 5×10^{-6} atm

For Ar, $\sigma = 3.6 \times 10^{-19} \text{ m}^2$ and $M = 0.040 \text{ kg mol}^{-1}$

a) $\lambda = \left(\frac{RT}{PN_A} \right) \frac{1}{\sqrt{2}\sigma} = \left(\frac{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{(0.5 \text{ atm})(6.022 \times 10^{23} \text{ mol}^{-1})} \right) \frac{1}{\sqrt{2}(3.6 \times 10^{-19} \text{ m}^2)} \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right)$

$\lambda = 1.60 \times 10^{-7} \text{ m}$

- b) Since the mean free path is inversely proportional to pressure, the result from part (a) can be used to determine the mean free path at pressures specified in parts (b) and (c) as follows:

Chapter 34/Kinetic Theory of Gases

$$\lambda_{0.005} = \lambda_{0.5} \left(\frac{0.5 \text{ atm}}{0.005 \text{ atm}} \right) = 1.60 \times 10^{-7} \text{ m} \quad (100)$$

$$\lambda_{0.005} = 1.60 \times 10^{-5} \text{ m}$$

c) $\lambda_{5 \times 10^{-6}} = \lambda_{0.5} \left(\frac{0.5 \text{ atm}}{5 \times 10^{-6} \text{ atm}} \right) = 1.60 \times 10^{-7} \text{ m} \quad (10^5)$

$$\lambda_{5 \times 10^{-6}} = 1.60 \times 10^{-2} \text{ m}$$

P34.27) Determine the mean free path at 500 K and 1 atm for the following:

- a) Ne
- b) Kr
- c) CH₄

Rather than simply calculating the mean free path for each species separately, instead develop an expression for the ratio of mean free paths for two species and use the calculated value for one species to determine the other two.

a) $\sigma_{\text{Ne}} = 2.4 \times 10^{-19} \text{ m}$

$$\lambda_{\text{Ne}} = \left(\frac{RT}{PN_A} \right) \frac{1}{\sqrt{2}\sigma} = \left(\frac{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1})(500 \text{ K})}{(1 \text{ atm})(6.022 \times 10^{23} \text{ mol}^{-1})} \right) \frac{1}{\sqrt{2}(2.4 \times 10^{-19} \text{ m})} \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right)$$

$$\lambda_{\text{Ne}} = 2.01 \times 10^{-7} \text{ m}$$

b) $\sigma_{\text{Kr}} = 5.2 \times 10^{-19} \text{ m}$

$$\lambda_{\text{Kr}} = \lambda_{\text{Ne}} \left(\frac{\sigma_{\text{Ne}}}{\sigma_{\text{Kr}}} \right) = (2.01 \times 10^{-7} \text{ m}) \left(\frac{2.4 \times 10^{-19} \text{ m}^2}{5.2 \times 10^{-19} \text{ m}^2} \right)$$

$$\lambda_{\text{Kr}} = 9.26 \times 10^{-8} \text{ m}$$

c) $\sigma_{\text{CH}_4} = 4.6 \times 10^{-19} \text{ m}^2$

$$\lambda_{\text{CH}_4} = \lambda_{\text{Ne}} \left(\frac{\sigma_{\text{Ne}}}{\sigma_{\text{CH}_4}} \right) = 2.01 \times 10^{-7} \text{ m} \left(\frac{2.4 \times 10^{-19} \text{ m}^2}{4.6 \times 10^{-19} \text{ m}^2} \right)$$

$$\lambda_{\text{CH}_4} = 1.05 \times 10^{-7} \text{ m}$$

P34.28) Consider the diagram of a molecular beam apparatus provided in the text.

In the design of the apparatus, it is important to ensure that the molecular beam effusing from the oven does not collide with other particles until the beam is well past the skimmer, a device that selects molecules that are traveling in the appropriate direction, resulting in the creation of a molecular beam. The skimmer is located 10 cm in front of the oven so that a mean free path of 20 cm will ensure that the molecules are well past the skimmer before a collision can occur. If the molecular beam consists of O₂ at a

temperature of 500 K, what must the pressure outside the oven be to ensure this mean free path?

$$\lambda = 0.20 \text{ m} = \left(\frac{RT}{PN_A} \right) \frac{1}{\sqrt{2}\sigma} \quad \sigma_{O_2} = 4.0 \times 10^{-19} \text{ m}^2$$

$$0.20 \text{ m} = \left(\frac{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1})(500 \text{ K})}{P(6.022 \times 10^{23} \text{ mol}^{-1})} \right) \frac{1}{\sqrt{2}(4.0 \times 10^{-19} \text{ m}^2)} \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right)$$

$$0.20 \text{ m} = \frac{1.20 \times 10^{-7} \text{ atm m}}{P}$$

$$P = \frac{1.21 \times 10^{-7} \text{ atm m}}{0.20 \text{ m}}$$

$$P = 6.03 \times 10^{-7} \text{ atm}$$

$$P = 4.58 \times 10^{-4} \text{ torr}$$

P34.29) A comparison of v_{ave} , v_{mp} , and v_{rms} for the Maxwell speed distribution reveals that these three quantities are not equal. Is the same true for the one-dimensional velocity distributions?

$$v_{avg} = \langle v \rangle = \int_{-\infty}^{\infty} v_x \left(\frac{M}{2\pi RT} \right)^{1/2} e^{-\frac{M}{2RT}v_x^2} dv_x$$

$$= \left(\frac{M}{2\pi RT} \right)^{1/2} \int_{-\infty}^{\infty} v_x e^{-\frac{M}{2RT}v_x^2} dv_x$$

$$v_{avg} = 0$$

$$v_{mp} \Rightarrow 0 = \frac{\partial}{\partial v_x} \left[\left(\frac{M}{2\pi RT} \right)^{1/2} e^{-\frac{M}{2RT}v_x^2} \right]$$

$$0 = \left(\frac{M}{2\pi RT} \right)^{1/2} \left(\frac{M}{2\pi RT} v_x \right) e^{-\frac{M}{2RT}v_x^2}$$

The above equality will be true when $v_x = 0$; therefore, $v_{mp} = 0$.

$$\begin{aligned}
 v_{\text{rms}} &= \langle v^2 \rangle^{1/2} = \left[\int_{-\infty}^{\infty} v_x^2 \left(\frac{M}{2\pi RT} \right)^{1/2} e^{-\frac{M}{2RT}v_x^2} dv_x \right]^{1/2} \\
 &= \left[\left(\frac{\beta}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} v_x^2 e^{-\beta v_x^2} dv_x \right]^{1/2} \quad \text{for } \beta = \frac{M}{2RT} \\
 &= \left[\left(\frac{\beta}{\pi} \right)^{1/2} \left(2 \int_0^{\infty} v_x^2 e^{-\beta v_x^2} dv_x \right) \right]^{1/2} \\
 &= \left[\left(\frac{\beta}{\pi} \right)^{1/2} \cdot \frac{1}{2} \left(\frac{\pi}{\beta^3} \right)^{1/2} \right]^{1/2} \\
 &= \left[\frac{1}{2} \beta^{-1} \right]^{1/2} \\
 v_{\text{rms}} &= \sqrt{\frac{RT}{M}}
 \end{aligned}$$

P34.30) At 30 km above the Earth's surface (roughly in the middle of the stratosphere), the pressure is roughly 0.013 atm and the gas density is 3.74×10^{23} molecules/m³. Assuming N₂ is representative of the stratosphere, using the collisional diameter information provided in Table 34.1 determine:

- The number of collisions a single gas particle undergoes in this region of the stratosphere in 1 s
- The total number of particles collisions that occur in 1 s
- The mean free path of a gas particle in this region of the stratosphere.

Using the ideal gas law, the temperature at 30 km can be determined as follows:

$$T = \frac{PV}{nR} = \frac{P}{\tilde{N}k} = \frac{(0.0120 \text{ atm})(1.01325 \times 10^5 \text{ Pa atm}^{-1})}{(3.74 \times 10^{23} \text{ m}^{-3})(1.38 \times 10^{-23} \text{ J K}^{-1})}$$

$$T = 235 \text{ K}$$

$$\begin{aligned}
 \text{a)} z_{11} &= \left(\frac{PN_A}{RT} \right) \sqrt{2} \sigma \left(\frac{8RT}{\pi M} \right)^{1/2} \\
 &= \frac{(0.012 \text{ atm})(6.022 \times 10^{23} \text{ mol}^{-1})}{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1})(235 \text{ K})} \\
 &\quad \times \sqrt{2} (4.3 \times 10^{-19} \text{ m}^2) \left(\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(235 \text{ K})}{\pi(0.028 \text{ kg mol}^{-1})} \right)^{1/2} \left(\frac{1000 \text{ L}}{1 \text{ m}^3} \right) \\
 z_{11} &= 9.60 \times 10^7 \text{ s}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \text{b) } Z_{11} &= \frac{1}{\sqrt{2}} \left(\frac{P N_A}{R T} \right)^2 \sigma \left(\frac{8 R T}{\pi M} \right)^{1/2} \\
 &= \frac{1}{\sqrt{2}} \left(\frac{(0.0120 \text{ atm})(6.022 \times 10^{23} \text{ mol}^{-1})}{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1})(235 \text{ K})} \right)^2 \\
 &\quad \times (4.3 \times 10^{-19} \text{ m}^2) \left(\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(235 \text{ K})}{\pi(0.028 \text{ kg mol}^{-1})} \right)^{1/2} \left(\frac{1000 \text{ K}}{1 \text{ m}^3} \right) \\
 Z_{11} &= 1.80 \times 10^{31} \text{ coll. m}^{-3} \text{ s}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \text{c) } \lambda &= \left(\frac{R T}{P N_A} \right) \frac{1}{\sqrt{2} \sigma} = \left(\frac{(8.21 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1})(235 \text{ K})}{(0.0120 \text{ atm})(6.022 \times 10^{23} \text{ mol}^{-1})} \right) \frac{1}{\sqrt{2}(4.3 \times 10^{-19} \text{ m}^2)} \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right) \\
 \lambda &= 4.39 \times 10^{-6} \text{ m}
 \end{aligned}$$

Chapter 35: Transport Phenomena

Problem numbers in italics indicate that the solution is included in the *Student's Solutions Manual*.

Questions on Concepts

Q35.1) What is the general relationship between the spatial gradient in a system property and the flux of that property?

The spatial gradient of a property is a continuous difference in a physical property such as pressure, temperature, or molecular distribution. The flux of the property is a change that occurs due to the spatial gradient, defined as the amount of a given property that passes through a specific area per unit time.

Q35.2) What is the expression for the diffusion coefficient, D , in terms of gas kinetic theory parameters? How is D expected to vary with an increase in molecular mass or collisional cross section?

The diffusion coefficient, D , is defined as

$$D = \frac{1}{3} v_{ave} \lambda$$

where v_{ave} is the average speed and λ is the mean free path of a gas particle, both as defined by the kinetic gas theory. The v_{ave} term is inversely proportional to the square root of the molar mass, therefore the diffusion coefficient will decrease as the molar mass increases. The mean free path is inversely proportional to the collisional cross section; therefore, the diffusion coefficient will decrease as the collisional cross section increases.

Q35.3) Particles are confined to a plane and then allowed to diffuse. How does the number density vary with distance away from the initial plane?

The number density of particles that diffuse from a fixed plane is given by the solution to Fick's Second Law of Diffusion,

$$\tilde{N} = \frac{N_0}{2A(\pi Dt)^{1/2}} \exp\left[\frac{-x^2}{4Dt}\right]$$

where N_0 is the number of particles initially confined to the plane, D is the diffusion coefficient, A is the area of the initial plane, and t is the time. The number density in the x-direction will decrease in accord with the exponential dependence on the square of distance away from the plane (so-called Gaussian dependence).

Q35.4) How does the root-mean-square diffusion distance vary with the diffusion coefficient? How does this quantity vary with time?

The root mean square diffusion distances depend on the square root of the both the time and the diffusion coefficient.

Q35.5) What is the expression for thermal conductivity in terms of particle parameters derived from gas kinetic theory?

The thermal conductivity, κ , is defined as

$$\kappa = \frac{1}{3} \frac{C_{v,m}}{N_A} v_{ave} \tilde{N} \lambda$$

where $C_{v,m}$ is the molar volume independent heat capacity, and v_{ave} and λ are the average speed and the mean free path, respectively.

Q35.6) Why is the thermal conductivity for an ideal gas expected to be independent of pressure? Why does the thermal conductivity for an ideal gas increase as $T^{1/2}$?

With reference to the equation provided in Question Q35.5 above, we see that the thermal conductivity depends on the product of the number density and the mean free path. For an ideal gas, the mean free path is dependent on the inverse of the pressure, while the number density is directly dependent on the pressure. As demonstrated below, the pressure term cancels, leaving the thermal conductivity independent of pressure for an ideal gas;

$$\tilde{N} \lambda = \left(\frac{P}{kT} \right) \left(\frac{RT}{PN_A} \frac{1}{\sqrt{2}\sigma} \right) = \frac{1}{\sqrt{2}\sigma}$$

The thermal conductivity is proportional to v_{ave} which varies as the square root of T .

Q35.7) In describing viscosity, what system quantity was transported? What is the expression for viscosity in terms of particle parameters derived from gas kinetic theory?

Viscosity arises due to the linear momentum gradient orthogonal to the direction of gas flow. Viscosity is the transport of linear momentum. The expression for viscosity is

$$\eta = \frac{1}{3} v_{ave} \tilde{N} \lambda m$$

where v_{ave} and λ are the average speed and mean free path as defined by the kinetic theory.

Q35.8) What observable is used to measure the viscosity of a gas or liquid?

The viscosity of a liquid or gas is measured by the flow rate of the substance, or the time it takes for a specified volume of the substance to pass through a column under specified pressure.

Q35.9) What is Brownian motion?

Brownian motion is the seemingly random motion of a large particle due to diffusion through a medium. The motion is driven by the force of particles from the medium colliding with the large particle.

Q35.10) In the Stokes–Einstein equation that describes particle diffusion for a spherical particle, how does the diffusion coefficient depend on fluid viscosity and particle size?

The Stokes–Einstein equation for the diffusion coefficient of a spherical particle is given as

$$D = \frac{kT}{6\pi\eta r}$$

As can be seen, the diffusion coefficient depends on the inverse of the viscosity of the fluid (η), as well as the inverse of the particle radius (r), were the particle is modeled as spherical.

Q35.11) What is the difference between a strong and weak electrolyte?

The difference between a strong and a weak electrolyte is the dependence of electrical conductivity of the electrolytic solution as a function of concentration and the degree of ionic dissociation. A strong electrolyte will dissociate with almost unit probability, with ionic salts such as NaCl serving as examples of these electrolytes. Weak electrolytes dissociate to only a limited extent. Weak acids such as acetic acid serve as examples of weak electrolytes.

Q35.12) According to Kohlrausch's law, how will the molar conductivity for a strong electrolyte change with concentration?

The Kohlrauch equation relates the change in molar ionic conductivity to the change in strong electrolyte concentration, and is expressed as

$$\Lambda_m = \Lambda_m^0 - K \sqrt{\frac{C}{C_0}}$$

So, the conductivity will decrease as a function of the square root of the ratio of the concentration at time t to the initial concentration. As the concentration increases, the conductivity decreases.

Problems

P35.1) The diffusion coefficient for CO₂ at 273 K and 1 atm is $1.00 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. Estimate the collisional cross section of CO₂ given this diffusion coefficient.

$$D_{CO_2} = 1.00 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} @ T = 273 \text{ K} \text{ is } P = 1 \text{ atm}$$

$$D = \frac{1}{3} v_{ave} \lambda$$

$$D = \frac{1}{3} \sqrt{\frac{8kT}{\pi M}} \left(\frac{RT}{PN_A} \right) \frac{1}{\sqrt{2}\sigma}$$

Rearranging the above equation to isolate the collisional cross section:

$$\sigma = \frac{1}{3} \sqrt{\frac{8RT}{\pi M}} \left(\frac{RT}{PN_A} \right) \frac{1}{\sqrt{2}D}$$

$$= \frac{1}{3\sqrt{2}} \sqrt{\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(273 \text{ K})}{\pi(0.044 \text{ kg mol}^{-1})}}$$

$$\times \left(\frac{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1}) \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right) (273 \text{ K})}{(1 \text{ atm})(6.022 \times 10^{23} \text{ mol}^{-1})} \right) \left(\frac{1}{1.00 \times 10^{-5} \text{ m}^2 \text{s}^{-1}} \right)$$

$$\sigma = 0.318 \text{ nm}^2$$

P35.2)

- a) The diffusion coefficient for Xe at 273 K and 1 atm is $0.5 \times 10^{-5} \text{ m}^2 \text{s}^{-1}$. What is the collisional cross section of Xe?
- b) The diffusion coefficient of N₂ is threefold greater than that of Xe under the same pressure and temperature conditions. What is the collisional cross section of N₂?

a)

$$D_{Xe} = 0.5 \times 10^{-5} \text{ m}^2 \text{s}^{-1} \text{ @ 273 K and 1 atm}$$

$$\sigma = \frac{1}{3} \sqrt{\frac{8kT}{\pi M}} \left(\frac{RT}{PN_A} \right) \frac{1}{\sqrt{2}D}$$

$$= \frac{1}{3\sqrt{2}} \sqrt{\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(273 \text{ K})}{\pi(0.131 \text{ kg mol}^{-1})}} \left(\frac{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1}) \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right) (273 \text{ K})}{(1 \text{ atm})(6.022 \times 10^{23} \text{ mol}^{-1})(0.5 \times 10^{-5} \text{ m}^2 \text{s}^{-1})} \right)$$

$$\sigma = 0.368 \text{ nm}^2$$

- b) The ratio of collisional cross sections is given by:

$$\begin{aligned}\frac{\sigma_{N_2}}{\sigma_{Xe}} &= \frac{D_{Xe}}{D_{N_2}} \sqrt{\frac{M_{Xe}}{M_{N_2}}} \\ \sigma_{N_2} &= \sigma_{Xe} \left(\frac{D_{Xe}}{D_{N_2}} \right) \sqrt{\frac{M_{Xe}}{M_{N_2}}} \\ &= (0.368 \text{ nm}^2) \left(\frac{1}{3} \right) \sqrt{\frac{0.131 \text{ kg mol}^{-1}}{0.028 \text{ kg mol}^{-1}}}\end{aligned}$$

$$\sigma_{N_2} = 0.265 \text{ nm}^2$$

P35.3)

- a) The diffusion coefficient of sucrose in water at 298 K is $0.522 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Determine the time it will take a sucrose molecule on average to diffuse an rms distance of 1 mm.
 b) If the molecular diameter of sucrose is taken to be 0.8 nm, what is the time per random walk step?

a) $D_{\text{sucrose}} = 0.522 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ @ $T = 298 \text{ K}$

$$\begin{aligned}r_{rms} &= (6Dt)^{1/2} \\ t &= \frac{r_{rms}^2}{6D} \\ &= \frac{1 \text{ mm}^2}{6(0.522 \times 10^{-9} \text{ m}^2 \text{ s}^{-1})} \cdot \left(\frac{1 \text{ m}}{10^3 \text{ mm}} \right)^2 \\ &= 319 \text{ s}\end{aligned}$$

b)

$$\begin{aligned}D &= \frac{x_0^2}{2\tau} \\ \tau &= \frac{x_0^2}{2D} \\ &= \frac{(0.8 \text{ nm})^2}{2(0.522 \times 10^{-9} \text{ m}^2 \text{ s}^{-1})} \cdot \left(\frac{1 \text{ m}}{10^9 \text{ nm}} \right)^2 \\ &= 6.13 \times 10^{-10} \text{ s}\end{aligned}$$

P35.4)

- a) The diffusion coefficient of the protein lysozyme (MW = 14.1 kg/mol) is $0.104 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. How long will it take this protein to diffuse an rms distance of 1 μm ? Model the diffusion as a three-dimensional process.
 b) You are about to perform a microscopy experiment in which you will monitor the

fluorescence from a single lysozyme molecule. The spatial resolution of the microscope is $1 \mu\text{m}$. You intend to monitor the diffusion using a camera that is capable of one image every 60 s. Is the imaging rate of the camera sufficient to detect the diffusion of a single lysozyme protein over a length of $1 \mu\text{m}$?

c) Assume that in the microscopy experiment of part (b) you use a thin layer of water such that diffusion is constrained to two dimensions. How long will it take a protein to diffuse an rms distance of $1 \mu\text{m}$ under these conditions?

$$\begin{aligned} \text{a)} \quad t &= \frac{r_{\text{rms}}^2}{6D} \\ &= \frac{(1 \mu\text{m})^2}{6(0.104 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})} \cdot \left(\frac{1 \text{ m}}{10^6 \mu\text{m}}\right)^2 \cdot \left(\frac{100 \text{ cm}}{1 \text{ m}}\right)^2 \\ t &= 1.60 \times 10^{-3} \text{ s} \end{aligned}$$

b) The time to diffuse by $1 \mu\text{m}$ is $1.6 \times 10^{-3} \text{ s}$; therefore, the time required for an image is much too large to deserve the diffusion over $1 \mu\text{m}$.

c) Similar to the extension of diffusion from one to three dimensions as presented in the text, we assume that the diffusion in either the x or y direction is equivalent. Therefore, the displacement in two dimensions is given by:

$$\begin{aligned} r^2 &= x^2 + y^2 = 2Dt + 2Dt = 4Dt \\ r_{\text{rms},2D} &= \sqrt{4Dt} \\ t &= \frac{(1.0 \mu\text{m})^2}{4 \cdot 0.104 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}} \left(\frac{1 \text{ m}}{10^6 \mu\text{m}}\right)^2 \left(\frac{100 \text{ cm}}{1 \text{ m}}\right)^2 \\ t &= 2.40 \times 10^{-3} \text{ s} \end{aligned}$$

P35.5) A solution consisting of 1 g of sucrose in 10 mL of water is poured into a 1-L graduated cylinder with a radius of 2.5 cm. Then the cylinder is filled with pure water.

a) The diffusion of sucrose can be considered diffusion in one dimension. Derive an expression for the average distance of diffusion, x_{ave} .

b) Determine x_{ave} and x_{rms} for sucrose for time periods of 1 s, 1 min, and 1 h.

a) The distribution first needs to be renormalized realizing that diffusion can only occur in one direction from the initial plane of sucrose molecules:

$$\begin{aligned}
1 &= C \int_0^{\infty} \frac{N_0}{2A(\pi Dt)^{1/2}} e^{-x^2/4Dt} dx \\
&= \frac{CN_0}{2A(\pi Dt)^{1/2}} \int_0^{\infty} e^{-x^2/4Dt} dx \\
&= \frac{CN_0}{2A(\pi Dt)^{1/2}} \left(\frac{1}{2} (4\pi Dt)^{1/2} \right) \\
1 &= \frac{CN_0}{2A} \\
\frac{2A}{N_0} &= C
\end{aligned}$$

Using the normalized distribution to determine $\langle x \rangle$:

$$\begin{aligned}
\langle x \rangle &= \int_0^{\infty} x \left(\frac{2A}{N_0} \frac{N_0}{2A(\pi Dt)^{1/2}} e^{-x^2/4Dt} \right) dx \\
&= \frac{1}{(\pi Dt)^{1/2}} \int_0^{\infty} xe^{-x^2/4Dt} dx \\
&= \frac{1}{(\pi Dt)^{1/2}} (2Dt) \\
\langle x \rangle &= 2\sqrt{\frac{Dt}{\pi}}
\end{aligned}$$

b) Now the values of x_{ave} can be calculated; assuming T = 298 K.

$$\begin{aligned}
t &= 1 \text{ sec.} \\
\langle x \rangle &= 2\sqrt{\frac{(0.522 \times 10^{-9} \text{ m}^2 \text{ s}^{-1})(1 \text{ s})}{\pi}} \\
&= 2.58 \times 10^{-5} \text{ m}
\end{aligned}$$

Similar calculations reveal that $\langle x \rangle = 1.00 \times 10^{-4}$ m at 60 s, and 1.54×10^{-3} m at 3600 s.

P35.6) A thermopane window consists of two sheets of glass separated by a volume filled with air (which we will model as N₂ where $\kappa = 0.0240 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}$). For a thermopane window that is 1 m² in area with a separation between glass sheets of 3 cm, what is the loss of energy when:

- a) the exterior of the window is at a temperature of 10°C and the interior of the window is at a temperature of 22°C?
- b) the exterior of the window is at a temperature of -20°C and the interior of the window is at a temperature of 22°C?

c) the same temperature differential as in part (b) is used but the window is filled with Ar ($\kappa = 0.0163 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}$) rather than N₂?

The energy flux is given by

$$J = -\kappa \left(\frac{dT}{dx} \right) = -\kappa \left(\frac{\Delta T}{\Delta x} \right)$$

The loss in energy is equal to the flux times the area (A) through which the energy loss occurs:

$$\Delta E = -\kappa \left(\frac{\Delta T}{\Delta x} \right) \cdot A$$

$$\begin{aligned} \text{a)} \quad \Delta E &= -\left(0.0240 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1} \right) \left(\frac{12 \text{ K}}{3 \text{ cm}} \right) \left(\frac{100 \text{ cm}}{1 \text{ m}} \right) (1 \text{ m}^2) \\ &= -9.60 \text{ J s}^{-1} \end{aligned}$$

$$\text{b)} \quad \Delta T = 42 \text{ K}$$

$$\begin{aligned} \Delta E &= -\left(0.0240 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1} \right) \left(\frac{42 \text{ K}}{3 \text{ cm}} \right) \left(\frac{100 \text{ cm}}{1 \text{ m}} \right) (1 \text{ m}^2) \\ &= -33.6 \text{ J s}^{-1} \end{aligned}$$

$$\text{c)} \quad \Delta T = 42 \text{ K} \quad \kappa = 0.0163 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}$$

$$\begin{aligned} \Delta E &= -\left(0.0163 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1} \right) \left(\frac{42 \text{ K}}{3 \text{ cm}} \right) \left(\frac{100 \text{ cm}}{1 \text{ m}} \right) (1 \text{ m}^2) \\ &= -22.8 \text{ J s}^{-1} \end{aligned}$$

P35.7) Two parallel metal plates separated by 1 cm are held at 300 and 298 K, respectively. The space between the plates is filled with N₂ ($\sigma = 0.430 \text{ nm}^2$ and $C_{V,m} = 5/2 R$). Determine the heat flow between the two plates in units of W cm⁻².

The flux is given by:

$$J = -\kappa \left(\frac{\Delta T}{\Delta x} \right)$$

where

$$\kappa = \frac{1}{3} \frac{C_{v,m}}{N_A} \nu_{ave} \tilde{N} \lambda = \frac{1}{3} \frac{C_{v,m}}{N_A} \left(\frac{8RT}{\pi M} \right)^{1/2} \frac{1}{\sqrt{2}\sigma}$$

Using the average temperature of 299 K to calculate the thermal conductivity, the flux is:

$$\begin{aligned}
J &= -\frac{1}{3} \left(\frac{5}{2} \frac{R}{N_A} \right) \left(\frac{8RT}{\pi M} \right)^{1/2} \frac{1}{\sqrt{2}\sigma} \left(\frac{\Delta T}{\Delta x} \right) \\
&= -\frac{5}{6} \left(\frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \right) \left(\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(299 \text{ K})}{\pi(0.028 \text{ kg mol}^{-1})} \right)^{1/2} \\
&\quad \times \frac{1}{\sqrt{2}(0.430 \text{ nm}^2)} \left(\frac{10^9 \text{ nm}}{1 \text{ m}} \right)^2 \left(\frac{2 \text{ K}}{1 \text{ cm}} \right) \left(\frac{1 \text{ m}}{100 \text{ cm}} \right) \\
&= -1.80 \times 10^{-4} \text{ J s}^{-1} \text{ cm}^{-2} = -1.80 \times 10^{-4} \text{ W cm}^{-2}
\end{aligned}$$

P35.8) Determine the thermal conductivity of the following species at 273 K and 1 atm:

- a) Ar ($\sigma = 0.36 \text{ nm}^2$)
- b) Cl₂ ($\sigma = 0.93 \text{ nm}^2$)
- c) SO₂ ($\sigma = 0.58 \text{ nm}^2$, geometry: bent)

You will need to determine $C_{V,m}$ for the species listed. You can assume that the translational and rotational degrees of freedom are in the high-temperature limit, and that the vibrational contribution to $C_{V,m}$ can be ignored at this temperature.

$$\kappa = \frac{1}{3} \frac{C_{vm}}{N_A} \cdot \left(\frac{8RT}{\pi M} \right)^{1/2} \frac{1}{\sqrt{2}\sigma}$$

a) $C_{V,m}^{Ar} = \frac{3}{2} R$

$$\begin{aligned}
\kappa &= \frac{1}{3} \left(\frac{3}{2} \frac{R}{N_A} \right) \cdot \left(\frac{8RT}{\pi M} \right)^{1/2} \frac{1}{\sqrt{2}\sigma} \\
&= \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{2(6.022 \times 10^{23} \text{ mol}^{-1})} \cdot \left(\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(273 \text{ K})}{\pi(0.040 \text{ kg mol}^{-1})} \right)^{1/2} \frac{1}{\sqrt{2}(0.36 \text{ nm}^2)} \cdot \left(\frac{10^9 \text{ nm}}{1 \text{ m}} \right)^2 \\
&= 0.00516 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}
\end{aligned}$$

b) $C_{V,m}^{Cl_2} = C_V^T + C_V^R = \frac{3}{2} R + R = \frac{5}{2} R$

$$\begin{aligned}
\kappa &= \frac{1}{3} \left(\frac{5}{2} \frac{R}{N_A} \right) \cdot \left(\frac{8RT}{\pi M} \right)^{1/2} \frac{1}{\sqrt{2}\sigma} \\
&= \frac{5(8.314 \text{ J mol}^{-1} \text{ K}^{-1})}{6(6.022 \times 10^{23} \text{ mol}^{-1})} \cdot \left(\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(273 \text{ K})}{\pi(0.071 \text{ kg mol}^{-1})} \right)^{1/2} \frac{1}{\sqrt{2}(0.93 \text{ nm}^2)} \left(\frac{10^9 \text{ nm}}{1 \text{ m}} \right)^2 \\
&= 0.00249 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}
\end{aligned}$$

$$\begin{aligned}
 c) \quad C_{V,m}^{SO_2} &= C_V^T + C_V^R = \frac{3}{2}R + \frac{3}{2}R = 3R \\
 \kappa &= \frac{1}{3} \left(\frac{3R}{N_A} \right) \left(\frac{8RT}{\pi M} \right)^{1/2} \frac{1}{\sqrt{2}\sigma} \\
 &= \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})}{3(6.022 \times 10^{23} \text{ mol}^{-1})} \left(\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(273 \text{ K})}{\pi(0.084 \text{ kg mol}^{-1})} \right)^{1/2} \frac{1}{\sqrt{2}(0.58 \text{ nm}^2)} \left(\frac{10^9 \text{ nm}}{1 \text{ m}} \right)^2 \\
 &= 0.0050 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}
 \end{aligned}$$

P35.9) The thermal conductivity of Kr is $0.0087 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}$ at 273 K and 1 atm. Estimate the collisional cross section of Kr.

Treating Kr as an ideal monatomic gas, $C_{V,m} = \frac{3}{2}R$, and the thermal conductivity is:

$$\kappa = \frac{1}{3} C_{V,m} V_{ave} \frac{1}{\sqrt{2}\sigma} = \frac{1}{3} \left(\frac{3}{2} \frac{R}{N_A} \right) \left(\frac{8RT}{\pi M} \right)^{1/2} \frac{1}{\sqrt{2}\sigma}$$

Rearranging to isolate the collisional cross section:

$$\begin{aligned}
 \sigma &= \frac{1}{3} C_{V,m} V_{ave} \frac{1}{\sqrt{2}\kappa} = \frac{1}{3} \left(\frac{3}{2} \frac{R}{N_A} \right) \left(\frac{8RT}{\pi M} \right)^{1/2} \frac{1}{\sqrt{2}\kappa} \\
 \sigma &= \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})}{2(6.022 \times 10^{23} \text{ mol}^{-1})} \left(\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(273 \text{ K})}{\pi(0.084 \text{ kg mol}^{-1})} \right)^{1/2} \frac{1}{\sqrt{2}(0.0087 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1})} \\
 &= 1.5 \times 10^{-19} \text{ m}^2
 \end{aligned}$$

P35.10) The thermal conductivity of Kr is roughly half that of Ar under identical pressure and temperature conditions. Both gases are monatomic such that $C_{V,m} = 3/2 R$.

- a) Why would one expect the thermal conductivity of Kr to be less than that of Ar?
- b) Determine the ratio of collisional cross sections for Ar relative to Kr assuming identical pressure and temperature conditions.
- c) For Kr at 273 K at 1 atm, $\kappa = 0.0087 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}$. Determine the collisional cross section of Kr.

- a) The thermal conductivity is defined as

$$\kappa = \frac{1}{3} \frac{C_v}{N_A} \cdot \left(\frac{8RT}{\pi M} \right)^{1/2} \frac{1}{\sqrt{2}\sigma}$$

The only gas specific value in κ are the molar mass and the collisional cross section. Since both the molar mass and the collisional cross section for Kr are larger than for Ar, the thermal conductivity of Kr should be less than that of Ar.

b)

$$\frac{\kappa_{Av}}{\kappa_{kv}} = \frac{\frac{C_{V,m}}{3N_A} \left(\frac{8RT}{\pi M_{Ar}} \right)^{1/2}}{\frac{C_{V,m}}{3N_A} \left(\frac{8RT}{\pi M_{Kr}} \right)^{1/2}} \frac{1}{\sqrt{2}\sigma_{Ar}}$$

$$\frac{\kappa_{Ar}}{\kappa_{Kr}} = \left(\frac{M_{Kr}}{M_{Ar}} \right)^{1/2} \frac{\sigma_{Kr}}{\sigma_{Ar}}$$

c)

$$\sigma = \frac{1}{3} C_{V,m} V_{ave} \frac{1}{\sqrt{2}\sigma} = \frac{1}{3} \left(\frac{3}{2} \frac{R}{N_A} \right) \left(\frac{8RT}{\pi M} \right)^{1/2} \frac{1}{\sqrt{2}\kappa}$$

$$\sigma = \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})}{2(6.022 \times 10^{23} \text{ mol}^{-1})} \left(\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(273 \text{ K})}{\pi(0.084 \text{ kg mol}^{-1})} \right)^{1/2} \frac{1}{\sqrt{2}(0.0087 \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1})}$$

$$= 1.5 \times 10^{-19} \text{ m}^2$$

P35.11)

- a) Determine the ratio of thermal conductivity for N₂ ($\sigma = 0.43 \text{ nm}^2$) at sea level ($T = 300 \text{ K}$, $P = 1 \text{ atm}$) versus the lower stratosphere ($T = 230 \text{ K}$, $P = 0.25 \text{ atm}$).
- b) Determine the ratio of thermal conductivity for N₂ at sea level if $P = 1 \text{ atm}$, but the temperature is reduced to 100 K. Which energetic degrees of freedom will be operative at the lower temperature, and how will this affect $C_{V,m}$?

a)

$$\frac{\kappa_{sea}}{\kappa_{strat}} = \frac{\frac{1}{3} \left(\frac{5}{2} \frac{R}{N_A} \right) \left(\frac{8RT_{sea}}{\pi M} \right)^{1/2}}{\frac{1}{3} \left(\frac{5}{2} \frac{R}{N_A} \right) \left(\frac{8RT_{strat}}{\pi M} \right)^{1/2}} \frac{1}{\sqrt{2}\sigma}$$

$$= \sqrt{\frac{T_{sea}}{T_{strat}}}$$

$$= \sqrt{\frac{300 \text{ K}}{230 \text{ K}}} = 1.14$$

- b) Even at 100 K, the translational and rotational degrees of freedom will be in the high temperature limit so that $C_{V,m}$ will be largely unaffected relative to 300 K.

$$\frac{\kappa_{sea}}{\kappa_{strat}} = \sqrt{\frac{100 \text{ K}}{230 \text{ K}}} = 0.659$$

P35.12) The thermal conductivities of acetylene (C_2H_2) and N_2 at 273 K and 1 atm are 0.01866 and $0.0240 \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}$, respectively. Based on these data, what is the ratio of the collisional cross section of acetylene relative to N_2 ?

$$\begin{aligned} \frac{\kappa_{\text{C}_2\text{H}_2}}{\kappa_{\text{N}_2}} &= \frac{\frac{C_{V,m}^{\text{C}_2\text{H}_2}}{3N_A} \left(\frac{8RT}{\pi M_{\text{C}_2\text{H}_2}} \right)^{1/2} \frac{1}{\sqrt{2}\sigma_{\text{C}_2\text{H}_2}}}{\frac{C_{V,m}^{\text{N}_2}}{3N_A} \left(\frac{8RT}{\pi M_{\text{N}_2}} \right)^{1/2} \frac{1}{\sqrt{2}\sigma_{\text{N}_2}}} \\ &= \frac{C_{V,m}^{\text{C}_2\text{H}_2}}{C_{V,m}^{\text{N}_2}} \left(\frac{M_{\text{N}_2}}{M_{\text{C}_2\text{H}_2}} \right)^{1/2} \frac{\sigma_{\text{N}_2}}{\sigma_{\text{C}_2\text{H}_2}} \end{aligned}$$

Rearranging to isolate the ratio of collisional cross sections:

$$\frac{\sigma_{\text{C}_2\text{H}_2}}{\sigma_{\text{N}_2}} = \frac{C_{V,m}^{\text{C}_2\text{H}_2}}{C_{V,m}^{\text{N}_2}} \left(\frac{M_{\text{N}_2}}{M_{\text{C}_2\text{H}_2}} \right)^{1/2} \frac{\kappa_{\text{N}_2}}{\kappa_{\text{C}_2\text{H}_2}}$$

Both C_2H_2 and N_2 are linear molecules, and will therefore have the same heat capacity value so that the collision cross section ratio depends only on the mass and thermal conductivity ratios:

$$\frac{\sigma_{\text{C}_2\text{H}_2}}{\sigma_{\text{N}_2}} = \left(\frac{0.028 \text{ kg mol}^{-1}}{0.026 \text{ kg mol}^{-1}} \right)^{1/2} \left(\frac{0.0240 \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}}{0.01866 \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}} \right)$$

$$\frac{\sigma_{\text{C}_2\text{H}_2}}{\sigma_{\text{N}_2}} = 1.33$$

P35.13)

- The viscosity of Cl_2 at 293 K and 1 atm is $132 \mu\text{P}$. Determine the collisional cross section of this molecule based on the viscosity.
- Given your answer in part (a), estimate the thermal conductivity of Cl_2 under the same pressure and temperature conditions.

a)

$$\eta = \frac{1}{3} \left(\frac{8RT}{\pi M} \right)^{1/2} \left(\frac{P}{kT} \right) \left(\frac{RT}{PN_A} \right) \frac{m}{\sqrt{2}\sigma}$$

$$= \frac{1}{3} \left(\frac{8RT}{\pi M} \right)^{1/2} \frac{1}{\sqrt{2}\sigma} \frac{M}{N_A}$$

Rearranging to isolate the collisional cross section:

$$\sigma = \frac{1}{3} \left(\frac{8RT}{\pi M} \right)^{1/2} \frac{1}{\sqrt{2}\eta} \frac{M}{N_A}$$

$$= \frac{1}{3} \left(\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(293 \text{ K})}{\pi(0.071 \text{ kg mol}^{-1})} \right)^{1/2} \frac{1}{\sqrt{2}(132 \times 10^{-6} \text{ Poise}) \left(\frac{0.1 \text{ kg m}^{-1} \text{ s}^{-1}}{1 \text{ Poise}} \right)} \left(\frac{0.071 \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \right)$$

$$\sigma = 6.23 \times 10^{-19} \text{ m}^2$$

b) $\kappa = \frac{1}{3} C_{V,m} V_{ave} \frac{1}{\sqrt{2}\sigma}$

$$= \frac{1}{3} \left(\frac{5}{2} \frac{R}{N_A} \right) \left(\frac{8RT}{\pi M} \right)^{1/2} \frac{1}{\sqrt{2}\sigma}$$

$$= \frac{5(8.314 \text{ J mol}^{-1} \text{ K}^{-1})}{6(6.022 \times 10^{23} \text{ mol}^{-1})} \left(\frac{8(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(293 \text{ K})}{\pi(0.071 \text{ kg mol}^{-1})} \right)^{1/2} \frac{1}{\sqrt{2}(6.23 \times 10^{-19} \text{ m}^2)}$$

$$= 0.00389 \text{ J K}^{-1} \text{s}^{-1} \text{m}^{-1}$$

P35.14)

- a) The viscosity of O₂ at 293 K and 1 atm is 204 μP . What is the expected flow rate through a tube having a radius of 2 mm, length of 10 cm, input pressure of 765 Torr, output pressure of 760 Torr, with the flow measured at the output end of the tube?
- b) If Ar were used in the apparatus ($\eta = 223 \mu\text{P}$) of part (a), what would be the expected flow rate? Can you determine the flow rate without evaluating Poiseuille's equation?

a)

$$\begin{aligned}\frac{\Delta V}{\Delta t} &= \frac{\pi r^4}{8\eta} \left(\frac{P_2 - P_1}{x_2 - x_1} \right) \\ &= \frac{\pi (2 \times 10^{-3} \text{ m})^4}{8(204 \times 10^{-6} \text{ Poise}) \left(\frac{0.1 \text{ kg m}^{-1} \text{ s}^{-1}}{\text{Poise}} \right)} \left(\frac{765 \text{ Torr} - 760 \text{ Torr}}{0.01 \text{ m}} \right) \left(\frac{133.32 \text{ Pa}}{1 \text{ Torr}} \right) \\ &= 2.05 \times 10^{-3} \text{ m}^3 \text{ s}^{-1}\end{aligned}$$

b)

$$\begin{aligned}\left(\frac{\Delta V}{\Delta t} \right)_{Ar} &= \left(\frac{\Delta V}{\Delta t} \right)_{Cl_2} \cdot \frac{\eta_{Cl_2}}{\eta_{Ar}} \\ \left(\frac{\Delta V}{\Delta t} \right)_{Ar} &= 2.05 \times 10^{-3} \text{ m}^3 \text{ s}^{-1} \left(\frac{204 \mu P}{223 \mu P} \right) \\ \left(\frac{\Delta V}{\Delta t} \right)_{Ar} &= 1.88 \times 10^{-3} \text{ m}^3 \text{ s}^{-1}\end{aligned}$$

P35.15) The Reynolds' number (Re) is defined as $Re = \frac{\rho \langle v_x \rangle d}{\eta}$, where ρ and η are the fluid density and viscosity, respectively; d is the diameter of the tube that the fluid which is flowing, and $\langle v_x \rangle$ is the average velocity. Laminar flow occurs when $Re < 2000$, the limit in which the equations for gas viscosity were derived in this chapter. Turbulent flow occurs when $Re > 2000$. For the following species, determine the maximum value of $\langle v_x \rangle$ for which laminar flow will occur:

- a) Ne at 293 K ($\eta = 313 \mu P$, ρ = that of an ideal gas) through a 2-mm-diameter pipe.
- b) Liquid water at 293 K ($\eta = 0.891 \text{ cP}$, $\rho = 0.998 \text{ g mL}^{-1}$) through a 2-mm-diameter pipe.

a) Laminar flow occurs when

$$2000 = \frac{\rho \langle v_x \rangle d}{\eta}$$

Therefore, the maximum velocity for laminar flow can be found from

$$\langle v_x \rangle = \frac{2000\eta}{\rho \cdot d}$$

First, calculating ρ :

$$\begin{aligned}\rho &= \frac{PM}{RT} = \frac{(1 \text{ atm})(0.020 \text{ kg mol}^{-1})}{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1})(293 \text{ K})} \left(\frac{1000 \text{ L}}{1 \text{ m}^3} \right) \\ &= 0.840 \text{ kg m}^{-3}\end{aligned}$$

With the gas density, the maximum average velocity is readily determined:

$$\langle v_x \rangle_{\max} = \frac{2000(313 \times 10^{-6} \text{ Poise})}{(0.840 \text{ kg m}^{-3})(2 \times 10^{-3} \text{ m})} \left(\frac{0.1 \text{ kg m}^{-1}\text{s}^{-1}}{1 \text{ Poise}} \right)$$

$$\langle v_x \rangle_{\max} = 37.3 \text{ m s}^{-1}$$

b)

$$\langle v_x \rangle_{\max} = \frac{2000(0.891 \times 10^{-2} \text{ Poise})}{(0.998 \text{ kg L}^{-1})(2 \times 10^{-3} \text{ m})} \left(\frac{0.1 \text{ kg m}^{-1}\text{s}^{-1}}{1 \text{ Poise}} \right) \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right)$$

$$= 0.893 \text{ m s}^{-1}$$

P35.16) The viscosity of H₂ at 273 K at 1 atm is 84 μP . Determine the viscosities of D₂ and HD.

The expression for viscosity is:

$$\eta = \frac{1}{3} \left(\frac{8RT}{\pi M} \right)^{1/2} \frac{1}{\sqrt{2}\sigma} \frac{M}{N_A}$$

Taking the ratio of viscosities for two species (denoted as 1 and 2) yields

$$\frac{\eta_2}{\eta_1} = \sqrt{\frac{M_2}{M_1}} \left(\frac{\sigma_1}{\sigma_2} \right)$$

Assuming that the collisional cross sections for the species are the same, the ratio of velocities reduces to:

$$\frac{\eta_2}{\eta_1} = \sqrt{\frac{M_2}{M_1}}$$

Substituting the molecular weights into the above expression yields the following viscosities for D₂ and HD:

$$\begin{aligned} \eta_{D_2} &= \eta_{H_2} \sqrt{\frac{M_{D_2}}{M_{H_2}}} \\ &= (84 \text{ } \mu\text{P}) \sqrt{\frac{4.04 \text{ g mol}^{-1}}{2.02 \text{ g mol}^{-1}}} \end{aligned}$$

$$\eta_{D_2} = 118 \text{ } \mu\text{P}$$

$$\begin{aligned} \eta_{HD} &= 84 \text{ } \mu\text{P} \sqrt{\frac{3.03 \text{ g mol}^{-1}}{2.02 \text{ g mol}^{-1}}} \\ &= 103 \text{ } \mu\text{P} \end{aligned}$$

P35.17) An Ostwald viscometer is calibrated using water at 20°C ($\eta = 1.0015 \text{ cP}$,

$\rho = 0.998 \text{ g mL}^{-1}$). It takes 15 s for the fluid to fall from the upper to the lower level of the viscometer. A second liquid is then placed in the viscometer and it takes 37 s for the fluid to fall between the levels. Finally, 100 mL of the second liquid weighs 76.5 g. What is the viscosity of the liquid?

The viscosity is determined using the following equation:

$$\eta = A\rho\Delta t$$

where A is the viscometer constant, ρ is the density of the fluid, and Δt is the time required to move through the viscometer. The viscometer constant is first determined using the data for water provided in the problem:

$$\begin{aligned} A &= \frac{\eta}{\rho\Delta t} \\ &= \frac{(1.0015 \times 10^{-2} \text{ P})}{(0.998 \text{ kg L}^{-1})(15 \text{ s})} \left(\frac{0.1 \text{ kg m}^{-1} \text{ s}^{-1}}{1 \text{ P}} \right) \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right) \\ &= 6.69 \times 10^{-8} \text{ m}^2 \text{ s}^{-2} \end{aligned}$$

With the viscometer constant, the viscosity of the second liquid can be determined:

$$\begin{aligned} \eta &= (6.69 \times 10^{-8} \text{ m}^2 \text{ s}^{-2}) \left(\frac{0.0765 \text{ kg}}{0.1 \text{ L}} \right) (37 \text{ s}) \\ &= 1.89 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \text{ kg L}^{-1} \left(\frac{1000 \text{ L}}{1 \text{ m}^3} \right) \\ &= 0.00189 \text{ kg m}^{-1} \text{ s}^{-1} \left(\frac{1 \text{ P}}{0.1 \text{ kg m}^{-1} \text{ s}^{-1}} \right) \\ &= 0.0189 \text{ P} \\ &= 1.89 \text{ cP} \end{aligned}$$

P35.18) How long will it take to pass 200 mL of H₂ at 273 K through a 10-cm-long capillary tube of 0.25 mm if the gas input and output pressures are 1.05 and 1.00 atm, respectively?

The flow rate is given as

$$\frac{\Delta V}{\Delta t} = \frac{\pi r^4}{8\eta} \left(\frac{P_2 - P_1}{x_2 - x_1} \right)$$

Substituting into this expression and solving for Δt yields:

$$\frac{(0.2 \text{ L})}{\Delta t} = \frac{\pi (2.5 \times 10^{-4} \text{ m})^4}{8(84 \times 10^{-6} \text{ P}) \left(\frac{0.1 \text{ kg m}^{-1}\text{s}^{-1}}{1 \text{ P}} \right)} \left(\frac{1.05 \text{ atm} - 1.00 \text{ atm}}{0.1 \text{ m}} \right)$$

$$\frac{(0.2 \text{ L})}{\Delta t} = 9.13 \times 10^{-11} \text{ m}^4 \text{ kg}^{-1} \text{ s} \cdot \frac{101,325 \text{ N m}^{-2}}{1 \text{ atm}}$$

$$\frac{(0.2 \text{ L})}{\Delta t} = 9.13 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$$

$$\frac{(0.2 \text{ L})}{9.13 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}} = 21.9 \text{ s} = \Delta t$$

P35.19)

- a) Derive the general relationship between the diffusion coefficient and viscosity for a gas.
- b) Given that the viscosity of Ar is 223 μP at 293 K and 1 atm, what is the diffusion coefficient?
- a) The diffusion coefficient is given as

$$D = \frac{1}{3} v_{ave} \lambda$$

And the viscosity is expressed as

$$\begin{aligned} \eta &= \frac{1}{3} v_{ave} \tilde{N} \lambda m \\ &= \frac{1}{3} v_{ave} \lambda (\tilde{N} m) \\ \eta &= D \tilde{N} m \end{aligned}$$

b)

$$\begin{aligned} D &= \frac{\eta}{\tilde{N} m} = \frac{\eta}{m} \left(\frac{kT}{P} \right) = \frac{\eta}{m} \left(\frac{RT}{PN_A} \right) = \frac{\eta RT}{MP} \\ &= \frac{(223 \times 10^{-6} \text{ Poise})(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1})(293 \text{ K})}{(0.040 \text{ kg mol}^{-1})(1 \text{ atm})} \\ &= 0.134 \text{ Poise L kg}^{-1} \left(\frac{0.1 \text{ kg m}^{-1}\text{s}^{-1}}{1 \text{ Poise}} \right) \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right) \\ &= 1.34 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} \end{aligned}$$

P35.20)

- a) Derive the general relationship between the thermal conductivity and viscosity.

b) Given that the viscosity of Ar is $223 \text{ } \mu\text{P}$ at 293 K and 1 atm, what is the thermal conductivity?

c) Given that the viscosity of Ar is $223 \text{ } \mu\text{P}$ at 293 K and 1 atm, what is the thermal conductivity of Ne under these same conditions?

a,b) The thermal conductivity is expressed as:

$$\kappa = \frac{1}{3} \frac{C_{V,m}}{N_A} \nu_{ave} \tilde{N} \lambda$$

and the viscosity is:

$$\eta = \frac{1}{3} \nu_{ave} \tilde{N} \lambda m$$

Therefore:

$$\begin{aligned}\kappa &= \frac{1}{3} \nu_{ave} \tilde{N} \lambda \frac{C_{V,m}}{N_A} \\ \kappa &= \frac{C_{V,m}}{m N_A} \eta = \frac{C_{V,m}}{M} \eta\end{aligned}$$

Substituting in the values provided in part (b) of the problem:

$$\begin{aligned}\kappa &= \frac{\frac{3}{2}(8.314 \text{ J mol}^{-1} \text{ K}^{-1})}{(0.040 \text{ kg mol}^{-1})} (223 \times 10^{-6} \text{ P}) \\ &= 0.0695 \text{ J} \cdot \text{kg}^{-1} \text{ K}^{-1} \text{ P} \left(\frac{0.1 \text{ kg m}^{-1} \text{ s}^{-1}}{1 \text{ P}} \right) \\ &= 6.95 \times 10^{-3} \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}\end{aligned}$$

c) The relation between two thermal conductivities for two gases with identical heat capacities is

$$\kappa_2 = \kappa_1 \sqrt{\frac{M_1}{M_2}} \frac{\sigma_1}{\sigma_2}$$

And so:

$$\begin{aligned}\kappa_{Ne} &= 6.95 \times 10^{-3} \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1} \cdot \sqrt{\frac{0.040 \text{ kg mol}^{-1}}{0.020 \text{ kg mol}^{-1}}} \left(\frac{0.36 \text{ nm}^2}{0.24 \text{ nm}^2} \right) \\ &= 1.47 \times 10^{-2} \text{ J K}^{-1} \text{ m}^{-1} \text{ s}^{-1}\end{aligned}$$

P35.21) As mentioned in the text, the viscosity of liquids decreases with increasing temperature. The empirical equation $\eta(T) = Ae^{E/RT}$ provides the relationship between

viscosity and temperature for a liquid. In this equation, A and E are constants, with E being referred to as the activation energy for flow.

- How can one use the equation provided to determine A and E given a series of viscosity versus temperature measurements?
- Use your answer in part (a) to determine A and E for liquid benzene given the following data:

T (K)	5	40	80	120	160
η (cP)	0.826	0.492	0.318	0.219	0.156

- Taking the natural log of both sides of the empirical equation provided in the problem:

$$\ln(\eta) = \ln(A) + \frac{E}{RT}$$

one obtains:

$$\ln(\eta) = \ln(A) + \frac{E}{RT}$$

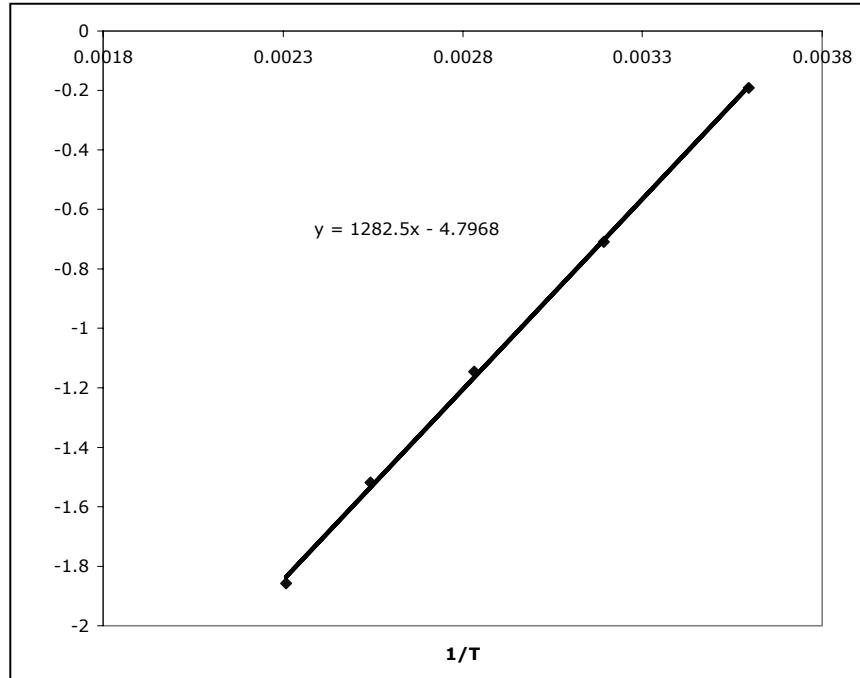
Therefore, a plot of the natural log of the viscosity versus, T^{-1} should yield a straight line with slope equal to $-E/R$ and y-intercept equal to $\ln(A)$.

- Converting the temperatures provided in the table to Kelvin, then taking the inverse, one can then plot $\ln(\eta)$ versus T^{-1} as shown below. Best fit by a straight line to the data yields a slope of 1282.5 K and y-intercept of -4.7968. Taking these values, E and A are determined as follows:

$$\begin{aligned} \frac{E}{R} &= 1282.5 \text{ K} \\ E &= R(1282.5 \text{ K}) = 10.7 \text{ kJ mol}^{-1} \end{aligned}$$

$$\ln(A) = -4.7968$$

$$A = 8.26 \times 10^{-3}$$



P35.22) Myoglobin is a protein that participates in oxygen transport. For myoglobin in water at 20°C, $\bar{s} = 2.04 \times 10^{-13}$ s, $D = 1.13 \times 10^{-10}$ m² s⁻¹, and $\bar{V} = 0.740$ cm³ g⁻¹. The density of water is 0.998 g cm⁻³ and the viscosity is 1.002 cP at this temperature.

- a) Using the information provided, estimate the size of myoglobin.
- b) What is the molecular weight of myoglobin?

- a) Using the Stokes-Einstein equation, the radius of myoglobin is:

$$r = \frac{kT}{6\pi\eta D}$$

$$\begin{aligned} r &= \frac{kT}{6\pi\eta D} \\ &= \frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(293 \text{ K})}{6\pi(0.01002 \text{ P}) \left(\frac{0.1 \text{ kg m}^{-1}\text{s}^{-1}}{1 \text{ P}} \right) (1.13 \times 10^{-10} \text{ m}^2 \text{ s}^{-1})} \\ &= 1.89 \times 10^{-9} \text{ m} \\ &= 1.89 \text{ nm} \end{aligned}$$

- b) The molecular weight of myoglobin can be found as follows:

$$\begin{aligned}
 M &= \frac{RT\bar{s}}{D(1-\bar{V}\rho)} \\
 &= \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(293 \text{ K})(2.04 \times 10^{-13} \text{ s})}{(1.13 \times 10^{-10} \text{ m}^2 \text{ s}^{-1})(1 - (0.740 \text{ cm g}^{-1})(0.998 \text{ g cm}^{-3}))} \\
 &= 16.8 \text{ kg mol}^{-1}
 \end{aligned}$$

P35.23) You are interested in purifying a sample containing the protein alcohol dehydrogenase obtained from horse liver; however, the sample also contains a second protein, catalase. These two proteins have the following transport properties:

	Catalase	Alcohol Dehydrogenase
\bar{s} (s)	11.3×10^{-13}	4.88×10^{-13}
D ($\text{m}^2 \text{ s}^{-1}$)	4.1×10^{-11}	6.5×10^{-11}
\bar{V} ($\text{cm}^3 \text{ g}^{-1}$)	0.715	0.751

- a) Determine the molecular weight of catalase and alcohol dehydrogenase.
- b) You have access to a centrifuge that can provide angular velocities up to 35,000 rpm. For the species you expect to travel the greatest distance in the centrifuge tube, determine the time it will take to centrifuge until a 3-cm displacement of the boundary layer occurs relative to the initial 5-cm location of the boundary layer relative to the centrifuge axis.
- c) To separate the proteins, you need a separation of at least 1.5 cm between the boundary layers associated with each protein. Using your answer to part (b), will it be possible to separate the proteins by centrifugation?

a) catalase

$$\begin{aligned}
 M &= \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})(11.3 \times 10^{-13} \text{ s})}{(4.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})(1 - (0.715 \text{ cm}^3 \text{ g}^{-1})(0.998 \text{ g cm}^{-3}))} \\
 &= 238 \text{ kg mol}^{-1}
 \end{aligned}$$

alcohol dehydrogenase

$$\begin{aligned}
 M &= \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(293 \text{ K})(4.88 \times 10^{-13} \text{ s})}{(6.5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})(1 - (0.751 \text{ cm}^3 \text{ g}^{-1})(0.998 \text{ g cm}^{-3}))} \\
 M &= 74.2 \text{ kg mol}^{-1}
 \end{aligned}$$

- b) The catalase should travel a greater distance. Using the following equation:

$$t = \frac{1}{\omega^2 \bar{s}} \ln \left(\frac{x_{b,t}}{x_{b,t=0}} \right)$$

$$t = \frac{1}{(3.5 \times 10^4 \text{ rev min}^{-1})^2 (11.3 \times 10^{-13} \text{ s})} \ln \left(\frac{5+3 \text{ cm}}{5 \text{ cm}} \right) \left(\frac{60 \text{ sec}}{1 \text{ min}} \right)^2 \left(\frac{1 \text{ rev}}{2\pi \text{ rad}} \right)^2$$

$$t = 3.10 \times 10^4 \text{ s}$$

c) The distance that alcohol dehydrogenase moves due to centrifugation in the same amount of time is determined as follows:

$$t = \frac{1}{\omega^2 \bar{s}} \ln \left(\frac{x_{b,t}}{x_{b,t=0}} \right)$$

$$t \omega^2 \bar{s} = \ln \left(\frac{x_{b,t}}{x_{b,t=0}} \right)$$

$$(3.10 \times 10^4 \text{ s}) (3.5 \times 10^4 \text{ rev min}^{-1})^2 (4.88 \times 10^{-13} \text{ s}) \left(\frac{\text{min}}{60 \text{ sec}} \right)^2 \left(\frac{2\pi \text{ rad}}{\text{rev}} \right)^2 = \ln \left(\frac{x_{b,t}}{5 \text{ cm}} \right)$$

$$0.203 = \ln \left(\frac{x_{b,t}}{5 \text{ cm}} \right)$$

$$1.23 = \left(\frac{x_{b,t}}{5 \text{ cm}} \right)$$

$$6.13 \text{ cm} = x_{b,t}$$

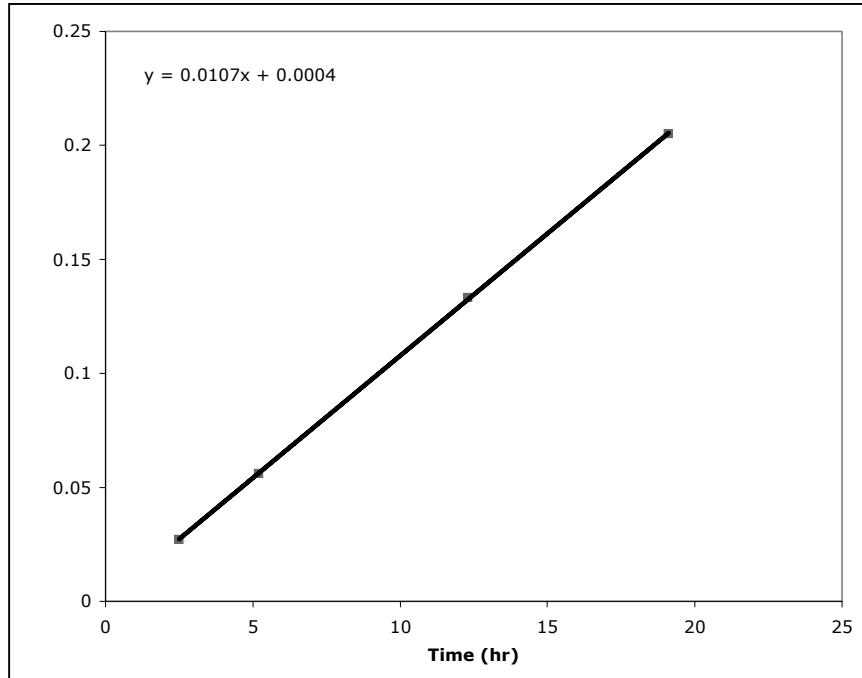
The separation between layers is 1.87 cm; therefore, the proteins can be separated.

P35.24) Boundary centrifugation is performed at an angular velocity of 40,000 rpm to determine the sedimentation coefficient of cytochrome *c* ($M = 13,400 \text{ g mol}^{-1}$) in water at 20°C ($\rho = 0.998 \text{ g cm}^{-3}$, $\eta = 1.002 \text{ cP}$). The following data are obtained on the position of the boundary layer as a function of time:

Time (h)	x_b (cm)
0	4.00
2.5	4.11
5.2	4.23
12.3	4.57
19.1	4.91

- a) What is the sedimentation coefficient for cytochrome *c* under these conditions?
- b) The specific volume of cytochrome *c* is $0.728 \text{ cm}^3 \text{ g}^{-1}$. Estimate the size of cytochrome *c*.

- a) Using the data from the table, a plot of $\ln\left(\frac{x_b}{x_{b,t=0}}\right)$ versus t can be constructed, the slope of which is equal to $\omega^2 \bar{s}$:



The slope from the best fit to the line is 0.0107 hr^{-1} . Using this slope, the sedimentation coefficient is determined as follows:

$$\begin{aligned}\omega^2 \bar{s} &= 0.0107 \text{ hr}^{-1} \\ \bar{s} &= \frac{0.0107 \text{ hr}^{-1}}{\omega^2} \left(\frac{1 \text{ hr}}{3600 \text{ s}} \right) = \frac{2.97 \times 10^{-6} \text{ s}^{-1}}{\omega^2} \\ &= \frac{2.97 \times 10^{-6} \text{ s}^{-1}}{(4.00 \times 10^4 \text{ rev min}^{-1})^2 \left(\frac{2\pi \text{ rad}}{1 \text{ rev}} \right)^2 \left(\frac{1 \text{ min}}{60 \text{ sec}} \right)^2} \\ &= 1.70 \times 10^{-13} \text{ s}\end{aligned}$$

- b) First, the frictional force is calculated as follows:

$$\begin{aligned}f &= \frac{m(1 - \bar{V}\rho)}{\bar{s}} \\ &= \frac{\left(\frac{13.4 \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \right) \left(1 - (0.728 \text{ cm}^3 \text{ g}^{-1})(0.998 \text{ g cm}^{-3}) \right)}{1.70 \times 10^{-13} \text{ s}} \\ f &= 3.58 \times 10^{-11} \text{ kg s}^{-1}\end{aligned}$$

With the frictional force, the particle radius can be determined:

$$6\pi\eta r = f$$

$$r = \frac{f}{6\pi\eta} = \frac{3.58 \times 10^{-11} \text{ kg s}^{-1}}{6\pi(0.01005 \text{ P}) \left(\frac{0.1 \text{ kg m}^{-1} \text{ s}^{-1}}{\text{P}} \right)}$$

$$= 1.89 \times 10^{-9} \text{ m}$$

$$= 1.89 \text{ nm}$$

P35.25) A current of 2.00 A is applied to a metal wire for 30 s. How many electrons pass through a given point in the wire during this time?

Current (I) is equal to the amount of charge (Q) that flows per unit time (t):

$$Q = It$$

$$= (2.00 \text{ A})(30 \text{ s})$$

$$= 60.0 \text{ C}$$

Coulombs of charge can be converted to number of electrons using the charge per electron as follows:

$$(60.0 \text{ C}) \left(\frac{1 e^-}{1.60 \times 10^{-19} \text{ C}} \right) = 3.75 \times 10^{20} e^-$$

P35.26) Use the following data to determine the conductance at infinite dilution for NaNO_3 :

$$\Lambda_m^0(\text{KCl}) = 0.0149 \text{ S m}^2 \text{ mol}^{-1}$$

$$\Lambda_m^0(\text{NaCl}) = 0.0127 \text{ S m}^2 \text{ mol}^{-1}$$

$$\Lambda_m^0(\text{KNO}_3) = 0.0145 \text{ S m}^2 \text{ mol}^{-1}$$

The above species are strong electrolytes, and the molar conductivity can be related to the individual ionic conductivities as follows:

$$\Lambda_m^0(\text{KCl}) = \lambda_{\text{K}} + \lambda_{\text{Cl}} \quad (\text{a})$$

$$\Lambda_m^0(\text{NaCl}) = \lambda_{\text{Na}} + \lambda_{\text{Cl}} \quad (\text{b})$$

$$\Lambda_m^0(\text{KNO}_3) = \lambda_{\text{K}} + \lambda_{\text{NO}_3} \quad (\text{c})$$

Subtracting (b) from (a) yields:

$$\Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{NaCl}) = \lambda_{\text{K}} - \lambda_{\text{Na}} \quad (\text{d})$$

Then, subtracting (c) from (d) yields:

$$\Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{NaCl}) - \Lambda_m^0(\text{KNO}_3) = -\lambda_{\text{Na}} - \lambda_{\text{NO}_3}$$

And so,

$$\begin{aligned}\Lambda_m^\circ(\text{NaNO}_3) &= -\Lambda_m^\circ(\text{KCl}) + \Lambda_m^\circ(\text{NaCl}) + \Lambda_m^\circ(\text{KNO}_3) \\ &= -0.0149 \text{ S m}^2 \text{ mol}^{-1} + 0.0127 \text{ S m}^2 \text{ mol}^{-1} + 0.0145 \text{ S m}^2 \text{ mol}^{-1} \\ &= 0.0123 \text{ S m}^2 \text{ mol}^{-1}\end{aligned}$$

P35.27) The following molar conductivity data are obtained for an electrolyte:

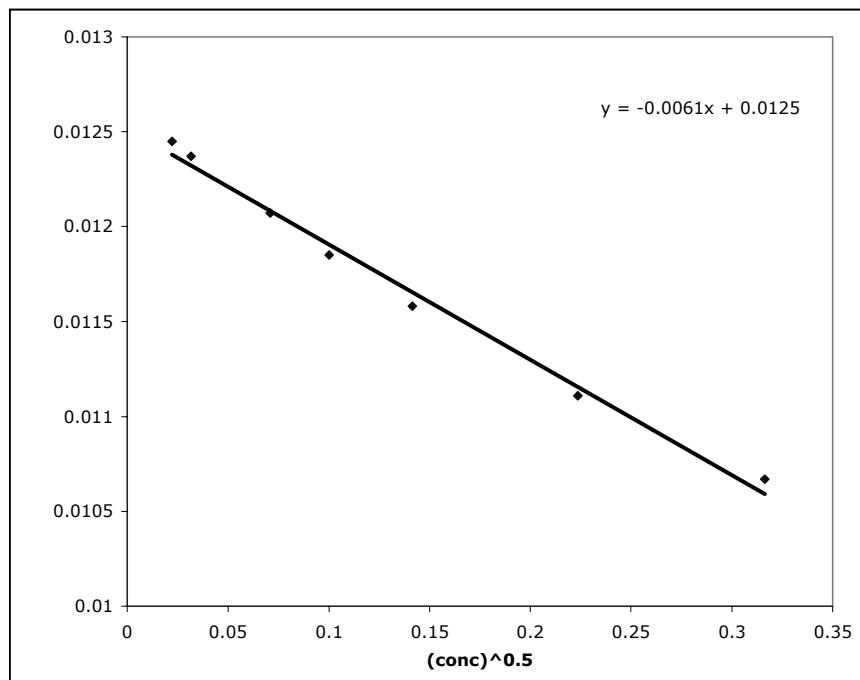
Concentration (M)	$\Lambda_m (\text{S m}^2 \text{ mol}^{-1})$
0.0005	0.01245
0.001	0.01237
0.005	0.01207
0.01	0.01185
0.02	0.01158
0.05	0.01111
0.1	0.01067

Determine if the electrolyte is strong or weak, and the conductivity of the electrolyte at infinite dilution.

According to **Kohlrausch's law**, a plot of conductivity versus $\sqrt{\frac{c}{c_0}}$ should yield a straight line for a strong electrolyte:

$$\Lambda_m = \Lambda_m^\circ - K \sqrt{\frac{c}{c_0}}$$

Using a reference concentration of 1 M, the following plot is obtained:



The best fit by a straight line to the data corresponds to the following equation:

$$\Lambda_m = 0.0126 - 0.0061 \sqrt{\frac{c}{1 \text{ M}}}$$

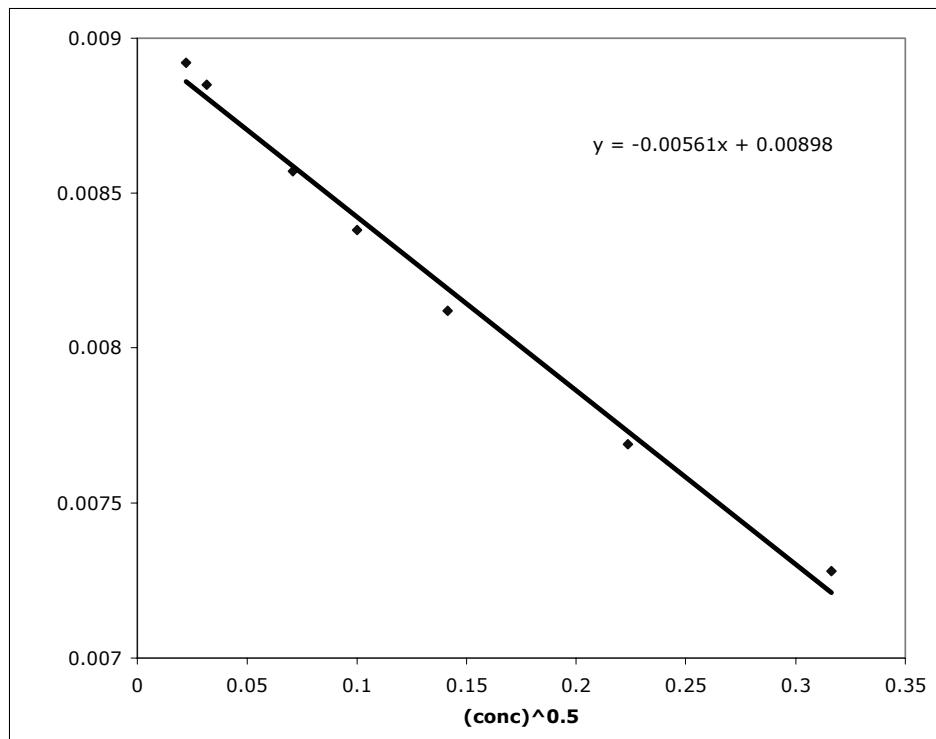
The near-linear behavior of the plot demonstrates that the electrolyte is strong, and from the fit $\Lambda_m^\circ = 0.0125 \text{ S m}^2 \text{ mol}^{-1}$.

P35.28) The molar conductivity of sodium acetate, CH_3COONa , is measured as a function of concentration in water at 298 K, and the following data are obtained:

Concentration (M)	$\Lambda_m (\text{S m}^2 \text{ mol}^{-1})$
0.0005	0.00892
0.001	0.00885
0.005	0.00857
0.01	0.00838
0.02	0.00812
0.05	0.00769
0.1	0.00728

Is sodium acetate a weak or strong electrolyte? Determine Λ_m^0 using appropriate methodology depending on your answer.

If the electrolyte is strong, a plot of Λ_m versus $\sqrt{\frac{c}{c_0}}$ (assuming $c_0 = 1 \text{ M}$) should yield a straight line. The corresponding plot is shown below:



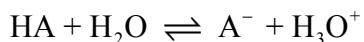
The linearity of the plot demonstrates that sodium acetate is a strong electrolyte. Best fit by a straight line yields the following:

$$\Lambda_m = -0.00561 \cdot \sqrt{\frac{c}{c_0}} + 0.00898$$

Therefore, for sodium acetate $\Lambda_m^0 = 0.00898 \text{ S m}^2 \text{ mol}^{-1}$.

P35.29) Starting with Equations (35.47) and (35.48), derive the Ostwald dilution law.

For a weak electrolyte like a weak acid, the following equilibrium exists in aqueous solution:



and the equilibrium constant, K_a , is equal to:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

The dissociation of the acid can be defined relative to the degree of ionization, α , as described in the text, and this definition results in the following expression for the equilibrium constant:

$$K_a = \frac{(ac)^2}{(1-\alpha)c} = \frac{\alpha^2 c}{1-\alpha}$$

Taking the inverse of the preceding expression yields:

$$\frac{1}{K_a} = \frac{1-\alpha}{\alpha^2 c}$$

Multiplying both sides of the preceding expression by αc and rearranging yields:

$$\frac{1}{\alpha} = \frac{\alpha c}{K_a} + 1$$

Now, the molar conductivity can be expressed as the product of the degree of ionization and the conductance at infinite dilution as follows:

$$\Lambda_m = \alpha \Lambda_m^\circ$$

Inverting the preceding expression results in the following:

$$\frac{1}{\Lambda_m} = \frac{1}{\alpha} \frac{1}{\Lambda_m^\circ}$$

Then, substituting for $\frac{1}{\alpha}$ the final expression of interest is obtained:

$$\begin{aligned}\frac{1}{\Lambda_m} &= \left(\frac{\alpha c}{K_a} + 1 \right) \frac{1}{\Lambda_m^\circ} \\ \frac{1}{\Lambda_m} &= \frac{1}{\Lambda_m^\circ} + (\alpha) \frac{c}{K_a \Lambda_m^\circ} \\ \frac{1}{\Lambda_m} &= \frac{1}{\Lambda_m^\circ} + \left(\frac{\Lambda_m}{\Lambda_m^\circ} \right) \frac{c}{K_a \Lambda_m^\circ} \\ \frac{1}{\Lambda_m} &= \frac{1}{\Lambda_m^\circ} + \frac{c \Lambda_m}{K_a (\Lambda_m^\circ)^2}\end{aligned}$$

P35.30) For a one-dimensional random walk, determine the probability that the particle will have moved six steps in either the $+x$ or $-x$ direction after 10, 20, and 100 steps.

To answer this question one needs to apply the following equations where Δ is the total number of steps and x is the number of steps representing the extent of displacement of interest ($x = 6$ in this case):

$$P = \frac{W}{2^\Delta} \quad W = \frac{\Delta!}{\left(\frac{\Delta+x}{2}\right)! \left(\Delta - \frac{\Delta+x}{2}\right)!}$$

For $\Delta = 10$, the probability is:

$$W = \frac{\Delta!}{\left(\frac{\Delta+x}{2}\right)!\left(\Delta-\frac{\Delta+x}{2}\right)!} = \frac{10!}{(8!)(2!)} = 45$$

$$P = \frac{W}{2^{10}} = \frac{45}{1024} = 4.39 \times 10^{-2}$$

Performing the same calculation for $\Delta = 20$ and 100 yields $P = 7.39 \times 10^{-2}$ and 6.66×10^{-2} , respectively.

P35.31) In the early 1990s, fusion involving hydrogen dissolved in palladium at room temperature, or *cold fusion*, was proposed as a new source of energy. This process relies on the diffusion of H_2 into palladium. The diffusion of hydrogen gas through a 0.005-cm-thick piece of palladium foil with a cross section of 0.750 cm^2 is measured. On one side of the foil, a volume of gas maintained at 298 K and 1 atm is applied, while a vacuum is applied to the other side of the foil. After 24 h, the volume of hydrogen has decreased by 15.2 cm^3 . What is the diffusion coefficient of hydrogen gas in palladium?

Beginning with the expression for flux:

$$J_x = -D \left(\frac{d\tilde{N}(x)}{dx} \right)$$

If the flux and gradient in number density are determined, then the diffusion coefficient can be defined. The flux is equal to the number of particles that pass through the foil area per unit time. First the number of particles that diffused through the foil is determined using the ideal gas law:

$$n_{\text{diffused}} = \frac{(1 \text{ atm})(15.2 \text{ cm}^3) \left(\frac{1 \text{ L}}{1000 \text{ cm}^3} \right)}{(8.21 \times 10^{-2} \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 6.21 \times 10^{-4} \text{ mol}$$

$$N_{\text{diffused}} = n_{\text{diffused}} \times N_A = 3.74 \times 10^{20}$$

Using the foil area and time for diffusion, the flux is determined as follows:

$$J_x = \frac{N_{\text{diffused}}}{At} = \frac{3.74 \times 10^{20}}{(0.750 \times 10^{-4} \text{ m}^2)(24 \text{ hr}) \left(\frac{3600 \text{ s}}{\text{hr}} \right)} = 5.77 \times 10^{19} \text{ m}^{-2} \text{ s}^{-1}$$

Next, the gradient in number density is equal to the difference in gas number density between each side of the foil divided by the foil thickness. The number density on the incident side of the foil is determined using the ideal gas law:

$$\tilde{N} = \frac{P}{kT} = \frac{101325 \text{ Pa}}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})} = 2.46 \times 10^{25} \text{ m}^{-3}$$

and the spatial gradient in number density is:

$$\left(\frac{d\tilde{N}}{dx} \right) = \frac{0 - 2.46 \times 10^{25} \text{ m}^{-3}}{5 \times 10^{-5} \text{ m}} = -4.93 \times 10^{29} \text{ m}^{-4}$$

Finally, the diffusion coefficient is calculated as follows:

$$D = - \frac{J_x}{\left(\frac{d\tilde{N}}{dx} \right)} = - \frac{5.77 \times 10^{19} \text{ m}^{-2} \text{ s}^{-1}}{(-4.93 \times 10^{29} \text{ m}^{-4})} = 1.17 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$$

P35.32) In the determination of molar conductivities, it is convenient to define the cell constant, K , as $K = \frac{l}{A}$, where l is the separation between the electrodes in the conductivity cell, and A is the area of the electrodes.

- a) A standard solution of KCl (conductivity or $\kappa = 1.06296 \times 10^{-6} \text{ S m}^{-1}$ at 298 K) is employed to standardize the cell, and a resistance of 4.2156Ω is measured. What is the cell constant?
- b) The same cell is filled with a solution of HCl and a resistance of 1.0326Ω is measured. What is the conductivity of the HCl solution?

a) The conductivity is defined as

$$\kappa = \frac{\ell}{R \cdot A} = \frac{K}{R}$$

where R is the resistance and K is the cell constant. Using this relationship, the cell constant is determined as follows:

$$\kappa = 1.06296 \times 10^{-6} \text{ S m}^{-1} \quad R = 4.2156 \Omega$$

$$K = \kappa R = (1.06296 \times 10^{-6} \text{ S m}^{-1})(4.2156 \Omega)$$

$$K = 4.48 \times 10^{-6} \text{ S m}^{-1} \Omega$$

b)

$$\kappa = \frac{K}{R} = \frac{4.48 \times 10^{-6} \text{ S m}^{-1} \Omega}{1.0326 \Omega}$$

$$= 4.34 \times 10^{-6} \text{ S m}^{-1}$$

P35.33) Conductivity measurements were one of the first methods used to determine the autoionization constant of water. The autoionization constant of water is given by the following equation:

$$K_w = a_{H^+} a_{OH^-} = \left(\frac{[H^+]}{1M} \right) \left(\frac{[OH^-]}{1M} \right)$$

where a is the activity of the species, which is equal to the actual concentration of the species divided by the standard state concentration at infinite dilution. This substitution

of concentrations for activities is a reasonable approximation given the small concentrations of H^+ and OH^- that result from autoionization.

a) Using the expression provided, show that the conductivity of pure water can be written

$$\text{as } \Lambda_m(H_2O) = (1M) K_w^{1/2} (\lambda(H^+) + \lambda(OH^-))$$

b) Kohlrausch and Heydweiller measured the conductivity of water in 1894 and determined that $\Lambda_m(H_2O) = 5.5 \times 10^{-6} \text{ S m}^{-1}$ at 298 K. Using the information provided in Table 35.2, determine K_w .

a) The conductivity of a weak electrolyte is given as

$$\Lambda_m = \alpha \Lambda_m^\circ$$

The degree of disassociation is given by the equilibrium expression

$$K_w = \frac{\alpha^2}{(1M)^2}$$

$$\alpha = (1M) K_w^{1/2}$$

And, Λ_m° is given as

$$\Lambda_m^\circ = \lambda(H^+) + \lambda(OH^-)$$

Combining the above expressions yields the relationship of interest:

$$\Lambda_m = (1M) K_w^{1/2} (\lambda(H^+) + \lambda(OH^-))$$

b)

$$\lambda(H^+) = 0.0350 \text{ S m}^2 \text{ mol}^{-1}$$

$$\lambda(OH^-) = 0.0199 \text{ S m}^2 \text{ mol}^{-1}$$

$$\Lambda_m = 5.5 \times 10^{-6} \text{ S m}^{-1}$$

Substituting these values in the expression derived in part (a) of this question and rearranging to isolate K_w yields:

$$\begin{aligned} K_w &= \left[\frac{\Lambda_m}{(1M)(\lambda(H^+) + \lambda(OH^-))} \right]^2 \\ &= \left[\frac{5.5 \times 10^{-6} \text{ S m}^{-1}}{1M(0.0350 \text{ S m}^2 \text{ mol}^{-1} + 0.0199 \text{ S m}^2 \text{ mol}^{-1})} \right]^2 \\ &= 1.00 \times 10^{-8} \cdot \frac{\text{mol}^2 \text{ L}^2}{\text{mol}^2 \text{ m}^6} \cdot \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right)^2 \\ &= 1.00 \times 10^{-14} \end{aligned}$$

Chapter 36: Elementary Chemical Kinetics

Questions on Concepts

Q36.1) Why is the stoichiometry of a reaction generally not sufficient to determine reaction order?

The order of a rate equation for a chemical reaction indicates the concentration dependence of the rate. The order is dependent on the mechanism of the reaction, and not on the proportionality of the reaction (i.e. the number of reactant molecules required to generate a specific number of product molecules).

Q36.2) What is an elementary chemical step, and how is one used in kinetics?

An elementary reaction step is a chemical process that occurs in a single step. Elementary reaction steps are combined to construct complex reaction mechanisms.

Q36.3) What is the difference between chemical and physical methods for studying chemical kinetics?

In chemical methods, a chemical process is used to quantify molecular concentrations. For example, a portion of the reaction sample may be removed, the reaction terminated, and the concentration of reactants or products is then measured. Physical methods involve measurement of some physical property of the system that changes as the reaction proceeds. Physical methods are in general more convenient, as the probe for the physical change are often located within the reaction vessel permitting measurement without having to disrupt or terminate the chemical reaction.

Q36.4) What is the method of initial rates, and why is it used in chemical kinetics studies?

In the method of initial rates a chemical reaction is initiated using a specific set of reactant concentrations and the reaction rate is measured. Subsequent measurements are in which the concentration of the reactant of interest is changed but all of the other concentrations are let the same. This process is repeated with varying initial concentrations of the reactant of interest while holding the other reactant concentrations constant. The variation in reaction rate with change in concentration of a single species can be used to determine the order of the reaction with respect to the species being changed. Finally, the reaction rates are measured at early times before the reactant concentrations have undergone substantial change from their initial value.

Q36.5) What is a rate law expression, and how is it determined?

The reaction rate law expression is a mathematical equation that expresses the reaction rate in terms of reactant concentrations and the microscopic rate constant of the reaction. Reaction rate law expressions must be determined experimentally.

Q36.6) What is the difference between a first-order reaction and a second-order reaction?

In a first order reaction the reaction rate depends linearly on the concentration of a single reactant species. In a second order reaction, the reaction rate depends either on a product of the concentration of two different reactant species with each concentration to the first power, or on the square of the concentration of a single reactant concentration.

Q36.7) What is a half-life? Is the half-life for a first-order reaction dependent on concentration?

The half-life of a chemical reaction is the time it takes for the initial reactant concentration to be reduced by exactly one half. The half-life for a first order reaction does not depend on initial reactant concentration.

Q36.8) In a sequential reaction, what is an intermediate?

The simplest sequential reaction involves two elementary reaction steps in which the reactant decays to form an intermediate species in the first step, then the intermediate proceeds to form product in the second step. An intermediate is a chemical species that is both produced during the course of the reaction, and subsequently decays resulting in product formation.

Q36.9) What is meant by the rate-determining step in a sequential reaction?

The rate determining step in a sequential chemical reaction is the elementary reaction step with the smallest reaction rate. This step is called rate limiting because no matter how large the reaction rates are for the other elementary steps, the overall reaction rate is determined by the smallest rate.

Q36.10) What is the steady-state approximation, and when is this approximation employed?

In the steady state approximation, the assumption is made that the concentrations of one or more intermediate species undergoes a negligible change with time. This approximation is generally valid when the elementary step that generates the intermediate is the rate determining step, and the subsequent step resulting in the

decay of intermediate is rapid ensuring that the intermediate undergoes decay as soon as it is formed so that the intermediate concentration is modest at all times.

Q36.11) In a branching reaction in which two products can be formed from the same reactant, what determines the extent to which one product will be formed over another?

The extent to which a product will be formed, or reaction yield, for a branching reaction depends on the reaction rate for the product channel of interest. The reaction yield is defined as the ratio of the rate constants for the given branches.

Q36.12) What is the kinetic definition of equilibrium?

The kinetic definition of equilibrium is the state at which the concentrations of reactants and products does not vary appreciably with time. This will occur when the forward and back reaction rates are equivalent.

Q36.13) In a temperature-jump experiment, why does a change in temperature result in a corresponding change in equilibrium?

The T-jump method relies on Arrhenius behavior of the reaction rates. In Arrhenius behavior, the rate constant is temperature dependent; therefore, when the temperature changes, the rate constant changes as well and a new equilibrium will exist. The system will relax to establish this new equilibrium

Q36.14) What is a transition state? How is the concept of a transition state used in activated complex theory set?

A transition state is position of maximum energy along the reaction. This maximum corresponds to an unstable configuration of the reaction (i.e., it does not correspond to a energetically-stable intermediate species).

Q36.15) What is the relationship between the parameters in the Arrhenius equation and in the Eyring equation?

The principle connection between the Arrhenius and Eyring equations is the relationship between the activation energy (E_a) in the Arrhenius expression and the enthalpy difference between the reactants and transition state (ΔH^\ddagger) which is:

$$E_a = RT + \Delta U^\ddagger \text{ with } \Delta U^\ddagger = \Delta H^\ddagger + \Delta(PV)^\ddagger$$

Where $\Delta(PV)^\ddagger$ is the difference in PV between reactants and the transition state. This term depends on the phase and type of reaction being considered.

Problems

P36.1) Express the rate of reaction with respect to each species in the following reactions:

- $2\text{NO}(g) + \text{O}_2(g) \longrightarrow \text{N}_2\text{O}_4(g)$
- $\text{H}_2(g) + \text{I}_2(g) \longrightarrow 2\text{HI}(g)$
- $\text{ClO}(g) + \text{BrO}(g) \longrightarrow \text{ClO}_2(g) + \text{Br}(g)$

a)

$$\begin{aligned} R &= -\frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{1}{2RT} \frac{dP_{\text{NO}}}{dt} \\ &= -\frac{d[\text{O}_2]}{dt} = -\frac{1}{RT} \frac{dP_{\text{O}_2}}{dt} \\ &= \frac{d[\text{N}_2\text{O}_4]}{dt} = \frac{1}{RT} \frac{dP_{\text{N}_2\text{O}_4}}{dt} \end{aligned}$$

b)

$$\begin{aligned} R &= -\frac{d[\text{H}_2]}{dt} = -\frac{1}{RT} \frac{dP_{\text{H}_2}}{dt} \\ &= -\frac{d[\text{I}_2]}{dt} = -\frac{1}{RT} \frac{dP_{\text{I}_2}}{dt} \\ &= \frac{1}{2} \frac{d[\text{HI}]}{dt} = \frac{1}{2RT} \frac{dP_{\text{HI}}}{dt} \end{aligned}$$

c)

$$\begin{aligned} R &= -\frac{d[\text{ClO}]}{dt} = -\frac{1}{RT} \frac{dP_{\text{ClO}}}{dt} \\ &= -\frac{d[\text{BrO}]}{dt} = -\frac{1}{RT} \frac{dP_{\text{BrO}}}{dt} \\ &= \frac{d[\text{ClO}_2]}{dt} = \frac{1}{RT} \frac{dP_{\text{ClO}_2}}{dt} \\ &= \frac{d[\text{Br}]}{dt} = \frac{1}{RT} \frac{dP_{\text{Br}}}{dt} \end{aligned}$$

P36.2) Consider the first-order decomposition of cyclobutane at 438°C at constant volume: $\text{C}_4\text{H}_8(g) \longrightarrow 2\text{C}_2\text{H}_4(g)$

- Express the rate of the reaction in terms of the change in total pressure as a function of time.
- The rate constant for the reaction is $2.48 \times 10^{-4} \text{ s}^{-1}$. What is the half-life?

c) After initiation of the reaction, how long will it take for the initial pressure of C₄H₈ to drop to 90% of its initial value?

a) The rate is given as

$$R = -\frac{1}{RT} \frac{dP_{C_4H_8}}{dt} = \frac{1}{2RT} \frac{dP_{C_2H_4}}{dt}$$

The pressure at time t is given as $P_t = P_{t=0} - P_{C_4H_8} + P_{C_2H_4}$. Where $P_{t=0}$ is the initial pressure, and $P_{C_4H_8}$ and $P_{C_2H_4}$ represent the pressures of the individual gases as a specific time. By stoichiometry $P_{C_4H_8} = \frac{1}{2}P_{C_2H_4}$ so that:

$$P_t = P_{t=0} - P_{C_2H_4} + 2P_{C_2H_4} = P_{t=0} + P_{C_2H_4}$$

Since $P_{C_2H_4}$ is dependent on time and the initial pressure is time independent:

$$\frac{dP_t}{dt} = \frac{dP_{C_2H_4}}{dt}$$

and

$$R = \frac{1}{2RT} \frac{dP_t}{dt}$$

b) The reaction is first order with respect to

$$t_{1/2} = \frac{\ln 2}{k}$$

so

$$t_{1/2} = \frac{0.693}{2.48 \times 10^{-4} \text{ s}^{-1}}$$

$$= 2.79 \times 10^3 \text{ s}$$

c) Using the integrated rate law

$$-kt = \ln\left(\frac{[A]}{[A]_0}\right)$$

where

$$\frac{[A]}{[A]_0} = 0.90$$

one finds

$$t = -\frac{\ln(0.90)}{2.48 \times 10^{-4} \text{ s}^{-1}}$$

$$= \frac{0.105}{2.48 \times 10^{-4} \text{ s}^{-1}}$$

$$= 425 \text{ s}$$

P36.3) As discussed in the text, the total system pressure can be used to monitor the progress of a chemical reaction. Consider the following reaction:

$\text{SO}_2\text{Cl}_2(g) \longrightarrow \text{SO}_2(g) + \text{Cl}_2(g)$. The reaction is initiated, and the following data are obtained:

Time (h)	0	3	6	9	12	15
P_{Total} (kPa)	11.07	14.79	17.26	18.90	19.99	20.71

- a) Is the reaction first or second order with respect to SO_2Cl_2 ?
b) What is the rate constant for this reaction?

a) As the reaction proceeds, stoichiometry dictates that every mole of SO_2Cl_2 that dissociates results in a mole of SO_2 and Cl_2 . Defining the extent of dissociation as ξ , and the initial pressure P_0 , the total pressure is given by:

$$P_{\text{total}} = P_{\text{SO}_2\text{Cl}_2} + P_{\text{SO}_2} + P_{\text{Cl}_2}$$

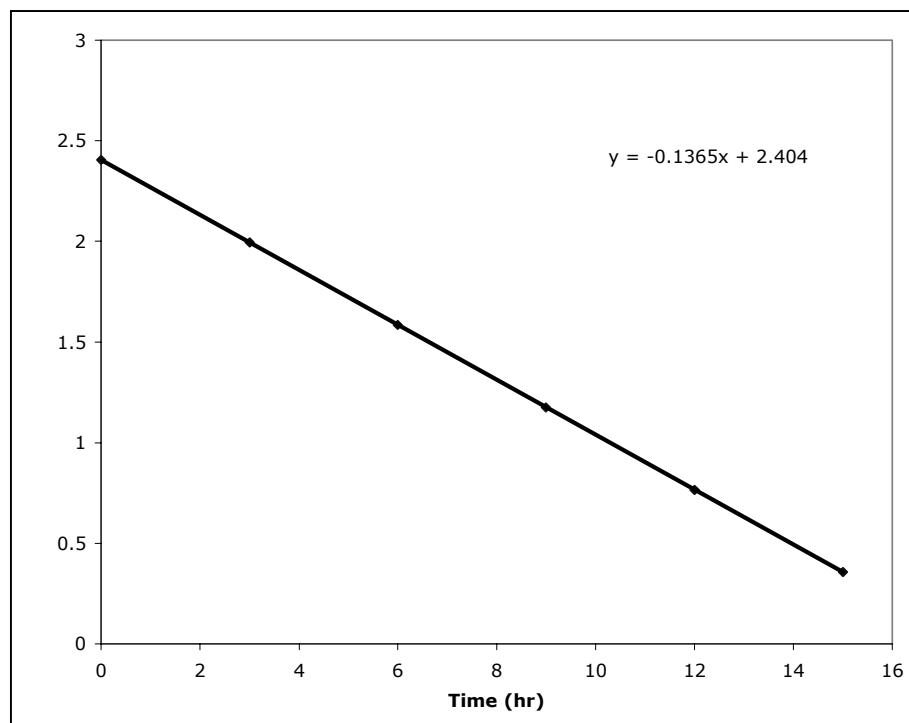
$$= (P_0 - \xi) + \xi + \xi = P_0 + \xi$$

$$P_{\text{total}} - P_0 = \xi$$

Therefore, the total pressure and initial pressure data in the table can be used to determine the extent of dissociation, and these quantities can be used to determine $P_{\text{SO}_2\text{Cl}_2}$. If the reaction is first order, a plot of $\ln(P_{\text{SO}_2\text{Cl}_2})$ versus time should yield a straight line. If the reaction is second order, a plot of $(P_{\text{SO}_2\text{Cl}_2})^{-1}$ versus time should yield a straight line. Therefore, the data provided in the table is used to determine the following:

t (hr)	$P_{\text{SO}_2\text{Cl}_2}$ (kPa)	$\ln(P_{\text{SO}_2\text{Cl}_2})$	$\frac{1}{P_{\text{SO}_2\text{Cl}_2}}$
0	11.07	2.404	0.090
3	7.35	1.995	0.136
6	4.88	1.585	0.205
9	3.24	1.176	0.309
12	2.15	0.765	0.465
15	1.43	0.358	0.699

A plot of $\ln(P_{SO_2Cl_2})$ vs. t is linear as shown below demonstrating that the reaction is first order in $P_{SO_2Cl_2}$.



- b) Best fit to the data presented in the above figure by a straight line yields a slope of -0.1365 hr^{-1} which is equal to the negative of the rate constant:

$$k = 0.1365 \text{ hr}^{-1} \left(\frac{1 \text{ hr}}{3600 \text{ s}} \right) = 3.79 \times 10^{-5} \text{ s}^{-1}$$

P36.4) Consider the following reaction involving bromophenol blue (BPB) and OH: $\text{BPB}(aq) + \text{OH}^-(aq) \longrightarrow \text{BPBOH}^-(aq)$.

The concentration of BPB can be monitored by following the absorption of this species and using the Beer–Lambert law. In this law, absorption, A , and concentration are linearly related.

- Express the reaction rate in terms of the change in absorbance as a function of time.
- Let A_0 be the absorbance due to BPB at the beginning of the reaction. Assuming that the reaction is first order with respect to both reactants, how is the absorbance of BPB expected to change with time?
- Given your answer to part (b), what plot would you construct to determine the rate constant for the reaction?

- a) Beer's Law states that

$$A = \epsilon b [\text{BPB}]$$

where ϵ is the molar absorptivity of BPB and b is the cell path length. The rate of reaction is

$$\text{Rate} = -\frac{d[\text{BPB}]}{dt}$$

Thus

$$\text{Rate} = -\frac{d[\text{BPB}]}{dt}$$

$$= -\frac{d\left\{\frac{A}{\epsilon b}\right\}}{dt}$$

$$\text{Rate} = -\frac{1}{\epsilon b} \frac{dA}{dt}$$

- b) Let A_0 be the initial absorbance of BPB and $A(t)$ be the absorbance at time, t . Since the reaction is a second order reaction of type II, the integrate rate equation has the form

$$\frac{1}{[\text{OH}^-]_0 - [\text{BPB}]_0} \ln \left(\frac{[\text{OH}^-]}{[\text{BPB}]} \right) = kt$$

Substituting into the above expression for [BPB] yields:

$$\frac{1}{[\text{OH}^-]_0 - \frac{A_0}{b\epsilon}} \ln \left(\frac{[\text{OH}^-]}{A/A_0} \right) = kt$$

$$\ln \left(\frac{A}{A_0} \right) = \ln \left(\frac{[\text{OH}^-]}{[\text{OH}^-]_0} \right) - \left([\text{OH}^-] - \frac{A_0}{b\epsilon} \right) kt$$

- c) A plot of $\ln \left(\frac{A}{A_0} \right)$ vs. t is predicted to be linear.

P36.5) For the following rate expressions, state the order of the reaction with respect to each species, the total order of the reaction, and the units of the rate constant, k :

a) $\text{Rate} = k[\text{ClO}][\text{BrO}]$

b) $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$

c) $\text{Rate} = k \frac{[\text{HI}]^2[\text{O}_2]}{[\text{H}^{+}]^{1/2}}$

a)

First order wrt ClO
 First order wrt BrO
 Second order overall
 Units of k: $s^{-1} M^{-1}$

b)

Second order wrt NO
 First order wrt O₂
 Third order overall
 Units of k: $s^{-1} M^{-2}$

c)

Second order wrt HI
 First order wrt O₂
 $-\frac{1}{2}$ order wrt H⁺
 2.5 order over all
 Units of k: $s^{-1} M^{-3/2}$

P36.6) What is the overall order of the reaction corresponding to the following rate constants:

- a) $k = 1.63 \times 10^{-4} M^{-1} s^{-1}$
- b) $k = 1.63 \times 10^{-4} M^{-2} s^{-1}$
- c) $k = 1.63 \times 10^{-4} M^{-1/2} s^{-1}$

- a) Second Order
- b) Third Order
- c) 1.5 Order

P36.7) The reaction rate as a function of initial reactant pressures was investigated for the reaction $2\text{NO}(g) + 2\text{H}_2(g) \longrightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g)$, and the following data were obtained

Run	$P_o \text{ H}_2$ (kPa)	$P_o \text{ N}_2$ (kPa)	Rate (kPa s ⁻¹)
1	53.3	40.0	0.137
2	53.3	20.3	0.033
3	38.5	53.3	0.213
4	19.6	53.3	0.105

What is the rate law expression for this reaction?

The rate law expression is:

$$\text{Rate} = k P_{\text{H}_2}^{\alpha} P_{\text{NO}}^{\beta}$$

Chapter 36/Elementary Chemical Kinetics

We first find the order of the reaction. Using the method of initial rates for the first two runs, the order of the reaction with respect to NO is:

$$\frac{Rate_1}{Rate_2} = \frac{P_{NO_1}^\beta}{P_{NO_2}^\beta} = \left(\frac{P_{NO_1}}{P_{NO_2}} \right)^\beta$$

$$\ln \left(\frac{Rate_1}{Rate_2} \right) = \beta \ln \left(\frac{P_{NO_1}}{P_{NO_2}} \right)$$

$$\frac{\ln \left(\frac{Rate_1}{Rate_2} \right)}{\ln \left(\frac{P_{NO_1}}{P_{NO_2}} \right)} = \beta$$

$$\frac{\ln \left(\frac{0.137}{0.033} \right)}{\ln \left(\frac{40}{20.3} \right)} = 2.09 \approx 2 = \beta$$

Next the second two runs, the order of the reaction with respect to H₂ is:

$$\frac{Rate_3}{Rate_4} = \frac{P_{H_2 \text{ run3}}^\alpha}{P_{H_2 \text{ run4}}^\alpha}$$

$$\ln \left(\frac{Rate_3}{Rate_4} \right) = \alpha \ln \left(\frac{P_{H_2 \text{ run3}}}{P_{H_2 \text{ run4}}} \right)$$

$$\frac{\ln \left(\frac{Rate_3}{Rate_4} \right)}{\ln \left(\frac{P_{H_2 \text{ run3}}}{P_{H_2 \text{ run4}}} \right)} = \alpha$$

$$\frac{\ln \left(\frac{0.213}{0.105} \right)}{\ln \left(\frac{38.5}{19.6} \right)} = 1.04 \approx 1 = \alpha$$

With the order dependence, the rate constant can be determined using the known concentrations (or pressures) of each species for a given run. Using the first run:

$$Rate_1 = k P_{H_2} P_{NO}^2$$

$$\frac{Rate_1}{P_{H_2} P_{NO}^2} = \frac{0.137 \text{ kPa s}^{-1}}{(53.3 \text{ kPa})(40.0 \text{ kPa})^2} = k$$

$$6.43 \times 10^{-5} \text{ kPa}^2 \text{ s}^{-1}$$

Therefore, the rate law expression is:

$$\text{Rate} = 6.43 \times 10^{-5} \text{ kPa}^{-2} \text{ s}^{-1} P_{H_2} P_{NO}^2$$

P36.8) (Challenging) The first-order thermal decomposition of chlorocyclohexane is as follows: $C_6H_{11}Cl(g) \longrightarrow C_6H_{10}(g) + HCl(g)$. For a constant volume system the following total pressure was measured as a function of time:

Time (s)	P (torr)	Time (min)	P (torr)
3	237.2	24	332.1
6	255.3	27	341.1
9	271.3	30	349.3
12	285.8	33	356.9
15	299.0	36	363.7
18	311.2	39	369.9
21	322.2	42	375.5

a) Derive the following relationship for a first-order reaction:

$P(t_2) - P(t_1) = (P(t_\infty) - P(t_0)) e^{-kt_1} (1 - e^{-k(t_2-t_1)})$. In this relation, $P(t_1)$ and $P(t_2)$ are the pressures at two specific times; $P(t_0)$ is the initial pressure when the reaction is initiated, $P(t_\infty)$ is the pressure at the completion of the reaction, and k is the rate constant for the reaction. To derive this relationship:

- Given the first-order dependence of the reaction, write down the expression for the pressure of chlorocyclohexane at a specific time t_1 .
- Write the expression for the pressure at another time t_2 , which is equal to $t_1 + \Delta$ where Δ is a fixed quantity of time.
- Write down expressions for $P(t_\infty) - P(t_1)$ and $P(t_\infty) - P(t_2)$.
- Subtract the two expressions from part (iii).

b) Using the natural log of the relationship from part (a) and the data provided in the table given earlier in this problem, determine the rate constant for the decomposition of chlorocyclohexane. (*Hint:* Transform the data in the table by defining $t_2 - t_1$ to be a constant value, for example, 9 s.)

a) Since the reaction is first order, we can write:

$$P_\infty - P_{t_1} = (P_\infty - P_0) e^{-kt_1}$$

$$P_\infty - P_{t_2} = (P_\infty - P_0) e^{-kt_2} = (P_\infty - P_0) e^{-k(t_1+\Delta)}$$

subtracting the two previous equations:

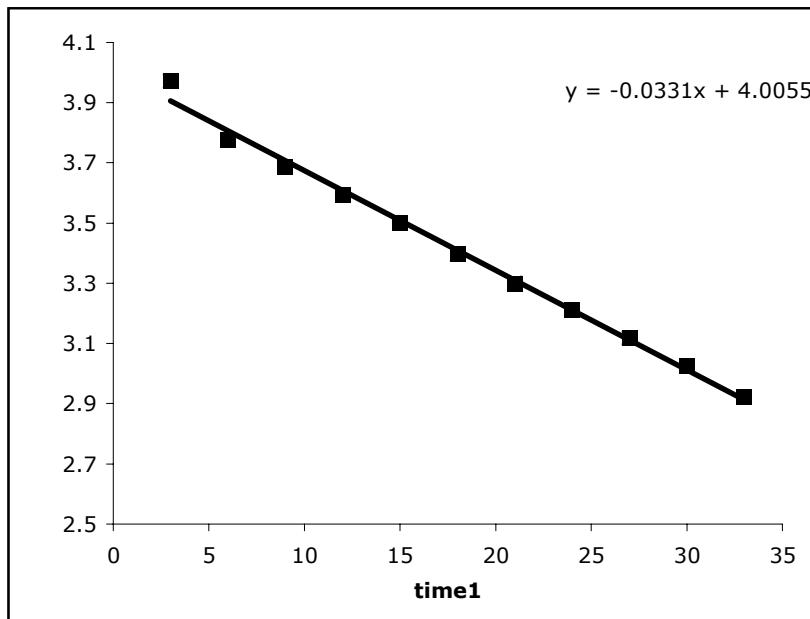
$$P_{t_2} - P_{t_1} = (P_\infty - P_0) e^{-kt_1} (1 - e^{-k\Delta})$$

where Δ is the difference in time between t_2 and t_1 .

b) Taking the natural log of the previous expression yields:

$$\begin{aligned}\ln(P_{t_2} - P_{t_1}) &= \ln(P_\infty - P_0) - kt_1 + \ln(1 - e^{-k\Delta t}) \\ &= \ln[(P_\infty - P_0)(1 - e^{-k\Delta t})] - kt_1\end{aligned}$$

Therefore, a plot of the difference in pressure at fixed difference in time versus t_1 should yield a straight line with slope equal to $-k$. Using a difference in time of 9 s yields the following table of the difference in pressures versus time:



The slope of the best fit line is -0.0311 min^{-1} ; therefore, the rate constant is 0.0311 min^{-1} , or $5.18 \times 10^{-4} \text{ s}^{-1}$.

P36.9) You are given the following data for the decomposition of acetaldehyde:

Initial Concentration (M)	9.72×10^{-3}	4.56×10^{-3}
Half-Life (s)	328	685

Determine the order of the reaction and the rate constant for the reaction.

Since the half-life depends on the initial concentration, the reaction cannot be first order. To see if it is second order, we can use the half-life information to solve for the rate constant as follows:

$$k = \frac{1}{t_{1/2} [A]_0}$$

For $[A]_0 = 9.72 \times 10^{-3}$

$$k = \left[(328 \text{ s}) (9.72 \times 10^{-3} \text{ M}) \right]^{-1}$$

$$k = 0.314 \text{ M}^{-1} \text{ s}^{-1}$$

at $[A]_0 = 4.56 \times 10^{-3}$

$$k = \left[(685 \text{ s}) (4.56 \times 10^{-3} \text{ M}) \right]^{-1}$$

$$k = 0.320 \text{ M}^{-1} \text{ s}^{-1}$$

The average value is $k = 0.317 \text{ M}^{-1} \text{ s}^{-1}$.

P36.10) Consider the schematic reaction $A \xrightarrow{k} P$.

- a) If the reaction is one-half order with respect to $[A]$, what is the integrated rate law expression for this reaction?
- b) What plot would you construct to determine the rate constant k for the reaction?
- c) What would be the half-life for this reaction? Will it depend on initial concentration of the reactant?

$$\text{a)} \frac{d[A]}{dt} = k[A]^{1/2}$$

$$[A]^{-1/2} d[A] = k dt$$

$$\int_{[A]_0}^{[A]} [A]^{-1/2} d[A] = k \int_0^t dt$$

$$2 \left([A]^{1/2} - [A]_0^{1/2} \right) = kt$$

$$[A]^{1/2} = [A]_0^{1/2} + \frac{kt}{2}$$

$$[A] = \left([A]_0^{1/2} + \frac{kt}{2} \right)^2$$

- b) A plot of $[A]^{1/2}$ vs. t will be linear, and the rate constant is equal to two times the slope of the line.

- c) At $t_{1/2}$, $[A] = 0.5[A]_0$

$$\frac{1}{2}[A]_0 = \left(\frac{1}{2}kt_{1/2} + [A]_0^{1/2} \right)^2$$

$$\frac{1}{\sqrt{2}}[A]_0^{1/2} = \frac{1}{2}kt_{1/2} + [A]_0^{1/2}$$

$$\frac{1}{2}kt_{1/2} = \left(\frac{1}{\sqrt{2}} - 1 \right) [A]_0^{1/2}$$

$$t_{1/2} = \frac{2}{k} \left(\frac{1}{\sqrt{2}} - 1 \right) [A]_0^{1/2}$$

$$t_{1/2} = \frac{1}{k} (\sqrt{2} - 2) [A]_0^{1/2}$$

The half-life depends on the square-root of the initial concentration.

P36.11) A certain reaction is first order, and 540 s after initiation of the reaction, 32.5% of the reactant remains.

- a) What is the rate constant for this reaction?
- b) At what time after initiation of the reaction will 10% of the reactant remain?

a) The integrated rate law is of the form

$$\ln[R] = \ln[R_0] - kt$$

or

$$\ln\left(\frac{[R]}{[R_0]}\right) = -kt$$

Thus at $t = 540$ s, $[A] = 0.325 [A]_0$

$$k = -\frac{1}{340 \text{ s}} \ln(0.325)$$

$$k = 0.00208 \text{ s}^{-1}$$

$$k = 2.08 \times 10^{-3} \text{ s}^{-1}$$

$$\begin{aligned} \text{b) } t &= -\frac{1}{k} \ln\left(\frac{[A]}{[A_0]}\right) \\ &= -\frac{1}{2.08 \times 10^{-3} \text{ s}^{-1}} \ln(0.1) \\ t &= 1.11 \times 10^3 \text{ s} \end{aligned}$$

P36.12) The half-life of ^{238}U is 4.5×10^9 years. How many disintegrations occur in 1 minute for a 10-mg sample of this element?

The rate constant can be found from the half-life:

$$t_{1/2} = \frac{\ln 2}{k} \quad \text{or} \quad k = \frac{\ln 2}{t_{1/2}}$$

Thus

$$k = \frac{0.693}{4.5 \times 10^9 \text{ yrs}} \left(\frac{1 \text{ yr}}{364.25 \text{ day}} \right) \left(\frac{1 \text{ day}}{24 \text{ hrs}} \right) \left(\frac{1 \text{ hr}}{60 \text{ min}} \right)$$

$$k = 2.94 \times 10^{-16} \text{ min}^{-1}$$

Converting 10 mgs into the number of ^{238}U atoms:

$$N_{^{238}\text{U}} = (1 \times 10^{-2} \text{ g}) (238 \text{ g mol}^{-1}) (6.022 \times 10^{23} \text{ mol}^{-1}) = 1.43 \times 10^{24}$$

Employing the rate law, the number of disintegrations in 1 minute is:

$$\begin{aligned} N &= N_0 e^{-kt} \\ &= (1.43 \times 10^{24}) e^{-2.94 \times 10^{-16} \text{ min}^{-1} \cdot 1 \text{ min}} \\ &= 1.43 \times 10^{24} \end{aligned}$$

The rate constant is so small that a negligible number of disintegrations occur in one minute.

P36.13) You are performing an experiment using ^3H (half-life = 4.5×10^3 days) labeled phenylalanine in which the five aromatic hydrogens are labeled. To perform the experiment, the initial activity cannot be lower than 10% of the initial activity when the sample was received. How long after receiving the sample can you wait before performing the experiment?

The rate constant can be found from the half-life:

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{4.5 \times 10^3 \text{ day}}$$

$$k = 1.54 \times 10^{-4} \text{ day}^{-1}$$

And so:

$$\ln \left(\frac{[A]}{[A]_0} \right) = -kt$$

$$t = -\frac{1}{1.54 \times 10^{-4} \text{ day}^{-1}} (\ln(0.10))$$

$$t = 1.50 \times 10^4 \text{ days} \approx 41 \text{ years}$$

P36.14) A convenient source of gamma rays for radiation chemistry research is ^{60}Co , which undergoes the following decay process: $^{60}_{27}\text{Co} \xrightarrow{k} ^{60}_{28}\text{Ni} + \beta^- + \gamma$. The half-life of ^{60}Co is 1.9×10^3 days.

a) What is the rate constant for the decay process?

b) How long will it take for a sample of ^{60}Co to decay to half of its original concentration?

a) The rate constant can be found from the half-life:

$$k = \frac{\ln 2}{t_{1/2}}$$

$$k = \frac{0.693}{1.9 \times 10^3 \text{ day}}$$

$$k = 3.65 \times 10^{-4} \text{ day}^{-1}$$

$$\text{b) } 1.9 \times 10^3 \text{ days} = 5.2 \text{ years}$$

P36.15) The growth of a bacterial colony can be modeled as a first-order process in

which the probability of cell division is linear with respect to time such that $\frac{dN}{N} = \zeta dt$,

where dN is the number of cells that divide in the time interval dt , and ζ is a constant.

a) Use the preceding expression to show that the number of cells in the colony is given by $N = N_0 e^{\zeta t}$, where N is the number of cell colonies and N_0 is the number of colonies present at $t = 0$.

b) The generation time is the amount of time it takes for the number of cells to double. Using the answer to part (a), derive an expression for the generation time.

c) In milk at 37°C , the bacteria *lactobacillus acidophilus* has a generation time of about 75 min.

Construct a plot of the acidophilus concentration as a function of time for time intervals of 15, 30, 45, 60, 90, 120, and 150 minutes after a colony of size N_0 is introduced to a container of milk.

$$\text{a) } \int_{N_0}^N \frac{dN}{N} = \zeta \int_0^t dt$$

$$\ln(N) - \ln(N_0) = \zeta t$$

$$\ln\left(\frac{N}{N_0}\right) = \zeta t$$

$$\frac{N}{N_0} = e^{\zeta t}$$

b) At the generation time, $N = 2N_0$. Thus,

$$2N_0 = N_0 e^{\xi t_{gen}}$$

or

$$2 = e^{\xi t_{gen}}$$

$$\ln 2 = \xi t_{gen}$$

$$\frac{\ln 2}{\xi} = t_{gen}$$

c) The value of ξ for $t_{gen} = 75$ min can be found.

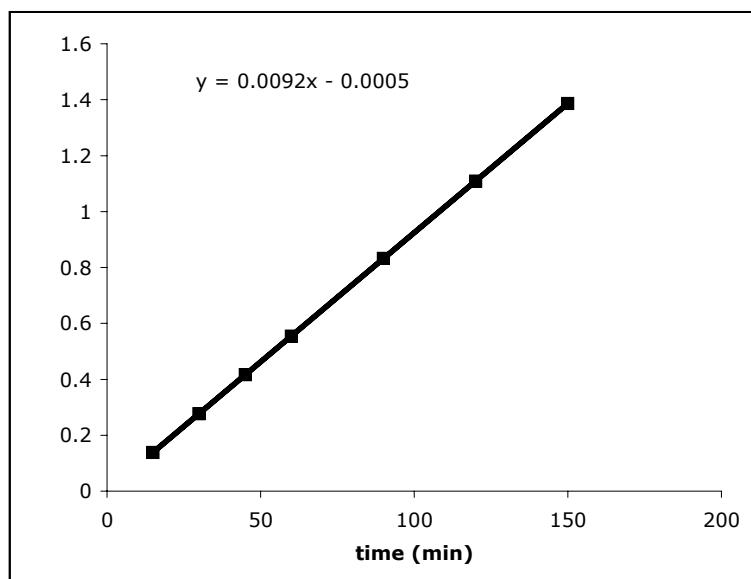
$$\xi = \frac{\ln 2}{75 \text{ min}}$$

$$\xi = 0.00924 \text{ min}^{-1}$$

Thus, the following table can be constructed:

t (min)	N/N ₀
15	1.148
30	1.319
45	1.515
60	1.741
90	2.297
120	3.031
150	4.000

And the plot of $\ln(N/N_0)$ versus time yields



The slope of the line is in agreement with part (b) of this problem.

P36.16) Show that the ratio of the half-life to the three-quarter life, $t_{1/2}/t_{3/4}$ for a reaction that is n th order ($n > 1$) in reactant A can be written as a function of n alone (that is, there is no concentration dependence in the ratio).

In general, for order n ,

$$kt = \frac{1}{n-1} \left\{ \frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right\}$$

$$t_{1/2} \Rightarrow [A] = \frac{1}{2} [A]_0$$

$$kt_{1/2} = \frac{1}{n-1} \left\{ \frac{2^{n-1}}{[A]_0^{n-1}} - \frac{1}{[A]_0^{n-1}} \right\}$$

and

$$t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}}$$

$$t_{3/4} \Rightarrow [A] = \frac{1}{4} [A]_0$$

$$kt_{3/4} = \frac{1}{n-1} \left\{ \frac{4^{n-1}}{[A]_0^{n-1}} - \frac{1}{[A]_0^{n-1}} \right\}$$

and

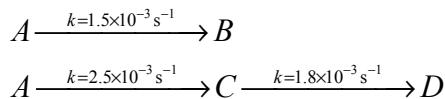
$$t_{3/4} = \frac{4^{n-1} - 1}{k(n-1)[A]_0^{n-1}}$$

Thus,

$$\frac{t_{1/2}}{t_{3/4}} = \frac{\frac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}}}{\frac{4^{n-1} - 1}{k(n-1)[A]_0^{n-1}}} = \frac{2^{n-1} - 1}{4^{n-1} - 1}$$

$$\frac{t_{1/2}}{t_{3/4}} = \frac{2^{n-1} - 1}{4^{n-1} - 1}$$

P36.17) Given the following kinetic scheme and associated rate constants, determine the concentration profiles of all species using Euler's method. Assume that the reaction is initiated with only the reactant A present at an initial concentration of 1 M. To perform this calculation, you may want to use a spreadsheet program such as Excel.



The differential rate expressions used in evaluating the kinetic scheme are:

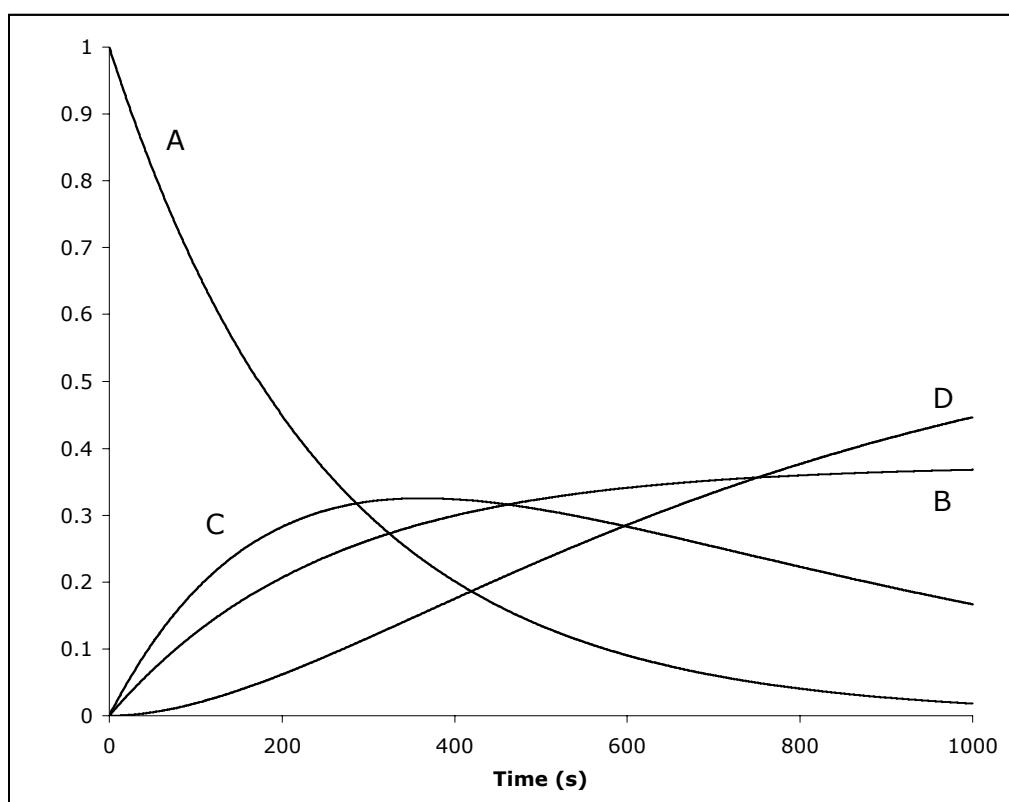
$$\frac{\Delta[A]}{\Delta t} = -\left[\left(1.5 \times 10^{-3} \text{ s}^{-1}\right) + \left(2.5 \times 10^{-3} \text{ s}^{-1}\right)\right][A]$$

$$\frac{\Delta[B]}{\Delta t} = \left(1.5 \times 10^{-3} \text{ s}^{-1}\right)[A]$$

$$\frac{\Delta[C]}{\Delta t} = \left(2.5 \times 10^{-3} \text{ s}^{-1}\right)[A] - \left(1.8 \times 10^{-3} \text{ s}^{-1}\right)[C]$$

$$\frac{\Delta[D]}{\Delta t} = \left(1.8 \times 10^{-3} \text{ s}^{-1}\right)[C]$$

Using these expressions and a time step size of 1 s, the following concentration profiles were obtained using Excel:



P36.18) For the sequential reaction $A \xrightarrow{k_A} B \xrightarrow{k_B} C$, the rate constants are $k_A = 5 \times 10^6 \text{ s}^{-1}$ and $k_B = 3 \times 10^6 \text{ s}^{-1}$. Determine the time at which $[B]$ is at a maximum.

For a sequential reaction,

$$[B] = \frac{k_A}{k_B - k_A} (e^{-k_A t} - e^{-k_B t}) [A_0]$$

The maximum occurs when

$$\frac{\partial[B]}{\partial t} = 0 = \frac{k_A}{k_B - k_A} [A_0] \frac{\partial}{\partial t} (e^{-k_A t} - e^{-k_B t})$$

$$0 = \frac{k_A}{k_B - k_A} [A_0] (-k_A e^{-k_A t} + k_B e^{-k_B t})$$

The above equality will be true when the term in parenthesis equals zero, therefore:

$$k_A e^{-k_A t} = k_B e^{-k_B t}$$

$$\ln k_A - k_A t = \ln k_B - k_B t$$

$$\ln k_A - \ln k_B = (k_A - k_B) t$$

$$\frac{1}{k_A - k_B} \ln \left(\frac{k_A}{k_B} \right) = t$$

Substituting the values of k_A and k_B into the previous expression yields:

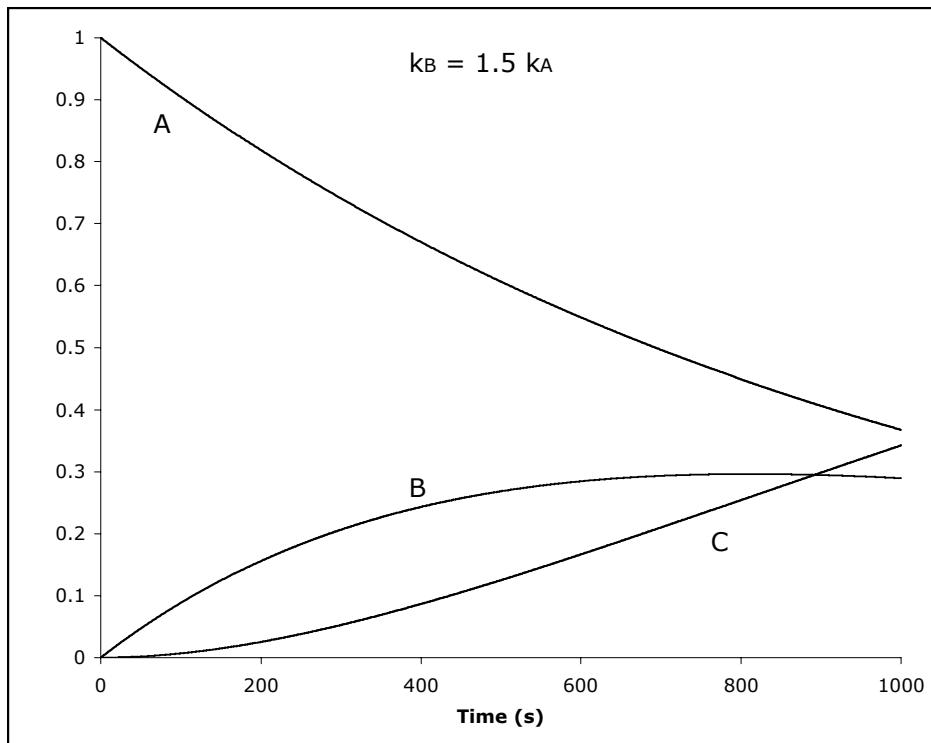
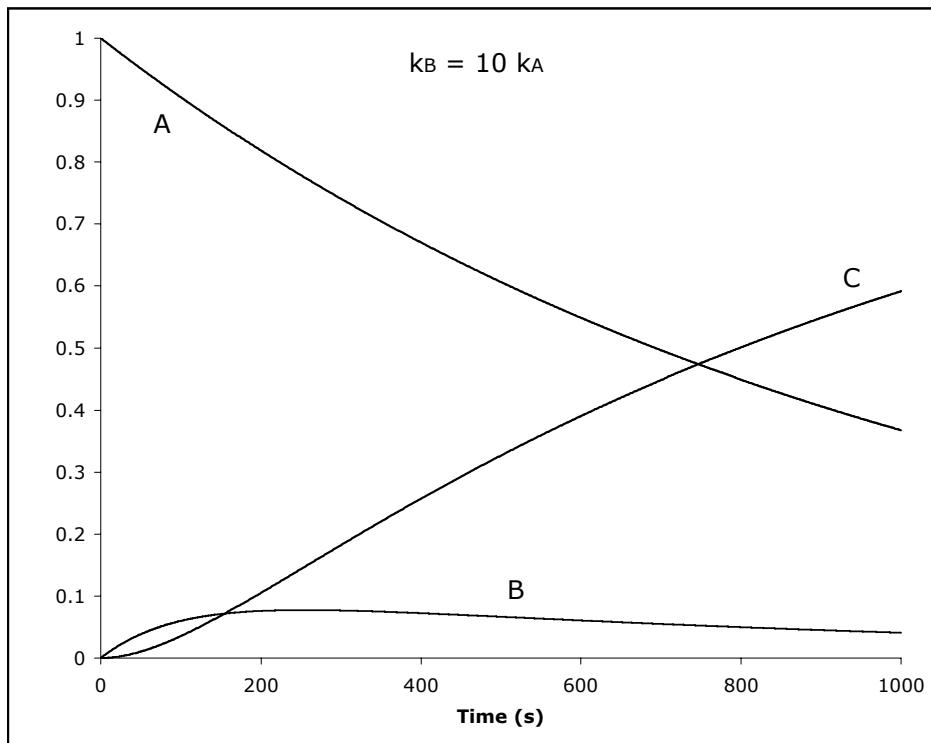
$$t = \frac{1}{(5 \times 10^6 \text{ s}^{-1}) - (3 \times 10^6 \text{ s}^{-1})} \ln \left(\frac{5 \times 10^6 \text{ s}^{-1}}{3 \times 10^6 \text{ s}^{-1}} \right)$$

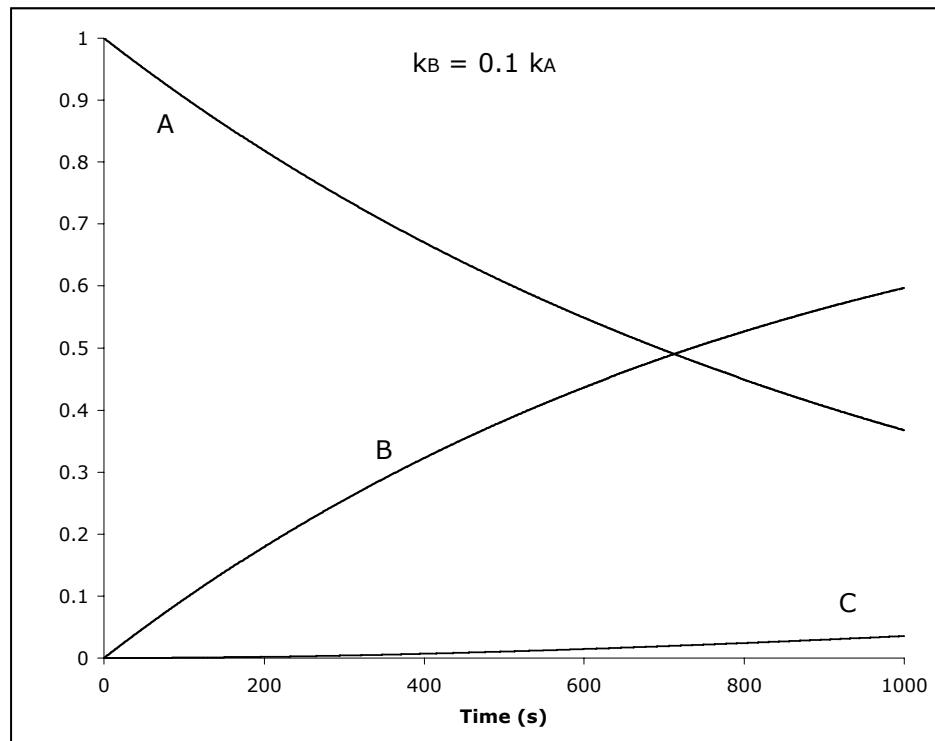
$$= (5 \times 10^{-7} \text{ s})(0.511)$$

$$t = 2.55 \times 10^{-7} \text{ s}$$

P36.19) For the sequential reaction $A \xrightarrow{k_A} B \xrightarrow{k_B} C$, $k_A = 1.00 \times 10^{-3} \text{ s}^{-1}$. Using a computer spreadsheet program such as Excel, plot the concentration of each species for cases where

$k_B = 10k_A$, $k_B = 1.5k_A$, and $k_B = 0.1k_A$. Assume that only the reactant is present when the reaction is initiated





P36.20) (Challenging) For the sequential reaction in Problem P36.19, plot the concentration of each species for the case where $k_B = k_A$. Can you use the analytical expression for $[B]$ in this case?

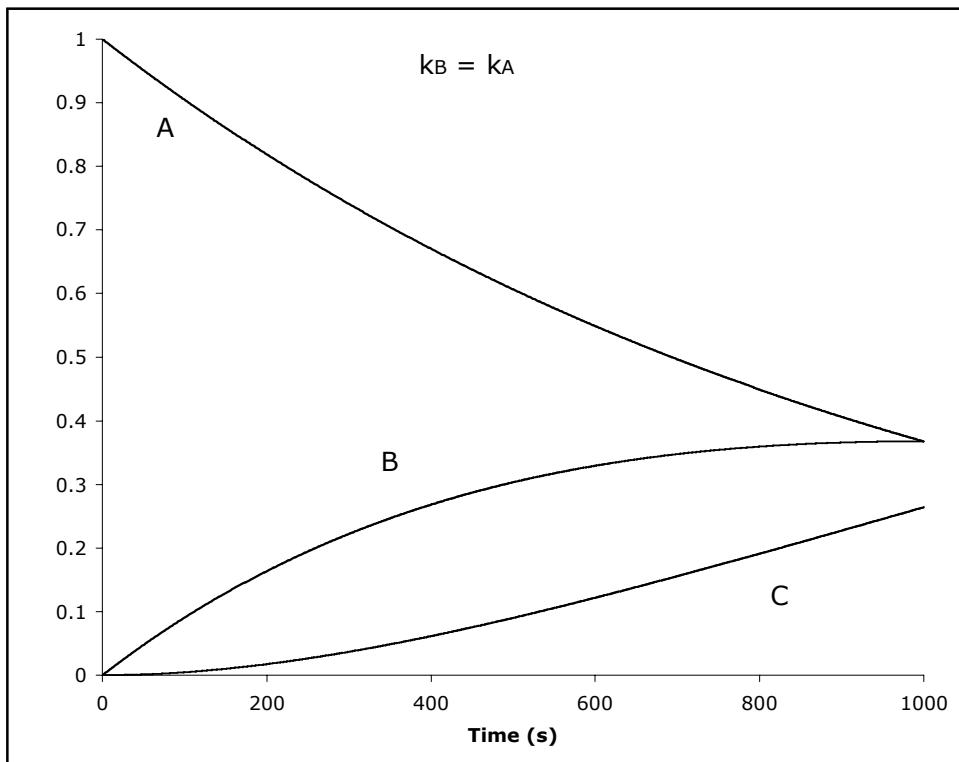
When $k_B = k_A$, the analytical expression for $[B]$ cannot be used since $k_B - k_A$ occurs in the denominator so that the analytical expression equals infinity in this case. In other words, the analytical expression for $[B]$ has a singularity at $k_B - k_A$. Instead, using Euler's method with the following differential rate expressions:

$$\frac{\Delta[A]}{\Delta t} = -(1 \times 10^{-3} \text{ s}^{-1})[A]$$

$$\frac{\Delta[B]}{\Delta t} = (1 \times 10^{-3} \text{ s}^{-1})[A] - (1 \times 10^{-3} \text{ s}^{-1})[B]$$

$$\frac{\Delta[C]}{\Delta t} = (1 \times 10^{-3} \text{ s}^{-1})[B]$$

Evaluating these expressions yields:



Notice that the concentration profiles follow the expected behavior given the results presented in Problem P36.19.

P36.21) For a type II second-order reaction, the reaction is 60% complete in 60 seconds when $[A]_0 = 0.1 \text{ M}$ and $[B]_0 = 0.5 \text{ M}$.

- What is the rate constant for this reaction?
- Will the time for the reaction to reach 60% completion change if the initial reactant concentrations are decreased by a factor of two?

- The integrated rate-law expression for a second-order reaction of type II is:

$$kt = \frac{1}{[B]_0 - [A]_0} \ln \left(\frac{[B]}{[B]_0} \right) \left(\frac{[A]}{[A]_0} \right)$$

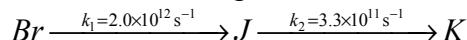
at $t = 60 \text{ s}$, $[A] = 0.04 \text{ M}$ with 1:1 stoichiometry so that $[B] = 0.44 \text{ M}$. Substituting these values into the above expression and using $t = 60 \text{ s}$ yields:

$$\begin{aligned}
 k &= \frac{1}{60 \text{ s} (0.5 \text{ M} - 0.1 \text{ M})} \ln \left(\frac{\frac{0.44 \text{ M}}{0.5 \text{ M}}}{\frac{0.04 \text{ M}}{0.1 \text{ M}}} \right) \\
 &= (0.0417 \text{ M}^{-1} \text{ s}^{-1})(0.788) \\
 &= 0.0329 \text{ M}^{-1} \text{ s}^{-1}
 \end{aligned}$$

b) The time will double, assuming the k value is the same. Numerically checking this expectation:

$$\begin{aligned}
 t &= \frac{1}{k([B]_0 - [A]_0)} \ln \left(\frac{[B]}{[B]_0} \right) \\
 &= \frac{1}{(0.0329 \text{ M}^{-1} \text{ s}^{-1})(0.25 \text{ M} - 0.05 \text{ M})} \ln \left(\frac{0.22 \text{ M}}{0.25 \text{ M}} \right) \\
 &= (152 \text{ s})(0.788) \\
 &= 120 \text{ s}
 \end{aligned}$$

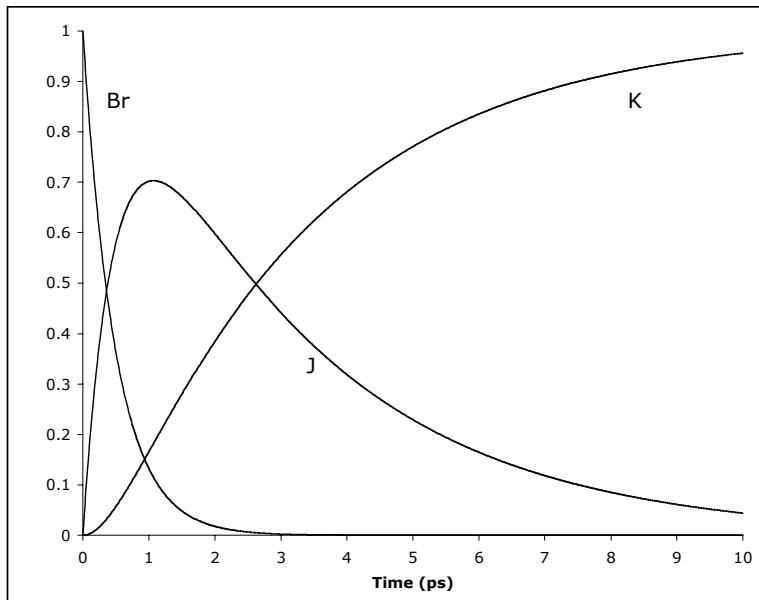
P36.22) Bacteriorhodopsin is a protein found in *Halobacterium halobium* that converts light energy into a transmembrane proton gradient that is used for ATP synthesis. After light is absorbed by the protein, the following initial reaction sequence occurs:



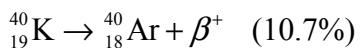
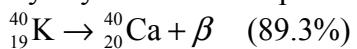
- a) At what time will the maximum concentration of the intermediate J occur?
 b) Construct plots of the concentration of each species versus time.

$$\begin{aligned}
 a) \quad t_{\max} &= \frac{1}{k_1 - k_2} \ln \left(\frac{k_1}{k_2} \right) \\
 &= \frac{1}{(2.0 \times 10^{12} \text{ s}^{-1}) - (3.3 \times 10^{11} \text{ s}^{-1})} \ln \left(\frac{2.0 \times 10^{12}}{3.3 \times 10^{11}} \right) \\
 &= (5.99 \times 10^{-13} \text{ s}^{-1})(1.80) \\
 &= 1.08 \times 10^{-12} \text{ s} = 1.08 \text{ ps}
 \end{aligned}$$

- b) First, using the expressions for a sequential reaction, the concentration profiles for Br, J, and K were determined using Excel as shown below:



P36.23) Bananas are somewhat radioactive due to the presence of substantial amounts of potassium. Potassium-40 decays by two different paths:



The half-life for potassium decay is 1.3×10^9 years. Determine the rate constants for the individual channels.

Since this is a branching reaction, we define k_1 as the rate constant for the Ca production, and k_2 as the rate constant for Ar production. Finally, the rate constant for K decay is equal to the sum of k_1 and k_2 so that:

$$k = k_1 + k_2 \quad \text{and} \quad \frac{[\text{Ca}]}{[\text{Ar}]} = \frac{k_1}{k_2}$$

Using the definition of the half-life, k is determined as follows:

$$k = \frac{\ln 2}{1.3 \times 10^9 \text{ yr}} = 5.33 \times 10^{-10} \text{ yr}^{-1}$$

Now $k = k_1 + k_2$ where $k_1 = \left(\frac{[\text{Ca}]}{[\text{Ar}]} \right) k_2$, $k_2 = \left(\frac{0.893}{0.107} \right) k_2$, $k_2 = 8.345 k_2$. Substituting this result into the expression for k yields:

$$k = k_1 + k_2$$

$$5.33 \times 10^{-10} \text{ yr}^{-1} = 8.345 k_2 + k_2$$

$$k_2 = \frac{5.33 \times 10^{-10} \text{ yr}^{-1}}{9.345}$$

$$k_2 = 5.70 \times 10^{-11} \text{ yr}^{-1}$$

$$k_1 = 4.76 \times 10^{-10} \text{ yr}^{-1}$$

P36.24) In the stratosphere, the rate constant for the conversion of ozone to molecular oxygen by atomic chlorine is $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$ $[(k = 1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})e^{-260K/T}]$.

a) What is the rate of this reaction at 20 km where $[\text{Cl}] = 5 \times 10^{-17} \text{ M}$, $[\text{O}_3] = 8 \times 10^{-9} \text{ M}$, and $T = 220 \text{ K}$?

b) The actual concentrations at 45 km are $[\text{Cl}] = 3 \times 10^{-15} \text{ M}$ and $[\text{O}_3] = 8 \times 10^{-11} \text{ M}$. What is the rate of the reaction at this altitude where $T = 270 \text{ K}$?

c) (Optional) Given the concentrations in part (a), what would you expect the concentrations at 45 km to be assuming that the gravity represents the operative force defining the potential energy?

a) Based on the units of k , the reaction is second order overall so that the rate law expression is:

$$\text{Rate} = k[\text{Cl}][\text{O}_3]$$

For $[\text{Cl}] = 5 \times 10^{-17} \text{ M}$, $[\text{O}_3] = 8 \times 10^{-9} \text{ M}$, and $T = 220 \text{ K}$

$$k = 1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} e^{-260K/220K}$$

$$k = 5.21 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

$$\begin{aligned} \text{Rate} &= 5.21 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} (5 \times 10^{-17} \text{ M})(8 \times 10^{-9} \text{ M}) \\ &= 2.08 \times 10^{-15} \text{ M s}^{-1} \end{aligned}$$

b) $[\text{Cl}] = 3 \times 10^{-15} \text{ M}$ $[\text{O}_3] = 8 \times 10^{-11} \text{ M}$ $T = 270 \text{ K}$

$$k = 1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} e^{-260K/270K}$$

$$k = 6.49 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

$$\begin{aligned} \text{Rate} &= 6.49 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} (3 \times 10^{-15} \text{ M})(8 \times 10^{-11} \text{ M}) \\ &= 1.56 \times 10^{-15} \text{ M s}^{-1} \end{aligned}$$

b) The ratio of pressures at two altitudes is given by:

$$\frac{[]_1}{[]_2} = e^{-\frac{mg(h_1 - h_2)}{kT}}$$

Using this expression to determine the difference in concentration for Cl at 45 versus 20 km yields:

$$\frac{[Cl]_{45}}{[Cl]_{20}} = e^{-\frac{(0.035 \text{ kg mol}^{-1}) \left(\frac{1}{N_A}\right) (9.80 \text{ m s}^{-2}) (2.5 \times 10^4 \text{ km})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(270 \text{ K})}} = 0.0219$$

$$[Cl]_{45} = (5 \times 10^{-17} \text{ M})(0.0219) = 1.10 \times 10^{-18} \text{ M}$$

Performing the same calculation for O₃:

$$\frac{[O_3]_{45}}{[O_3]_{20}} = e^{-\frac{(0.048 \text{ kg mol}^{-1}) \left(\frac{1}{N_A}\right) (9.80 \text{ m s}^{-2}) (2.5 \times 10^4 \text{ km})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(270 \text{ K})}} = 0.0053$$

$$[O_3]_{45} = (8 \times 10^{-9} \text{ M})(0.0053) = 4.24 \times 10^{-11} \text{ M}$$

Finally, the rate is:

$$\begin{aligned} \text{Rate} &= 6.49 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} (1.10 \times 10^{-18} \text{ M})(4.24 \times 10^{-11} \text{ M}) \\ &= 3.03 \times 10^{-19} \text{ M s}^{-1} \end{aligned}$$

Notice that since this simple model for the concentration dependence versus altitude significantly underestimates the concentration of Cl, the rate of ozone depletion by reaction with Cl is also significantly underestimated.

P36.25) An experiment is performed on the branching reaction depicted in the text. Two things are determined: (1) The yield for B at a given temperature is found to be 0.3 and (2) the rate constants are described well by an Arrhenius expression with the activation to B and C formation being 27 and 34 kJ mol⁻¹, respectively, and with identical preexponential factors. Demonstrate that these two statements are inconsistent with each other.

The yield for B is given as

$$\Phi_B = \frac{k_B}{k_B + k_C} = 0.3$$

or

$$k_B = 0.3(k_B + k_C)$$

$$\frac{k_B}{k_C} = \frac{0.3}{0.7} k_C$$

$$\frac{k_B}{k_C} = 0.429$$

Next, the ratio of rate constants is given by:

$$\frac{k_B}{k_C} = \frac{A e^{-27 \text{ kJ mol}^{-1}/RT}}{A e^{-34 \text{ kJ mol}^{-1}/RT}}$$

$$\frac{k_B}{k_C} = e^{\frac{7 \text{ kJ mol}^{-1}}{RT}}$$

Setting the rate constant ratios equal and solving for temperature:

$$e^{\frac{7 \text{ kJ mol}^{-1}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})T}} = 0.429$$

$$\frac{7 \text{ kJ mol}^{-1}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})T} = -0.846$$

$$-995 \text{ K} = T$$

Since absolute temperature can not be a negative quantity, the two statements are inconsistent.

P36.26) A standard “rule of thumb” for thermally activated reactions is that the reaction rate doubles for every 10 K increase in temperature. Is this statement true independent of the activation energy (assuming that the activation energy is positive and independent of temperature)?

The analysis is best performed numerically

$$\frac{k_2}{k_1} = \frac{e^{-E_a/RT_2}}{e^{-E_a/RT_1}} = e^{-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

T ₁ (K)	T ₂ (K)	E _a (J mol ⁻¹)	$\frac{k_2}{k_1}$
100	110	50,000	236
300	310	50,000	1.91
1000	1010	50,000	1.06
300	310	500,000	6.43
300	310	5,000	1.06

Inspection of the table demonstrates that the rule is only valid for temperatures around room temperature, and moderate E_a values (~50,000 – 70,000 J mol⁻¹).

P36.27) Calculate the ratio of rate constants for two thermal reactions that have the same Arrhenius preexponential term, but with activation energies that differ by 1, 10, and 30 kJ/mol.

a) $E_a' = E_a + 1 \text{ kJ mol}^{-1}$

$$\frac{k'}{k} = \frac{Ae^{-(E_a+1 \text{ kJ mol}^{-1})/RT}}{Ae^{-E_a/RT}}$$

$$\frac{k'}{k} = \frac{e^{-E_a/RT} e^{-1 \text{ kJ mol}^{-1}/RT}}{e^{-E_a RT}}$$

$$\frac{k'}{k} = e^{-1 \text{ kJ mol}^{-1}/RT}$$

b) $E_a' = E_a + 10$

$$\frac{k'}{k} = \frac{Ae^{-(E_a+10 \text{ kJ mol}^{-1})/RT}}{Ae^{-E_a/RT}}$$

$$\frac{k'}{k} = \frac{e^{-E_a/RT} e^{-10 \text{ kJ mol}^{-1}/RT}}{e^{-E_a RT}}$$

$$\frac{k'}{k} = e^{-10 \text{ kJ mol}^{-1}/RT}$$

c) $E_a' = E_a + 30$

$$\frac{k'}{k} = \frac{Ae^{-(E_a+30 \text{ kJ mol}^{-1})/RT}}{Ae^{-E_a/RT}}$$

$$\frac{k'}{k} = \frac{e^{-E_a/RT} e^{-30 \text{ kJ mol}^{-1}/RT}}{e^{-E_a RT}}$$

$$\frac{k'}{k} = e^{-30 \text{ kJ mol}^{-1}/RT}$$

P36.28) The rate constant for the reaction of hydrogen with iodine is $2.45 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ at 302°C and $0.950 \text{ M}^{-1} \text{ s}^{-1}$ at 508°C .

- Calculate the activation energy and Arrhenius preexponential factor for this reaction.
- What is the value of the rate constant at 400°C ?

a)

$$k(575 \text{ K}) = 2.45 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$$

$$k(781 \text{ K}) = 0.950 \text{ M}^{-1}\text{s}^{-1}$$

$$2.45 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1} = A e^{-E_a/(8.314 \text{ J mol}^{-1}\text{K}^{-1})(575 \text{ K})}$$

$$2.45 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1} = A e^{-E_a/4781 \text{ J mol}^{-1}}$$

$$0.950 \text{ M}^{-1} \text{ s}^{-1} = A e^{-E_a/(8.314 \text{ J mol}^{-1}\text{K}^{-1})(781 \text{ K})}$$

$$0.950 \text{ M}^{-1} \text{ s}^{-1} = A e^{-E_a/6494 \text{ J mol}^{-1}}$$

Taking the ratio of the two rates yields the following for the activation energy:

$$\frac{2.45 \times 10^{-4}}{0.950} = 2.58 \times 10^{-4} = \frac{e^{-\frac{E_a}{4781 \text{ J mol}^{-1}}}}{e^{-\frac{E_a}{6494 \text{ J mol}^{-1}}}} = e^{-E_a \left(\frac{1}{4781 \text{ J mol}^{-1}} - \frac{1}{6494 \text{ J mol}^{-1}} \right)}$$

$$\ln(2.58 \times 10^{-4}) = -E_a \left(\frac{1}{4781 \text{ J mol}^{-1}} - \frac{1}{6494 \text{ J mol}^{-1}} \right) = -E_a (5.52 \times 10^{-5} \text{ J}^{-1} \text{ mol})$$

$$E_a = 1.50 \times 10^5 \text{ J mol}^{-1}$$

Using the activation energy, the pre-exponential factor is determined as follows:

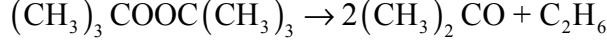
$$A = (0.950 \text{ M}^{-1}\text{s}^{-1}) e^{1.50 \times 10^5 \text{ J mol}^{-1}/(8.314 \text{ J mol}^{-1}\text{K}^{-1})(781 \text{ K})}$$

$$A = 1.02 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$

b)

$$\begin{aligned} k_{673 \text{ K}} &= (1.02 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}) e^{-1.50 \times 10^5 \text{ J mol}^{-1}/(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(673 \text{ K})} \\ &= (1.02 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}) (2.30 \times 10^{-12}) \\ &= 0.0234 \text{ M}^{-1} \text{ s}^{-1} \end{aligned}$$

P36.29) Consider the thermal decomposition of 1 atm of $(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3$ to acetone ($\text{CH}_3)_2\text{CO}$ and ethane (C_2H_6), which occurs with a rate constant of 0.0019 s^{-1} . After initiation of the reaction, at what time would you expect the pressure to be 1.8 atm?



The stoichiometry of the reaction is such that for every reactant molecule that decays (x), two acetone ($2x$) and one ethane (x) are produced. Using this, the extent of reactant decomposition when the pressure is 1.8 atm can be determined as follows:

$$1.8 \text{ atm} = (1 \text{ atm} - x) + 2x + x$$

$$1.8 \text{ atm} = 1 \text{ atm} + 2x$$

$$x = 0.4 \text{ atm}$$

$$\text{Thus, } P_{\text{reactant}} = 1 \text{ atm} - 0.4 \text{ atm} = 0.6 \text{ atm}$$

Using the integrated rate law expression for a first-order reaction (as indicated by the units of the rate constant), the time is determined as follows:

$$[\text{Reactant}] = [\text{Reactant}]_0 e^{-kt}$$

$$(0.6 \text{ atm}) = (1 \text{ atm}) e^{-(1.9 \times 10^{-3} \text{ s}^{-1})t}$$

$$0.6 = e^{-(1.9 \times 10^{-3} \text{ s}^{-1})t}$$

$$\frac{\ln(0.6)}{-1.9 \times 10^{-3} \text{ s}^{-1}} = t$$

$$269 \text{ s} = t$$

P36.30) At 552.3 K, the rate constant for the thermal decomposition of SO_2Cl_2 is $1.02 \times 10^{-6} \text{ s}^{-1}$. If the activation energy is 210 kJ mol $^{-1}$, calculate the Arrhenius preexponential factor and determine the rate constant at 600 K.

$$k_{552.3 \text{ K}} = 1.02 \times 10^{-6} \text{ s}^{-1} \quad E_a = 210 \text{ kJ mol}^{-1}$$

$$1.02 \times 10^{-6} \text{ s}^{-1} = Ae^{-2.10 \times 10^5 \text{ J mol}^{-1}/(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(552.3 \text{ K})}$$

$$A = (1.02 \times 10^{-6} \text{ s}^{-1}) e^{2.10 \times 10^5 \text{ J mol}^{-1}/(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(552.3 \text{ K})}$$

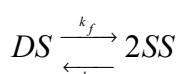
$$A = 7.38 \times 10^{13} \text{ s}^{-1}$$

$$k_{600 \text{ K}} = (7.38 \times 10^{13} \text{ s}^{-1}) e^{-2.10 \times 10^5 \text{ J mol}^{-1}/(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(600 \text{ K})}$$

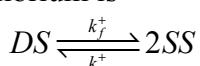
$$= (7.38 \times 10^{13} \text{ s}^{-1})(5.23 \times 10^{-19})$$

$$= 3.86 \times 10^{-5} \text{ s}^{-1}$$

P36.31) The melting of double-strand DNA into two single strands can be initiated using temperature-jump methods. Derive the expression for the T-jump relaxation time for the following equilibrium involving double-strand (DS) and single-strand (SS) DNA:



After the temperature jump, the equilibrium is



The rate law expression at equilibrium is:

$$\frac{d[DS]_{eq}}{dt} = 0 = -k_f^+ [DS]_{eq} + k_r^+ [SS]_{eq}^2$$

$$k_f^+ [DS]_{eq} = k_r^+ [SS]_{eq}^2$$

The adjusted equilibrium can be expressed in terms of the concentration shift, ξ , $[A] - \xi = [A]_{eg}$ and $[B] + 2\xi = [B]_{eg}$.

As in the text, the differential rate expression with respect to the concentration shift is:

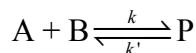
$$\begin{aligned}\frac{d\xi}{dt} &= -k_f^+ [DS]_{eq} + k_r^+ [SS]_{eq}^2 \\ &= -k_f^+ ([DS]_{eq} + \xi) + k_r^+ ([SS]_{eq} - 2\xi)^2 \\ &= -k_f^+ [DS]_{eq} + k_r^+ [SS]_{eq}^2 - k_f^+ \xi - 4k_r^+ [SS]_{eq} \xi + 4k_r^+ \xi^2 \\ &= -\xi (k_f^+ + 4k_r^+ [SS]_{eq})\end{aligned}$$

where we have ignored terms on the order of ξ^2 . Integration of the first-order differential equation suggests the following definition for the relaxation time:

$$\tau = (k_f^+ + 4k_r^+ [SS]_{eq})^{-1}$$

P36.32) Consider the reaction $A + B \xrightleftharpoons[k]{k'} P$. A temperature-jump experiment is

performed where the relaxation time constant is measured to be $310 \mu\text{s}$, resulting in an equilibrium where $K_{eq} = 0.7$ with $[P]_{eq} = 0.2 \text{ M}$. What are k and k' ? (Watch the units!)



$$\tau = 310 \times 10^{-6} \text{ s} \quad K_{eg} = 0.7 \quad [P]_{eg} = 0.2 \text{ M}$$

Assuming the following rate law,

$$\frac{d[A]}{dt} = -k^+ [A][B] + k'^+ [P] = 0,$$

The post-jump equilibrium concentrations with respect to the initial concentrations and concentration shift are:

$$[A] - \xi = [A]_{eq}$$

$$[B] - \xi = [B]_{eq}$$

$$[P] + \xi = [P]_{eq}$$

Therefore, the differential rate expression for the concentration shift, ξ , is:

$$\frac{d\xi}{dt} = -k^+ ([A]_{eq} + \xi) ([B]_{eq} + \xi) + k'^+ ([P]_{eq} - \xi)$$

$$\begin{aligned}\frac{d\xi}{dt} &= -\xi \left(k^+ [A]_{eq} + k^+ [B]_{eq} + k^+ \xi + k^{+'} \right) \\ &= -\xi \left(k^+ ([A]_{eq} + k^+ [B]_{eq}) + k^{+'} \right) + O(\xi^2)\end{aligned}$$

Ignoring terms on the order ξ^2 , the relaxation time is:

$$\tau = \left[k^+ ([A]_{eq} + k^+ [B]_{eq}) + k^{+'} \right]^{-1}$$

Next, the equilibrium constant is given by:

$$K = \frac{k^+}{k^{+'}} = \frac{[P]_{eq}}{[A]_{eq} [B]_{eq}} = 0.7$$

If we assume that $[A]_o = [B]_o$ then $[A]_{eg} = [B]_{eg}$ and

$$0.7 = \frac{0.2 \text{ M}}{x^2} \Rightarrow x = 0.535 \text{ M} = [A]_{eq} = [B]_{eq}$$

And using the expression for K , we know that $k^+ = 0.7 k^{+'}$. Use these last two results in the expression for the relaxation time yields:

$$310 \times 10^{-6} \text{ s} = \frac{1}{k^+ (0.535 + 0.535) + k^{+'}}$$

$$310 \times 10^{-6} \text{ s} = \frac{1}{(0.7k^{+'})(1.070) + k^{+'}}$$

$$310 \times 10^{-6} \text{ s} = \frac{1}{k^{+'}(1.749)}$$

$$k^{+'} = 1845 \text{ s}^{-1}$$

$$k^+ = 0.7k^{+'} = 1291 \text{ M}^{-1} \text{ s}^{-1}$$

The units of the rate constants are consistent with the forward reaction being second order, and the reverse reaction being first order.

P36.33) The unimolecular decomposition of urea in aqueous solution is measured at two different temperatures and the following data are observed:

Trial Number	Temperature (°C)	$k (\text{s}^{-1})$
1	60.0	1.2×10^{-7}
2	71.5	4.40×10^{-7}

- a) Determine the Arrhenius parameters for this reaction.
- b) Using these parameters, determine ΔH^\ddagger and ΔS^\ddagger as described by the Eyring equation.
- c) The activation energy is determined by taking the ratio of the rate constants as described by the Arrhenius expression.

Chapter 36/Elementary Chemical Kinetics

$$\frac{k_1}{k_2} = \frac{Ae^{-\frac{E_a}{RT_1}}}{Ae^{-\frac{E_a}{RT_1}}} = e^{-\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$\frac{1.2 \times 10^{-7}}{4.40 \times 10^{-7}} = e^{-\frac{E_a}{R}\left(\frac{1}{333 \text{ K}} - \frac{1}{345 \text{ K}}\right)}$$

$$0.273 = e^{-E_a(1.20 \times 10^{-5} \text{ J}^{-1} \text{ mol})}$$

$$1.30 = E_a(1.20 \times 10^{-5} \text{ J}^{-1} \text{ mol})$$

$$108 \text{ kJ mol}^{-1} = E_a$$

Using the activation energy and the rate constant for the first trial, the pre-exponential factor is:

$$1.2 \times 10^{-7} \text{ s}^{-1} = Ae^{-\frac{1.08 \times 10^5 \text{ J mol}^{-1}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(333 \text{ K})}}$$

$$1.2 \times 10^{-7} \text{ s}^{-1} = A(1.14 \times 10^{-17})$$

$$1.05 \times 10^{10} \text{ s}^{-1} = A$$

For a unimolecular reaction in solution:

$$A = \frac{ek_B T}{h} e^{\frac{\Delta S^\ddagger}{R}}$$

$$1.05 \times 10^{10} \text{ s}^{-1} = \frac{(2.303)(1.38 \times 10^{-23} \text{ J K}^{-1})(333 \text{ K})}{(6.626 \times 10^{-34} \text{ J s})} e^{\frac{\Delta S^\ddagger}{R}}$$

$$1.05 \times 10^{10} \text{ s}^{-1} = (1.60 \times 10^{13} \text{ s}^{-1}) e^{\frac{\Delta S^\ddagger}{R}}$$

$$6.56 \times 10^{-4} = e^{\frac{\Delta S^\ddagger}{R}}$$

$$-7.32 = \frac{\Delta S^\ddagger}{R}$$

$$\Delta S^\ddagger = -60.8 \text{ J mol K}^{-1}$$

Furthermore:

$$E_a = \Delta H^\ddagger + RT$$

$$\Delta H^\ddagger = E_a - RT = 108 \text{ kJ mol}^{-1} - (8.314 \text{ J mol}^{-1} \text{ K}^{-1})(333 \text{ K}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right)$$

$$= 105.2 \text{ kJ mol}^{-1}$$

P36.34) The gas-phase decomposition of ethyl bromide is a first-order reaction, occurring with a rate constant that demonstrates the following dependence on temperature:

Trial Number	Temperature (K)	$k \text{ (s}^{-1}\text{)}$
1	800	0.036
2	900	1.410

- a) Determine the Arrhenius parameters for this reaction.
 b) Using these parameters, determine ΔH^\ddagger and ΔS^\ddagger as described by the Eyring equation.

a) The activation energy is determined by taking the ratio of the rate constants as described by the Arrhenius expression.

$$\frac{k_1}{k_2} = \frac{Ae^{\frac{-E_a}{RT_1}}}{Ae^{\frac{-E_a}{RT_2}}} = e^{\frac{-E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)}$$

$$\frac{0.036}{1.410} = e^{\frac{-E_a}{R} \left(\frac{1}{800 \text{ K}} - \frac{1}{900 \text{ K}} \right)}$$

$$0.0255 = e^{-E_a (1.67 \times 10^{-5} \text{ J}^{-1} \text{ mol})}$$

$$3.67 = E_a (1.67 \times 10^{-5} \text{ J}^{-1} \text{ mol})$$

$$219 \text{ kJ mol}^{-1} = E_a$$

Using the activation energy and the rate constant for the first trial, the pre-exponential factor is:

$$0.036 \text{ s}^{-1} = Ae^{\frac{2.19 \times 10^5 \text{ J mol}^{-1}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(800 \text{ K})}}$$

$$0.036 \text{ s}^{-1} = A (5.00 \times 10^{-15})$$

$$7.20 \times 10^{12} \text{ s}^{-1} = A$$

b) For a unimolecular reaction in solution:

$$A = \frac{ek_B T}{h} e^{\frac{\Delta S^\ddagger}{R}}$$

$$7.20 \times 10^{12} \text{ s}^{-1} = \frac{(2.303)(1.38 \times 10^{-23} \text{ J K}^{-1})(800 \text{ K})}{(6.626 \times 10^{-34} \text{ J s})} e^{\frac{\Delta S^\ddagger}{R}}$$

$$7.20 \times 10^{12} \text{ s}^{-1} = (3.84 \times 10^{13} \text{ s}^{-1}) e^{\frac{\Delta S^\ddagger}{R}}$$

$$0.188 = e^{\frac{\Delta S^\ddagger}{R}}$$

$$-1.67 = \frac{\Delta S^\ddagger}{R}$$

$$\Delta S^\ddagger = -14.0 \text{ J mol K}^{-1}$$

Furthermore:

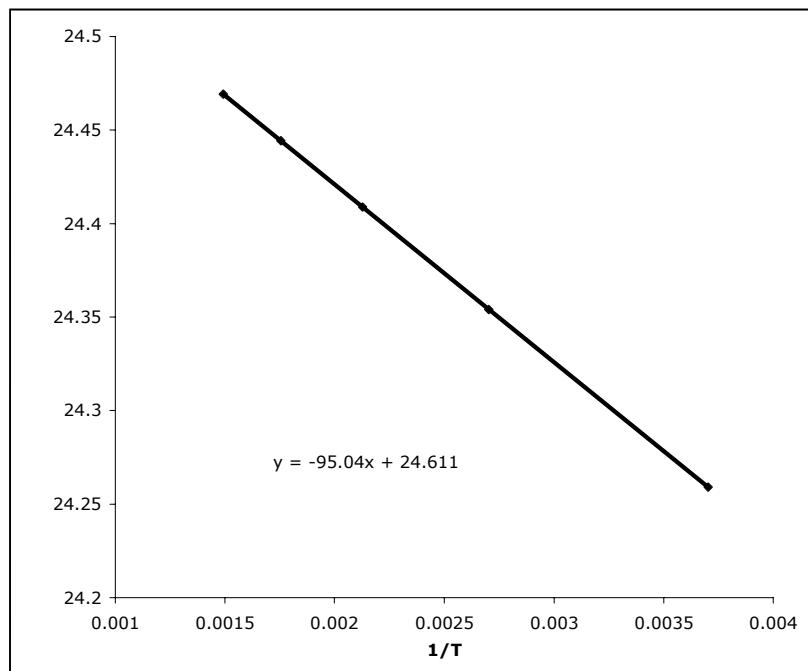
$$E_a = \Delta H^\ddagger + RT$$

$$\begin{aligned}\Delta H^\ddagger &= E_a - RT = 219 \text{ kJ mol}^{-1} - (8.314 \text{ J mol}^{-1} \text{ K}^{-1})(800 \text{ K})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \\ &= 212.4 \text{ kJ mol}^{-1}\end{aligned}$$

P36.35) Hydrogen abstraction from hydrocarbons by atomic chlorine is a mechanism for Cl loss in the stratosphere. Consider the reaction of Cl with ethane: $\text{C}_2\text{H}_6(g) + \text{Cl}(g) \longrightarrow \text{C}_2\text{H}_5(g) + \text{HCl}(g)$. This reaction was studied in the laboratory, and the following data was obtained.

$T(\text{K})$	$10^{-10} k (\text{M}^{-2}\text{s}^{-1})$
270	3.43
370	3.77
470	3.99
570	4.13
670	4.23

- a) Determine the Arrhenius parameters for this reaction.
 - b) At the tropopause (the boundary between the troposphere and stratosphere located approximately 11 km above the surface of the Earth), the temperature is roughly 220 K. What do you expect the rate constant to be at this temperature?
 - c) Using the Arrhenius parameters obtained in part (a), determine the Eyring parameters ΔH^\ddagger and ΔS^\ddagger for this reaction.
- a) A plot of $\ln k$ versus T^{-1} should yield a straight line if the Arrhenius expression is a valid description of the temperature dependence of the rate constant. This plot is given below:



The slope of the line yields the activation energy:

$$-\frac{E_a}{R} = \text{slope}$$

$$\begin{aligned} E_a &= -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(-95.04 \text{ K}) \\ &= 790 \text{ J mol}^{-1} \end{aligned}$$

And the y -intercept of the graph yields $\ln(A)$:

$$y - \text{int} = \ln(A)$$

$$e^{24.611} = A$$

$$A = 4.88 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$

b)

$$k = A e^{-E_a/RT}$$

$$\begin{aligned} &= (4.88 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}) \exp^{\frac{-790 \text{ J mol}^{-1}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(220 \text{ K})}} \\ &= (4.88 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})(0.649) \\ &= 3.17 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \end{aligned}$$

c) For a second order gas phase reaction:

$$\begin{aligned}
 E_a &= \Delta H^\ddagger + 2RT \\
 \Delta H^\ddagger &= E_a - 2RT \\
 &= 790 \text{ J mol}^{-1} - 2(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(220 \text{ K}) \\
 &= -2.87 \text{ kJ mol}^{-1} \\
 A &= \frac{e^2 k_B T}{hc^\circ} e^{\Delta S^\ddagger / R} \\
 \Delta S^\ddagger &= R \ln \left(\frac{A h c^\circ}{e^2 k T} \right) \\
 &= (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln \left(\frac{(3.17 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})(6.626 \times 10^{-34} \text{ J s})(1 \text{ M})}{e^2 (1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})} \right) \\
 &= -57.8 \text{ J mol}^{-1} \text{ K}^{-1}
 \end{aligned}$$

P36.36) Consider the “unimolecular” isomerization of methylcyanide, a reaction that will be discussed in detail in the subsequent chapter:



The Arrhenius parameters for this reaction are $A = 2.5 \times 10^{16} \text{ s}^{-1}$ and $E_a = 272 \text{ kJ mol}^{-1}$. Determine the Eyring parameters ΔH^\ddagger and ΔS^\ddagger for this reaction with $T = 300 \text{ K}$.

For a unimolecular gas phase reaction

$$\begin{aligned}
 E_a &= \Delta H^\ddagger + RT \\
 \Delta H^\ddagger &= 272 \times 10^3 \text{ J mol}^{-1} - (8.314 \text{ J mol}^{-1} \text{ K}^{-1})(300 \text{ K}) \\
 &= 272 \times 10^3 \text{ J mol}^{-1} - 2.49 \times 10^3 \text{ J mol}^{-1} \\
 &= 269.5 \times 10^3 \text{ J mol}^{-1} \\
 A &= \frac{ek_B T}{h} e^{\Delta S^\ddagger / R} \\
 \Delta S^\ddagger &= R \ln \left(\frac{Ah}{ek_B T} \right) \\
 &= 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \ln \left(\frac{(2.5 \times 10^{16} \text{ s}^{-1})(6.626 \times 10^{-34} \text{ J s})}{e(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})} \right) \\
 &= (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln(1737) \\
 &= 62.0 \text{ J mol}^{-1} \text{ K}^{-1}
 \end{aligned}$$

P36.37) Reactions involving hydroxyl radical (OH) are extremely important in atmospheric chemistry. The reaction of hydroxyl radical with molecular hydrogen is as follows:



Determine the Eyring parameters ΔH^\ddagger and ΔS^\ddagger for this reaction where $A = 8 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1}$ and $E_a = 42 \text{ kJ mol}^{-1}$.

$$E_a = \Delta H^\ddagger + 2RT$$

$$\Delta H^\ddagger = E_a - 2RT$$

$$= 4.2 \times 10^4 \text{ J mol}^{-1} - 2(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(300 \text{ K})$$

$$= 3.7 \times 10^4 \text{ J mol}^{-1} = 37 \text{ kJ mol}^{-1}$$

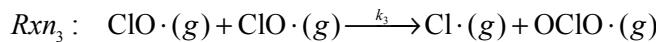
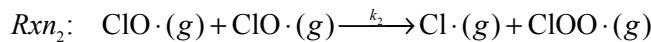
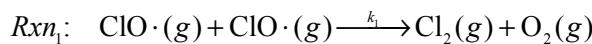
$$A = \frac{e^2 k_B T}{hc^\circ} e^{\Delta S^\ddagger / R}$$

$$\Delta S^\ddagger = R \ln\left(\frac{A h c^\circ}{e^2 k T}\right)$$

$$= (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln\left(\frac{(8 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1})(6.626 \times 10^{-34} \text{ J s})(1 \text{ M})}{e^2 (1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}\right)$$

$$= 7.33 \text{ J mol}^{-1} \text{ K}^{-1}$$

P36.38) Chlorine monoxide (ClO) demonstrates three bimolecular self-reactions:



The following table provides the Arrhenius parameters for this reaction:

	$A (\text{M}^{-1} \text{ s}^{-1})$	$E_a (\text{kJ/mol})$
Rxn_1	6.08×10^8	13.2
Rxn_2	1.79×10^{10}	20.4
Rxn_3	2.11×10^8	11.4

a) For which reaction is ΔH^\ddagger greatest and by how much relative to the next closest reaction?

b) For which reaction is ΔS^\ddagger the smallest and by how much relative to the next closest reaction?

a) These are all bimolecular gas phase reactions; therefore, the relationship between ΔH^\ddagger and E_a is equivalent. Since each ΔH^\ddagger depends linearly on the T and E_a , at the same T, the largest E_a corresponds to the largest ΔH^\ddagger . Therefore, Rxn₂ will have the largest ΔH^\ddagger by 7.2 kJ mol^{-1} relative to Rxn₁.

b) ΔS^\ddagger depends linearly on $\ln A$; therefore, the smallest ΔS^\ddagger corresponds to the reaction with the smallest A, or Rxn₃. The next smallest ΔS^\ddagger is Rxn₁, and the difference is:

$$\ln(6.08 \times 10^8) - \ln(2.11 \times 10^8) = \ln\left(\frac{6.08}{2.11}\right) = \ln(2.88) = 1.06$$

Chapter 37: Complex Reaction Mechanisms

Questions on Concepts

Q37.1) How is a simple reaction different from a complex reaction?

A simple reaction is any reaction that consists of the single reaction step. A complex reaction is any reaction that occurs in two or more elementary steps.

Q37.2) For a reaction mechanism to be considered correct, what property must it demonstrate?

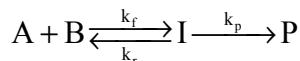
In order to be valid, a proposed reaction mechanism must agree with the experimentally determined rate law.

Q37.3) What is a reaction intermediate? Can an intermediate be present in the rate law expression for the overall reaction?

A reaction intermediate is a chemical species that is formed during the course of a reaction, but decays as the reaction proceeds resulting in product formation. The reaction intermediates must be consumed prior to the completion of the reaction, therefore reaction intermediates will not appear in the overall reaction expression.

Q37.4) What is the preequilibrium approximation, and under what conditions is it considered valid?

The pre-equilibrium approximation is somewhat related to the steady state approximation. The pre-equilibrium approximation assumes a complex reaction of the form



The principle assumption of the pre-equilibrium approximation is that equilibrium is established between reactants A, B and the intermediate species I. I then undergoes reaction to form the product P. This approximation is valid when the reaction rate for the decomposition of I into A and B is much faster than the decomposition of I into P (in other words, $k_f \gg k_p$).

Q37.5) What is the one main assumption in the Lindemann mechanism for unimolecular reactions?

The principle assumption of the Lindemann reaction is that an activated complex is formed during the course of the reaction. This activated complex can then

deactivate resulting in reformation of the reactant, or it can decompose resulting in product formation. This activated complex assumption allows for the decomposition to be a linear function of the concentration of the activated reactant; therefore, the Lindemann mechanism is consistent with the experimentally determined unimolecularity of the reaction.

Q37.6) How is a catalyst defined, and how does such a species increase the reaction rate?

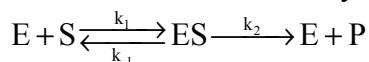
A catalyst is a chemical species that increases the rate of a chemical reaction without being consumed during the reaction. The catalyst serves to set up an additional reaction coordinate for which the activation energy is reduced relative to the uncatalyzed reaction.

Q37.7) What is an enzyme? What is the general mechanism describing enzyme catalysis?

An enzyme is essentially a biological catalyst. The "lock and key" model of enzyme activity is discussed in the text where the catalyst binds a substrate in a very specific location and orientation. Once the enzyme-substrate complex is formed, the product is produced and free enzyme is regenerated.

Q37.8) What is the Michaelis–Menten rate law? What is the maximum reaction rate predicated by this rate law?

The Michaelis-Menten mechanism that describes enzyme catalysis is as follows:



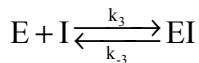
where E is the enzyme, S is the substrate, ES is the enzyme-substrate complex and P is the product. The Michaelis-Menten rate law is derived based on the assumption that the initial concentration of the substrate ($[S]_0$) is much greater than the initial concentration of the enzyme ($[E]_0$). The rate law is expressed as

$$R_0 = \frac{k_2 [S]_0 [E]_0}{[S]_0 + K_m}$$

where K_m is the Michaelis constant, which combines the rate constants.

Q37.9) How is the standard enzyme kinetic scheme modified to incorporate competitive inhibition? What plot is used to establish competitive inhibition and to determine the kinetic parameters associated with inhibition?

A competitive inhibitor is a molecule that structurally resembles the substrate of interest, but does not react. A competitive inhibitor binds to the active site of the enzyme. The kinetics is changed in that a third reaction step must be considered, the equilibrium of the docking of the inhibitor, expressed as



The consequence of competitive inhibition is a decreased reaction rate. As with the Michaelis-Menten kinetics, a modified Lineweaver-Burke plot is employed.

Q37.10) What is the difference between a homogeneous and a heterogeneous catalyst? For a homogeneous catalysis both the catalyst and the substrate exist in the same phase. Heterogeneous catalysis occurs when the catalyst and the substrate molecules exist in different phases.

Q37.11) What are the inherent assumptions in the Langmuir model of surface adsorption?

The Langmuir model arises from three assumptions,

- (1) Adsorption finishes once one monolayer of coverage results.
- (2) The surface is uniform and all adsorption sites are equivalent.
- (3) The occupancy of a site will not affect the adsorption or desorption processes in adjacent sites.

Q37.12) What is a radical? What elementary steps are involved in a reaction mechanism involving radicals?

Radicals are chemical species that contain an unpaired electron. The general mechanism for radical reactions involve three steps:

- (1) Initiation—the radical species is formed from a precursor.
- (2) Propagation—one radical species generates a second radical species, generally by abstraction of an atom or larger moiety.
- (3) Termination—the radical species eventually recombines with a second radical to form a non-radical species.

Q37.13) In what ways are radical polymerization reactions similar to radical reactions in general?

The radical polymerizations are very similar to the general radical reaction mechanisms in that they involve initiation, propagation, and termination steps.

Q37.14) What is photochemistry? How does one calculate the energy of a photon?

Photochemistry is the initiation of a chemical reaction through the absorption of energy in the form of a photon. The photon is a quantum particle of light with energy:

$$E_{\text{photon}} = h\nu$$

where h is Planck's constant and v is the frequency of the light.

Q37.15) What depopulation pathways occur from the first excited singlet state? For the first excited triplet state?

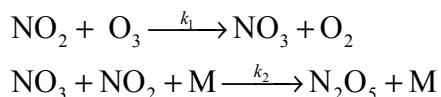
There are three main pathways for decay of the first excited singlet state: emitting a photon or fluorescence, non-radiative decay or internal conversion, and intersystem crossing to the triplet state. The first excited triplet state decays by emitting a photon or phosphorescence, and non-radiative decay or internal conversion.

Q37.16) What is the expected variation in excited state lifetime with quencher concentration in a Stern–Volmer plot?

The fluorescence lifetime is inversely proportional to the concentration of the quenching species. As the quencher concentration increases, the fluorescence lifetime decreases. The slope of the plot is the rate constant for quenching.

Problems

P37.1) A proposed mechanism for the formation of N_2O_5 from NO_2 and O_3 is



Determine the rate law expression for the production of N_2O_5 given this mechanism.

$$\begin{aligned}\frac{d[\text{N}_2\text{O}_5]}{dt} &= k_2 [\text{NO}_2][\text{NO}_3] \\ \frac{d[\text{NO}_3]}{dt} &= k_2 [\text{NO}_2][\text{O}_3] - k_2 [\text{NO}_2][\text{NO}_3]\end{aligned}$$

Applying the steady state approximation to the intermediate NO_3 and substituting back into the differential rate expression for N_2O_5 yields:

$$\frac{d[\text{NO}_3]}{dt} = 0 = k_1[\text{NO}_2][\text{O}_3] - k_2[\text{NO}_2][\text{NO}_3]$$

$$k_2[\text{NO}_2][\text{NO}_3] = k_1[\text{NO}_2][\text{O}_3]$$

$$[\text{NO}_3] = \frac{k_1}{k_2}[\text{O}_3]$$

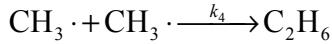
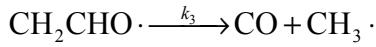
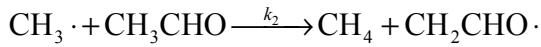
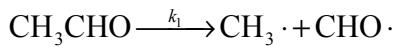
$$\frac{d[\text{N}_2\text{O}_5]}{dt} = k_2[\text{NO}_2][\text{NO}_3]$$

$$= k_2[\text{NO}_2]\left(\frac{k_1}{k_2}[\text{O}_3]\right)$$

$$= k_1[\text{NO}_2][\text{O}_3]$$

The mechanism predicts that the reaction is first order in NO_2 and O_3 , second order overall.

P37.2) The Rice-Herzfeld mechanism for the thermal decomposition of acetaldehyde (CH_3CO) is



Using the steady-state approximation, determine the rate of methane (CH_4) formation.

The differential rate expressions for methane and relevant intermediate species are:

$$\frac{d[\text{CH}_4]}{dt} = k_2[\text{CH}_3^-][\text{CH}_3\text{CHO}]$$

$$\frac{d[\text{CH}_2\text{CHO}]}{dt} = k_2[\text{CH}_3][\text{CH}_3\text{CHO}] - k_3[\text{CH}_2\text{CHO}]$$

$$\frac{d[\text{CH}_3]}{dt} = k_1[\text{CH}_3\text{CHO}] - k_2[\text{CH}_3][\text{CH}_3\text{CHO}] + k_3[\text{CH}_2\text{CHO}] - 2k_4[\text{CH}_3]^2$$

Applying the steady state approximation to the differential rate expressions for the intermediates:

$$\frac{d[\text{CH}_2\text{CHO}]}{dt} = \frac{d[\text{CH}_3]}{dt} = 0$$

or

$$0 = k_2 [\text{CH}_3][\text{CH}_3\text{CHO}] - k_3 [\text{CH}_2\text{CHO}]$$

$$0 = k_1 [\text{CH}_3\text{CHO}] - k_2 [\text{CH}_3][\text{CH}_3\text{CHO}] + k_3 [\text{CH}_2\text{CHO}] - 2k_4 [\text{CH}_3]^2$$

Adding the above two equations yields the following expression:

$$2k_4 [\text{CH}_3]^2 = k_1 [\text{CH}_3\text{CHO}]$$

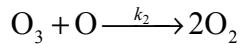
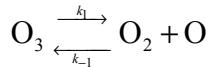
$$[\text{CH}_3] = \sqrt{\frac{k_1}{2k_4}} [\text{CH}_3\text{CHO}]^{1/2}$$

Substitution into the rate expression for $[\text{CH}_4]$ yields

$$\frac{d[\text{CH}_4]}{dt} = k_2 \left[\sqrt{\frac{k_1}{2k_4}} [\text{CH}_3\text{CHO}]^{1/2} \right] [\text{CH}_3\text{CHO}]$$

$$\frac{d[\text{CH}_4]}{dt} = k_{\text{eff}} [\text{CH}_3\text{CHO}]^{3/2} \quad \text{where } k_{\text{eff}} = k_2 \sqrt{\frac{k_1}{2k_4}}$$

P37.3) Consider the following mechanism for ozone thermal decomposition:



- a) Derive the rate law expression for the loss of O_3 .
- b) Under what conditions will the rate law expression for O_3 decomposition be first order with respect to O_3 ?

a)

$$\frac{d[\text{O}_3]}{dt} = -k_1 [\text{O}_3] + k_{-1} [\text{O}_2][\text{O}] - k_2 [\text{O}_3][\text{O}]$$

- b) Atomic oxygen is the intermediate species, and the differential rate expression for this species is:

$$\frac{d[\text{O}]}{dt} = k_1 [\text{O}_3] - k_{-1} [\text{O}_2][\text{O}] - k_2 [\text{O}_3][\text{O}]$$

Applying the steady-state approximation to the differential rate expression for O yields:

$$\frac{d[\text{O}]}{dt} = 0 = k_1[\text{O}_3] - k_{-1}[\text{O}_2][\text{O}] - k_2[\text{O}_3][\text{O}]$$

$$k_1[\text{O}_3] = k_{-1}[\text{O}_2][\text{O}] + k_2[\text{O}_3][\text{O}]$$

$$\frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} = [\text{O}]$$

Substituting this result into the differential rate expression for ozone yields:

$$\begin{aligned}\frac{d[\text{O}_3]}{dt} &= -k_1[\text{O}_3] + k_{-1}[\text{O}_2][\text{O}] - k_2[\text{O}_3][\text{O}] \\ &= -k_1[\text{O}_3] + [\text{O}](k_{-1}[\text{O}_2] - k_2[\text{O}_3]) \\ &= -k_1[\text{O}_3] + \left(\frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} \right) (k_{-1}[\text{O}_2] - k_2[\text{O}_3]) \\ &= -k_1[\text{O}_3] + \left(\frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} \right) (k_{-1}[\text{O}_2] - k_2[\text{O}_3]) \\ &= -k_1[\text{O}_3] \left(1 + \frac{-k_{-1}[\text{O}_2] + k_2[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} \right) \\ &= -k_1[\text{O}_3] \left(\frac{k_{-1}[\text{O}_2] + k_2[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} + \frac{-k_{-1}[\text{O}_2] + k_2[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} \right) \\ &= -\frac{2k_1k_2[\text{O}_3]^2}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]}\end{aligned}$$

if $k_2[\text{O}_3] \gg k_{-1}[\text{O}_2]$

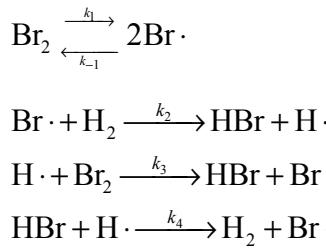
$$\frac{d[\text{O}_3]}{dt} = -2k_1[\text{O}_3]$$

P37.4) The hydrogen-bromine reaction corresponds to the production of HBr from H₂ and Br₂ as follows: H₂ + Br₂ ⇌ 2HBr. This reaction is famous for its complex rate law, determined by Bodenstein and Lind in 1906:

$$\frac{d[\text{HBr}]}{dt} = \frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1 + \frac{m[\text{HBr}]}{[\text{Br}_2]}}$$

where k and m are constants. It took 13 years for the correct mechanism of this reaction to be proposed, and this feat was accomplished simultaneously by Christiansen, Herzfeld, and Polanyi. The mechanism is as follows:

Chapter 37/Complex Reaction Mechanisms



Construct the rate law expression for the hydrogen-bromine reaction by performing the following steps:

- Write down the differential rate expression for [HBr].
- Write down the differential rate expressions for [Br] and [H].
- Because Br and H are reaction intermediates, apply the steady-state approximation to the result of part (b).
- Add the two equations from part (c) to determine [Br] in terms of [Br₂].
- Substitute the expression for [Br] back into the equation for [H] derived in part (c) and solve for [H].
- Substitute the expressions for [Br] and [H] determined in part (e) into the differential rate expression for [HBr] to derive the rate law expression for the reaction.

$$a) \frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{HBr}][\text{H}]$$

$$b) \frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - 2k_{-1}[\text{Br}]^2 - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{HBr}][\text{H}]$$

$$\frac{d[\text{H}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{HBr}][\text{H}]$$

- Applying the steady state approximation to [Br·] and [H·] and adding yields

$$0 = 2k_1[\text{Br}_2] - 2k_{-1}[\text{Br}]^2 - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{HBr}][\text{H}]$$

$$0 = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{HBr}][\text{H}]$$

d)

$$0 = 2k_1[\text{Br}_2] - 2k_{-1}[\text{Br}]^2$$

$$[\text{Br}] = \sqrt{\frac{k_1}{k_{-1}}} [\text{Br}_2]^{1/2}$$

e)



$$\frac{k_2 [\text{Br}][\text{H}_2]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} = [\text{H}]$$

$$\frac{k_2 \sqrt{\frac{k_1}{k_{-1}}} [\text{Br}_2]^{1/2} [\text{H}_2]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} = [\text{H}]$$

f) Now, substitution into (a) yields

$$\begin{aligned} \frac{d[\text{HBr}]}{dt} &= k_2 [\text{Br}][\text{H}_2] + k_3 [\text{H}][\text{Br}_2] - k_4 [\text{HBr}][\text{H}] \\ &= k_2 \sqrt{\frac{k_1}{k_{-1}}} [\text{Br}_2]^{1/2} [\text{H}_2] + \frac{k_3 k_2 \sqrt{\frac{k_1}{k_{-1}}} [\text{Br}_2]^{3/2} [\text{H}_2]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} - \frac{k_4 k_2 \sqrt{\frac{k_1}{k_{-1}}} [\text{Br}_2]^{1/2} [\text{H}_2][\text{HBr}]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} \\ &= k_2 \sqrt{\frac{k_1}{k_{-1}}} [\text{Br}_2]^{1/2} [\text{H}_2] \left(\frac{k_3 [\text{Br}_2] + k_4 [\text{HBr}]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} \right) + \frac{k_3 k_2 \sqrt{\frac{k_1}{k_{-1}}} [\text{Br}_2]^{3/2} [\text{H}_2]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} \\ &\quad - \frac{k_4 k_2 \sqrt{\frac{k_1}{k_{-1}}} [\text{Br}_2]^{1/2} [\text{H}_2][\text{HBr}]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} \\ &= \frac{2 k_3 k_2 \sqrt{\frac{k_1}{k_{-1}}} [\text{Br}_2]^{3/2} [\text{H}_2]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} \\ &= \frac{2 k_2 \sqrt{\frac{k_1}{k_{-1}}} [\text{Br}_2]^{1/2} [\text{H}_2]}{1 + \frac{k_4 [\text{HBr}]}{k_3 [\text{Br}_2]}} \end{aligned}$$

P37.5)

a) For the hydrogen-bromine reaction presented in Problem P37.4, imagine initiating the reaction with only Br_2 and H_2 present. Demonstrate that the rate law expression at $t = 0$ reduces to

$$\left(\frac{d[\text{HBr}]}{dt} \right)_{t=0} = 2 k_2 \left(\frac{k_1}{k_5} \right)^{1/2} [\text{H}_2]_0 [\text{Br}_2]_0^{1/2}$$

b) The activation energies for the rate constants are as follows:

Rate Constant	ΔE_a (kJ/mol)
k_1	192
k_2	0
k_5	74

What is the overall activation energy for this reaction?

c) How much will the rate of the reaction change if the temperature is increased to 400 K from 298 K?

a) At $t = 0$ $[Br_2] = [Br_2]_0$ $[H_2] = [H_2]_0$ $[HBr] = 0$
 Thus:

$$\left(\frac{d[HBr]}{dt} \right)_{t=0} = \frac{k [Br_2]_0^{1/2} [H_2]_0}{1 + m \cdot \frac{0}{[Br_2]_0}} = k [Br_2]_0^{1/2} [H_2]_0$$

$$\left(\frac{d[HBr]}{dt} \right)_{t=0} = 2k_2 \sqrt{\frac{k_1}{k_{-1}}} [Br_2]_0^{1/2} [H_2]_0$$

$$b) k = 2k_2 \sqrt{\frac{k_1}{k_{-1}}} = 2A_2 e^{-Ea_2/RT} \left(\frac{A_1 e^{-Ea_1/RT}}{A_{-1} e^{-Ea_{-1}/RT}} \right)^{1/2}$$

$$k = 2A_2 \left(\frac{A_1}{A_{-1}} \right)^{1/2} \left(e^{-\frac{2Ea_2+Ea_1-Ea_{-1}}{RT}} \right)^{1/2}$$

$$k = 2A_2 \left(\frac{A_1}{A_{-1}} \right)^{1/2} \left(e^{-\frac{2(74 \text{ kJ mol}^{-1})+(192 \text{ kJ mol}^{-1})-0}{RT}} \right)^{1/2}$$

$$k = 2A_2 \left(\frac{A_1}{A_{-1}} \right)^{1/2} \left(e^{-\frac{340 \text{ kJ mol}^{-1}}{RT}} \right)^{1/2}$$

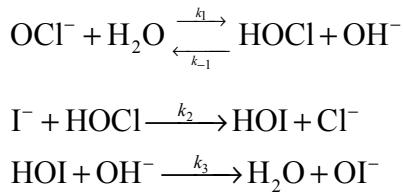
$$k = 2A_2 \left(\frac{A_1}{A_{-1}} \right)^{1/2} e^{-\frac{170 \text{ kJ mol}^{-1}}{RT}}$$

Therefore, $E_a = 170 \text{ kJ mol}^{-1}$

$$c) \frac{\text{rate}_{400 \text{ K}}}{\text{rate}_{298 \text{ K}}} = \frac{e^{\frac{1.7 \times 10^5 \text{ J mol}^{-1}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(400 \text{ K})}}}{e^{\frac{1.7 \times 10^5 \text{ J mol}^{-1}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}}}$$

$$= 3.98 \times 10^7$$

P37.6) For the reaction $I^-(aq) + OCl^-(aq) \rightleftharpoons OI^-(aq) + Cl^-(aq)$ occurring in aqueous solution, the following mechanism has been proposed:



- a) Derive the rate law expression for this reaction based on this mechanism. (*Hint: $[OH^-]$ should appear in the rate law.*)
- b) The initial rate of reaction was studied as a function of concentration by Chia and Connick [*J. Phys. Chem.* 63 (1959), 1518], and the following data were obtained:

$[I^-]_0$ (M)	$[OCl^-]_0$ (M)	$[OH^-]_0$ (M)	Initial Rate (M s ⁻¹)
2.0×10^{-3}	1.5×10^{-3}	1.00	1.8×10^{-4}
4.0×10^{-3}	1.5×10^{-3}	1.00	3.6×10^{-4}
2.0×10^{-3}	3.0×10^{-3}	2.00	1.8×10^{-4}
4.0×10^{-3}	3.0×10^{-3}	1.00	7.2×10^{-4}

Is the predicted rate law expression derived from the mechanism consistent with these data?

$$a) \frac{d[OI^-]}{dt} = k_3 [HOI][OH^-]$$

The intermediate species have rate expressions (with steady state approximation)

$$\frac{d[HOCl]}{dt} = 0 = k_1 [OCl^-][H_2O] - k_1 [HOCl][OH^-] - k_2 [I^-][HOCl]$$

$$\frac{d[HOI]}{dt} = k_2 [I^-][HOCl] - k_3 [HOI][OH^-] = 0$$

Solving the last expression for $[HOI]$ and substituting into the differential rate expression for $[OI^-]$ yields:

$$\frac{d[OI^-]}{dt} = k_2 [I^-][HOCl]$$

Next, $[HOCl]$ must be expressed in terms of reactants and $[OH^-]$. Rearranging the steady-state approximation applied to the differential rate expression for $[HOCl]$ results in the following:

$$[\text{HOCl}] = \frac{k_1 [\text{OCl}^-][\text{H}_2\text{O}]}{k_1 [\text{OH}^-] + k_2 [\text{I}^-]}$$

This result is substituted into the differential rate expression for $[\text{OI}^-]$ to yield:

$$\frac{d[\text{OI}^-]}{dt} = \frac{k_1 k_2 [\text{OCl}^-][\text{H}_2\text{O}][\text{I}^-]}{k_1 [\text{OH}^-] + k_2 [\text{I}^-]}$$

Inspection of the concentrations employed in the table suggests that $k_2[\text{I}^-] \ll k_1[\text{OI}^-]$ resulting in:

$$\frac{d[\text{OI}^-]}{dt} = \frac{k_2 [\text{I}^-][\text{OCl}^-][\text{H}_2\text{O}]}{[\text{OH}^-]}$$

A markedly similar expression is obtained using the pre-equilibrium approximation to determine $[\text{HOCl}]$

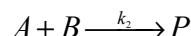
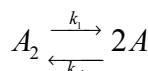
b) Consider set 1 & 2: $[\text{I}^-]_0$ is doubled, doubling the rate.

set 1 & 3: Doubling $[\text{OCl}^-]$ and $[\text{OH}^-]$ results in no net change in rate.

set 1 & 4: Doubling $[\text{I}^-]$ and $[\text{OCl}^-]$ quadruples the rate.

These results confirm the rate expression.

P37.7) Using the preequilibrium approximation, derive the predicted rate law expression for the following mechanism:



The rate expression for the formation of the product is

$$\frac{d[P]}{dt} = k_2 [A][B]$$

The equilibrium constant can be expressed as

$$K_{eg} = \frac{k_1}{k_{-1}} = \frac{[A]^2}{[A_2]}$$

therefore,

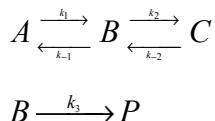
$$[A] = \left(\frac{k_1}{k_{-1}} \cdot [A_2] \right)^{1/2}$$

Substituting this into the rate expression for P yields:

$$\frac{d[P]}{dt} = k_2 \left(\frac{k_1}{k_{-1}} \right)^{1/2} [A_2]^{1/2} [B]$$

$$\frac{d[P]}{dt} = k_{eff} [A_2]^{1/2} [B] \quad \text{where } k_{eff} = k_2 \left(\frac{k_3}{k_{-1}} \right)^{1/2}$$

P37.8) Consider the following mechanism, which results in the formation of product *P*:



If only the species *A* is present at *t* = 0, what is the expression for the concentration of *P* as a function of time? You can apply the preequilibrium approximation in deriving your answer.

Using the pre-equilibrium approximation, we can express [B] and [C] in terms of [A] as follows:

$$[B] = \frac{k_1}{k_{-1}} [A] = K_1 [A]$$

$$[C] = \frac{k_2}{k_{-2}} [B] = K_2 [B] = K_1 K_2 [A]$$

$$\frac{d[P]}{dt} = k_3 [B] = k_3 K_1 [A]$$

Next, from mass conservation:

$$[A]_0 = [A] + [B] + [C] + [P]$$

$$\frac{d[A]_0}{dt} = 0 = \frac{d[A]}{dt} + \frac{d[B]}{dt} + \frac{d[C]}{dt} + \frac{d[P]}{dt}$$

$$\frac{d[P]}{dt} = - \left(\frac{d[A]}{dt} + \frac{d[B]}{dt} + \frac{d[C]}{dt} \right)$$

$$\frac{d[P]}{dt} = - \left(\frac{d[A]}{dt} + \frac{d(K_1 [A])}{dt} + \frac{d(K_1 K_2 [A])}{dt} \right)$$

$$= -(1 + K_1 + K_1 K_2) \frac{d[A]}{dt}$$

Setting the two differential rate expressions for [P] and integrating yields:

$$-\left(1+K_1+K_1K_2\right)\frac{d[A]}{dt}=k_3K_1[A]$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \int_0^t \frac{-k_3K_1}{(1+K_1+K_1K_2)} dt$$

$$[A] = [A]_0 e^{\frac{-k_3K_1 t}{(1+K_1+K_1K_2)}}$$

If a pre-equilibrium is established rapidly before any product formation:

$$[A]_0 = [A]_0^{eq} + [B]_0^{eq} + [C]_0^{eq}$$

$$= (1+K_1+K_1K_2)[A]_0^{eq}$$

$$[P] = [A]_0 - ([A] + [B] + [C])$$

$$= [A]_0 - (([A] + K_1[A] + K_1K_2[A]))$$

$$= [A]_0 - (1+K_1+K_1K_2)[A]$$

$$= [A]_0 - (1+K_1+K_1K_2) \frac{[A]_0}{(1+K_1+K_1K_2)} e^{\frac{-k_3K_1 t}{(1+K_1+K_1K_2)}}$$

$$= [A]_0 \left(1 - e^{\frac{-k_3K_1 t}{(1+K_1+K_1K_2)}} \right)$$

P37.9) Consider the gas-phase isomerization of cyclopropane. Are the following data of the observed rate constant as a function of cyclopropane pressure consistent with the Lindemann mechanism?

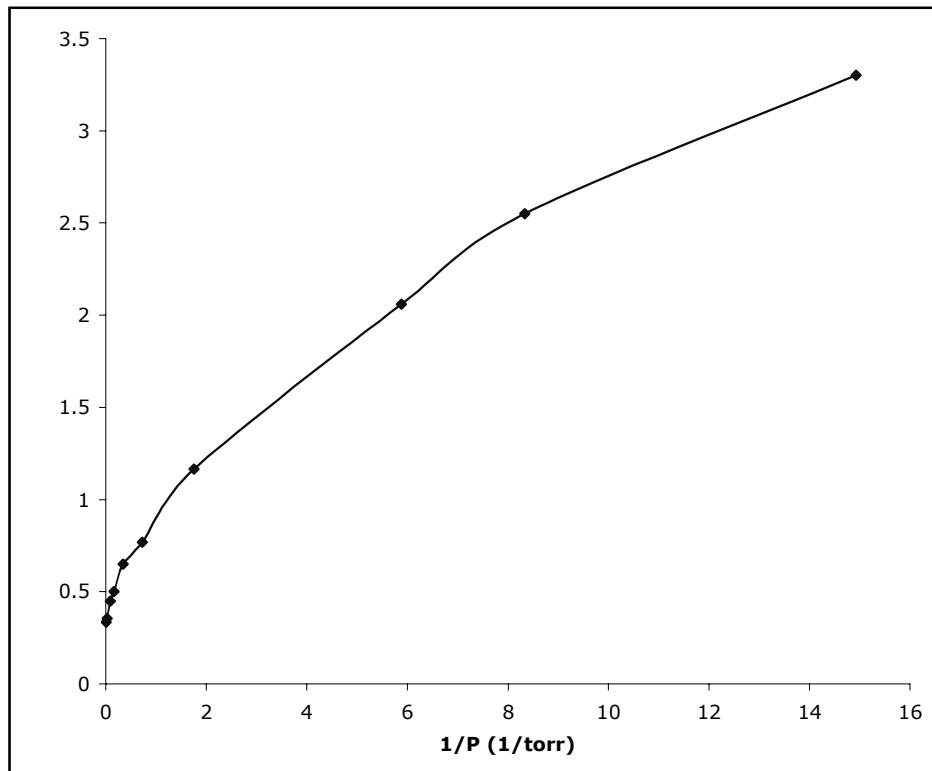
P (Torr)	k (10^4 s $^{-1}$)	P (Torr)	k (10^4 s $^{-1}$)
84.1	2.98	1.37	1.30
34.0	2.82	0.569	0.857
11.0	2.23	0.170	0.486
6.07	2.00	0.120	0.392
2.89	1.54	0.067	0.303

If the data obeyed the Lindemann mechanism, then a plot of the data would fit the equation

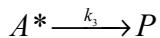
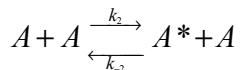
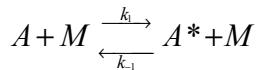
$$\frac{1}{k_{uni}} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1} \frac{1}{[M]}$$

$$\frac{1}{k_{uni}} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1} \frac{RT}{P}$$

Therefore, the Lindemann mechanism predicts that a plot of $\frac{1}{k_{uni}}$ versus $\frac{1}{P}$ should be a straight line. This plot is provided below, and demonstrates that the plot shows significant curvature so that the Lindemann mechanism does not provide an adequate description of the reaction mechanism.



P37.10) In the discussion of the Lindemann mechanism, it was assumed that the rate of activation by collision with another reactant molecule, A , was the same as collision with a nonreactant molecule, M , such as a buffer gas. What if the rates of activation for these two processes are different? In this case, the mechanism becomes



a) Demonstrate that the rate law expression for this mechanism is

$$R = \frac{k_3(k_1[A][M] + k_2[A]^2)}{k_{-1}[M] + k_{-2}[A] + k_{-3}}$$

b) Does this rate law reduce to the expected form when $[M] = 0$?

$$\text{a) } \frac{d[\text{P}]}{dt} = k_3 [\text{A}^*]$$

$$\frac{d[\text{A}^*]}{dt} = k_1 [\text{A}][\text{M}] - k_{-1} [\text{A}^*][\text{M}] + k_2 [\text{A}]^2 - k_{-2} [\text{A}^*][\text{A}] - k_3 [\text{A}^*]$$

Applying steady state theory to A^* yields

$$k_3 [\text{A}^*] + k_{-1} [\text{A}^*][\text{M}] + k_{-2} [\text{A}^*][\text{A}] = k_1 [\text{A}][\text{M}] + k_2 [\text{A}]^2$$

$$[\text{A}^*] = \frac{k_1 [\text{A}][\text{M}] + k_2 [\text{A}]^2}{k_{-1} [\text{M}] + k_{-2} [\text{A}] + k_3}$$

Substituting back into the differential rate expression for the product yields:

$$R = \frac{d[\text{P}]}{dt} = \frac{k_3 (k_1 [\text{A}][\text{M}] + k_2 [\text{A}]^2)}{k_{-1} [\text{M}] + k_{-2} [\text{A}] + k_3}$$

b) If the concentration of M goes to 0, then

$$R = \frac{k_3 (k_2 [\text{A}]^2)}{k_{-2} [\text{A}] + k_3}$$

which is the Lindemann rate expression.

P37.11) In the unimolecular isomerization of cyclobutane to butylene, the following values for k_{uni} as a function of cyclobutane pressure were measured:

P_0 (Torr)	110	210	390	760
k_{uni} (s^{-1})	9.58	10.3	10.8	11.1

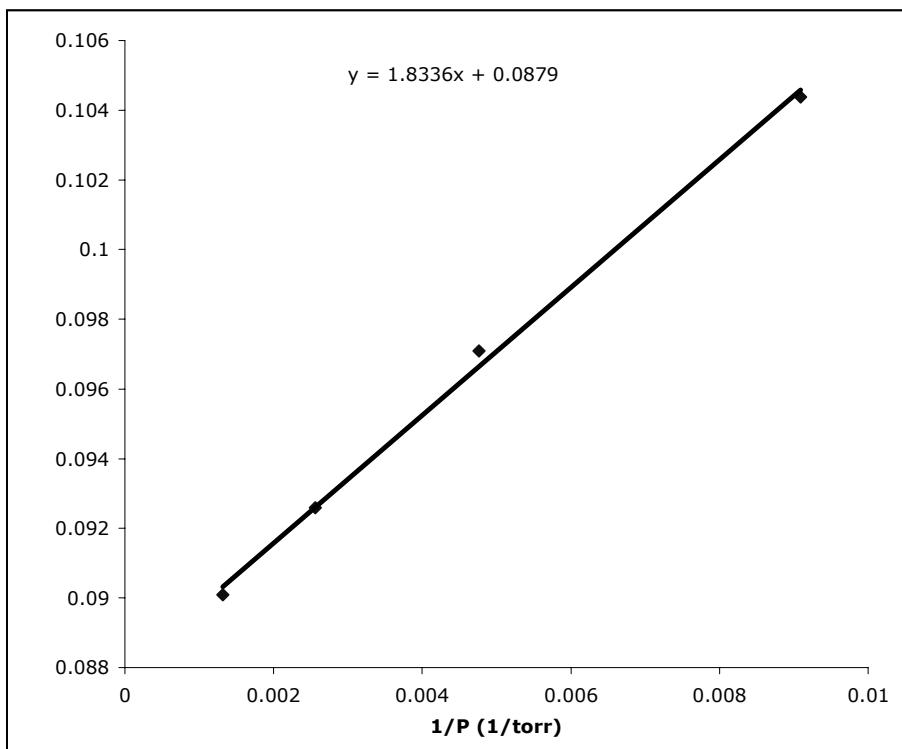
Assuming that the Lindemann mechanism accurately describes this reaction, determine k_1 and the ratio k_{-1}/k_2 .

The Lindemann mechanism predicts the following relationship between the unimolecular rate constant for the reaction and the concentration of reactant:

$$\frac{1}{k_{uni}} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1} \frac{1}{[\text{M}]}$$

$$\frac{1}{k_{uni}} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1} \frac{RT}{P}$$

Therefore, a plot of k_{uni}^{-1} versus P^{-1} should yield a straight line, as shown below:



$$\frac{1}{k_{uni}} = 1.834 \text{ s torr} \frac{1}{P} + 0.0879$$

Thus, k_1 can be related to the slope

$$k_1 = \frac{RT}{\text{slope}} = \frac{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(350 \text{ K})}{(1.834 \text{ s torr}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right)}$$

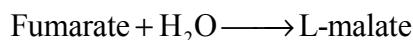
$$k_1 = 1.19 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$$

The ratio $\frac{k_{-1}}{k_2}$ is related to the intercept

$$\frac{k_{-1}}{k_2} = (y - \text{int})(k_1) = (0.0879 \text{ s})(1.19 \times 10^4 \text{ M}^{-1} \text{ s}^{-1})$$

$$\frac{k_{-1}}{k_2} = 1.05 \times 10^3 \text{ M}^{-1}$$

P37.12) The enzyme fumarase catalyzes the hydrolysis of fumarate:



The turnover number for this enzyme is $2.5 \times 10^3 \text{ s}^{-1}$, and the Michaelis constant is $4.2 \times 10^{-6} \text{ M}$. What is the rate of fumarate conversion if the initial enzyme concentration is $1 \times 10^{-6} \text{ M}$ and the fumarate concentration is $2 \times 10^{-4} \text{ M}$?

Recognizing that k_2 is the turnover number, the values provided in the problem can be used directly in the rate expression to determine the initial rate of reaction:

$$\begin{aligned} k_2 &= 2.5 \times 10^3 \text{ s}^{-1} & K_m &= 4.2 \times 10^{-6} \text{ M} \\ [E]_0 &= 1 \times 10^{-6} \text{ M} & [S]_0 &= 2 \times 10^{-4} \text{ M} \\ rate_o &= \frac{k_2 [S]_0 [E]_0}{[S]_0 + K_m} \\ &= \frac{(2.5 \times 10^3 \text{ s}^{-1})(2 \times 10^{-4} \text{ M})(1 \times 10^{-6} \text{ M})}{(2 \times 10^{-4} \text{ M}) + (4.2 \times 10^{-6} \text{ M})} \\ &= 2.45 \times 10^{-3} \text{ M s}^{-1} \end{aligned}$$

P37.13) The enzyme catalase catalyzes the decomposition of hydrogen peroxide. The following data are obtained regarding the rate of reaction as a function of substrate concentration:

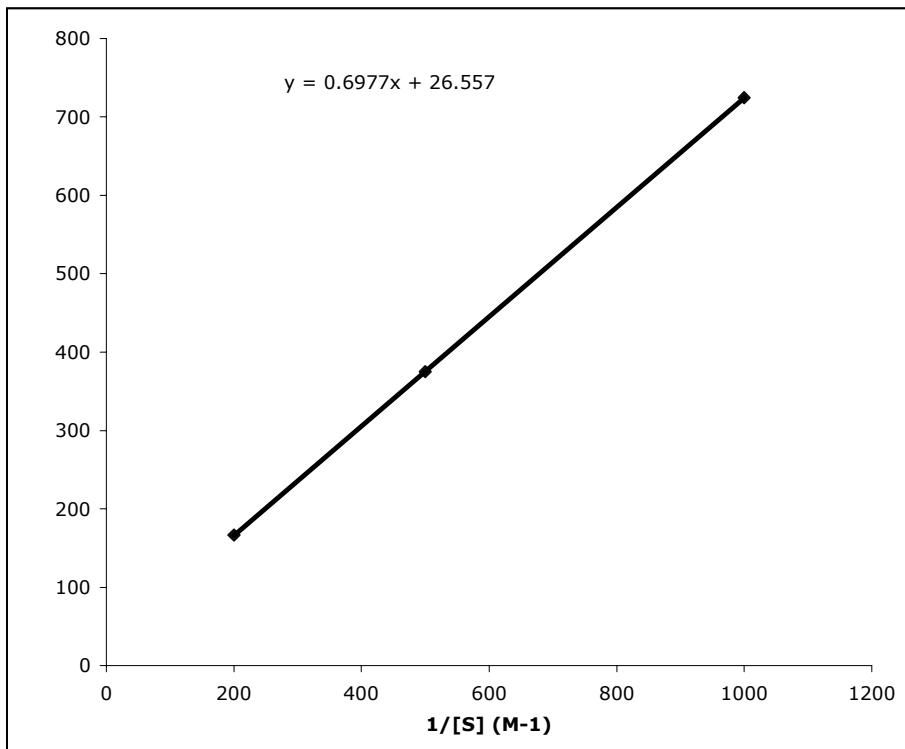
[H ₂ O ₂] ₀ (M)	0.001	0.002	0.005
Initial Rate (M s ⁻¹)	1.38 × 10 ⁻³	2.67 × 10 ⁻³	6.00 × 10 ⁻³

The concentration of catalase is 3.5×10^{-9} M. Use these data to determine $rate_{max}$, K_m , and the turnover number for this enzyme.

Analyzing the data using the Lineweaver-Burk plot:

$$\frac{1}{rate_o} = \frac{1}{rate_{max}} + \frac{K_m}{rate_{max}} \frac{1}{[S]_0}$$

The corresponding plot of $rate_o^{-1}$ versus $[H_2O_2]^{-1}$ is as follows:



Best fit to the data by a straight line yields the following equation:

$$\frac{1}{rate_0} = (0.698 \text{ s}) \frac{1}{[S]_0} + 26.6 \text{ s M}^{-1} \text{ s}$$

The $rate_{max}$ is related to the intercept

$$rate_{max} = \frac{1}{y - \text{int}} = \frac{1}{26.6 \text{ M}^{-1} \text{ s}}$$

$$rate_{max} = 3.75 \times 10^{-2} \text{ M s}^{-1}$$

With $rate_{max}$, the Michaelis constant is determined using the slope:

$$K_m = \text{slope} \cdot rate_{max} = (0.698 \text{ s}) (3.75 \times 10^{-2} \text{ M s}^{-1})$$

$$K_m = 2.63 \times 10^{-2} \text{ M}$$

Finally, the turnover number is determined using $rate_{max}$ and $[E]_0$ as follows:

$$rate_{\max} = k_2 [E]_0$$

$$\frac{rate_{\max}}{[E]_0} = k_2$$

$$\frac{3.75 \times 10^{-2} \text{ M s}^{-1}}{3.5 \times 10^{-9} \text{ M}} = k_2$$

$$1.08 \times 10^7 \text{ s}^{-1} = k_2$$

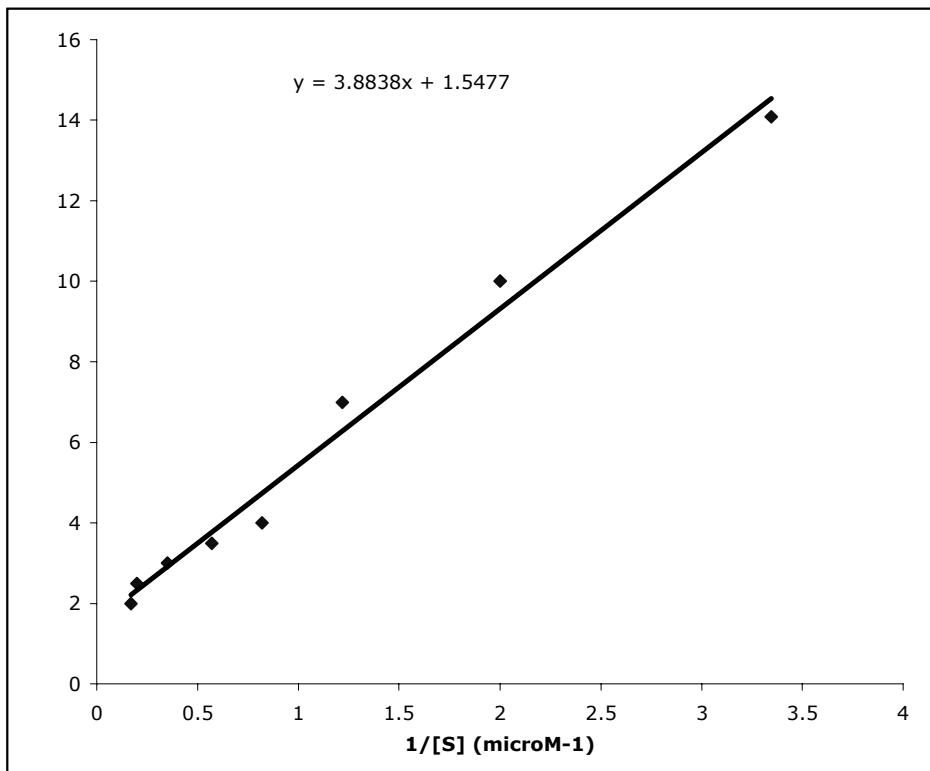
P37.14) Protein tyrosine phosphatases (PTPases) are a general class of enzymes that are involved in a variety of disease processes including diabetes and obesity. In a study by Z.-Y. Zhang and coworkers [*J. Medicinal Chemistry* 43 (2000), 146], computational techniques were used to identify potential competitive inhibitors of a specific PTPase known as PTP1B. The structure of one of the identified potential competitive inhibitors is shown in the text.

The reaction rate was determined in the presence and absence of inhibitor, I , and revealed the following initial reaction rates as a function of substrate concentration:

[S] (μM)	Rate ₀ ($\mu\text{M s}^{-1}$), [I] = 0	Rate ₀ ($\mu\text{M s}^{-1}$) [I] = 200 μM
0.299	0.071	0.018
0.500	0.100	0.030
0.820	0.143	0.042
1.22	0.250	0.070
1.75	0.286	0.105
2.85	0.333	0.159
5.00	0.400	0.200
5.88	0.500	0.250

- Determine K_m and $rate_{\max}$ for PTP1B.
- Demonstrate that the inhibition is competitive, and determine K_i .

- Performing a Lineweaver-Burke plot for the uninhibited reaction yields:



Best fit to the data by a straight line yields the following equation:

$$\frac{1}{\text{rate}_0} = 3.88 \times 10^6 \text{ s} \frac{1}{[S]_0} + 1.55 \times 10^6 \text{ M}^{-1} \text{ s}$$

The maximum rate is equal to the inverse of the y-intercept:

$$\text{rate}_{\max} = \frac{1}{y - \text{int}} = \frac{1}{1.55 \times 10^6 \text{ M}^{-1} \text{ s}}$$

$$\text{rate}_{\max} = 6.45 \times 10^{-7} \text{ M s}^{-1}$$

With rate_{\max} , the Michaelis constant is determined from the slope:

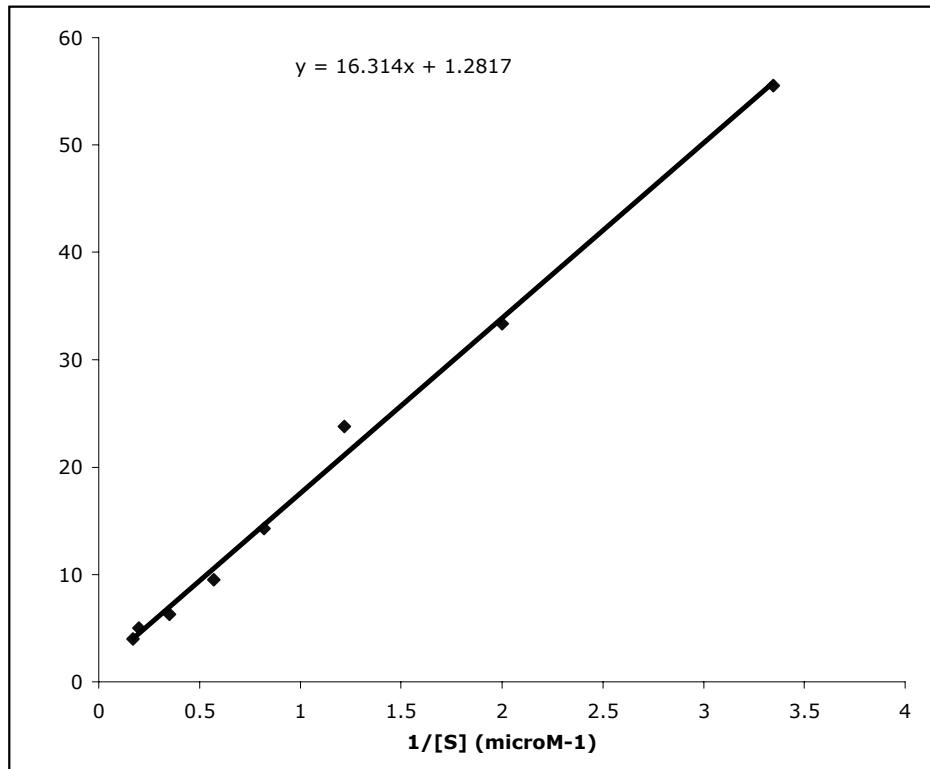
$$K_m = (\text{slope})(\text{rate}_{\max}) = (3.88 \times 10^6 \text{ s}) (6.45 \times 10^{-7} \text{ M s}^{-1})$$

$$K_m = 2.5 \text{ M}$$

b) With the inhibitor present, the modified Lineweaver-Burke equation is used where:

$$\frac{I}{\text{rate}_0} = \frac{I}{\text{rate}_{\max}} + \frac{K_m^*}{\text{rate}_{\max}} \frac{I}{[S]_0}$$

Again, a plot of the inverse of the initial rate with the inverse of substrate concentration should yield a straight line. The plot is as follows:



Best fit to the data by a straight line yields the following equation:

$$\frac{1}{\text{rate}_0} = 1.63 \times 10^7 \text{ s} \frac{1}{[S]} + 1.28 \times 10^6 \text{ M}^{-1} \text{ s}$$

The maximum rate is given by the inverse of the y-intercept:

$$\text{rate}_{\max} = \frac{1}{y - \text{int}} = \frac{1}{1.26 \times 10^6 \text{ M}^{-1} \text{s}}$$

$$\text{rate}_{\max} = 7.94 \times 10^{-7} \text{ M s}^{-1}$$

With rate_{\max} and the slope of the line the apparent Michaelis constant is:

$$K_m^* = (\text{slope}) (\text{rate}_{\max}) = (1.63 \times 10^7 \text{ s}) (1.28 \times 10^{-6} \text{ M s}^{-1})$$

$$= 20.9 \text{ M}$$

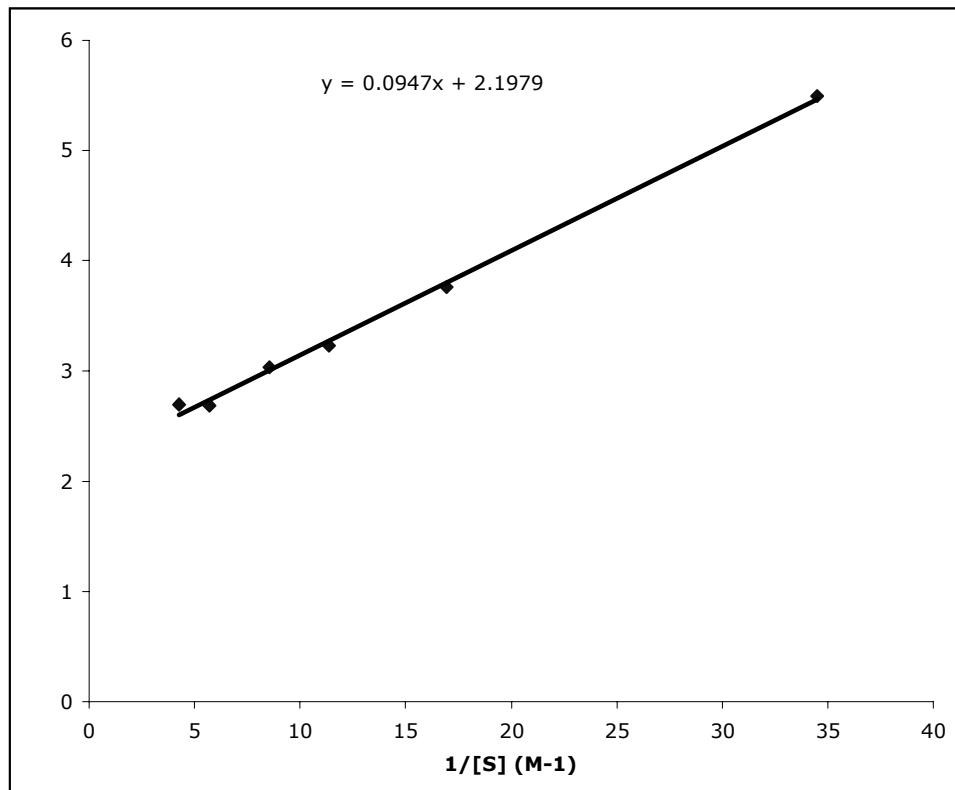
With K_m , K_m^* and $[I]$, K_I is determined as follows:

$$\begin{aligned} K_I &= \frac{[I]}{\frac{K_m^*}{K_m} - 1} \\ &= \frac{200 \times 10^{-6} \text{ M}}{\left(\frac{20.9 \text{ M}}{2.5 \text{ M}}\right) - 1} \\ &= 2.71 \times 10^{-5} \text{ M} \end{aligned}$$

P37.15) The rate of reaction can be determined by measuring the change in optical rotation of the sample as a function of time if a reactant or product is chiral. This technique is especially useful for kinetic studies of enzyme catalysis involving sugars. For example, the enzyme invertase catalyzes the hydrolysis of sucrose, an optically active sugar. The initial reaction rates as a function of sucrose concentration are as follows:

[Sucrose] ₀ (M)	Rate (M s ⁻¹)
0.029	0.182
0.059	0.266
0.088	0.310
0.117	0.330
0.175	0.372
0.234	0.371

Use these data to determine the Michaelis constant for invertase. The Lineweaver-Burk plot and best fit to the data is as follows:



The equation for the best-fit line is:

$$\frac{1}{\text{rate}_0} = 0.0947 \text{ s} \frac{1}{[S]_0} + 2.1979 \text{ M}^{-1}\text{s}$$

The maximum rate is equal to the inverse of the y-intercept

$$\text{rate}_{\max} = \frac{1}{\text{int}} = \frac{1}{2.20 \text{ M}^{-1}\text{s}}$$

$$\text{rate}_{\max} = 0.455 \text{ M s}^{-1}$$

The Michaelis constant is equal to the product of rate_{\max} and the slope:

$$K_m = \text{slope} \cdot \text{rate}_{\max} = 0.0947 \text{ s} \cdot 0.455 \text{ Ms}^{-1}$$

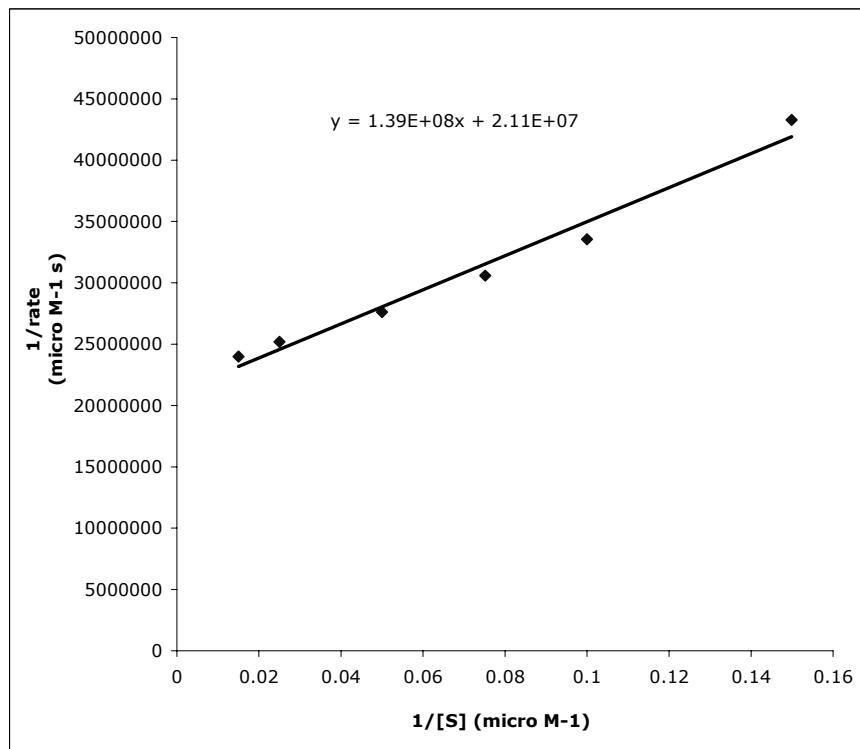
$$K_m = 0.0431 \text{ M}$$

P37.16) The enzyme glycogen synthase kinase (GSK-3 β) plays a central role in Alzheimer's disease. The onset of Alzheimer's disease is accompanied by the production of highly phosphorylated forms of a protein referred to as " τ ." GSK-3 β contributes to the hyperphosphorylation of τ such that inhibiting the activity of this enzyme represents a pathway for the development of an Alzheimer's drug. A compound known as Ro 31-8220 is a competitive inhibitor of GSK-3 β . The following data were obtained for the rate of GSK-3 β activity in the presence and absence of Ro 31-8220 [A. Martinez *et al.*, *J. Medicinal Chemistry* 45 (2002), 1292]:

[S] (μM)	$\text{Rate}_0 (\mu\text{M s}^{-1})$, $[I] = 0$	$\text{Rate}_0 (\mu\text{M s}^{-1})$, $[I] = 200 \mu\text{M}$
66.7	4.17×10^{-8}	3.33×10^{-8}
40.0	3.97×10^{-8}	2.98×10^{-8}
20.0	3.62×10^{-8}	2.38×10^{-8}
13.3	3.27×10^{-8}	1.81×10^{-8}
10.0	2.98×10^{-8}	1.39×10^{-8}
6.67	2.31×10^{-8}	1.04×10^{-8}

Determine K_m and rate_{\max} for GSK-3 β and, using the data with the inhibitor, determine K_m^* and K_i .

Analyzing the data without inhibitor using a Lineweaver-Burk plot yields:



The best-fit straight line to the data yields the following equation:

$$\frac{1}{rate_0} = 1.39 \times 10^8 \text{ s} \frac{1}{[S]_0} + 2.11 \times 10^7 \mu\text{M}^{-1} \text{ s}$$

The maximum rate is equal to the inverse of the y -intercept:

$$rate_{max} = \frac{1}{y-int} = \frac{1}{2.11 \times 10^7 \mu\text{M}^{-1}\text{s}}$$

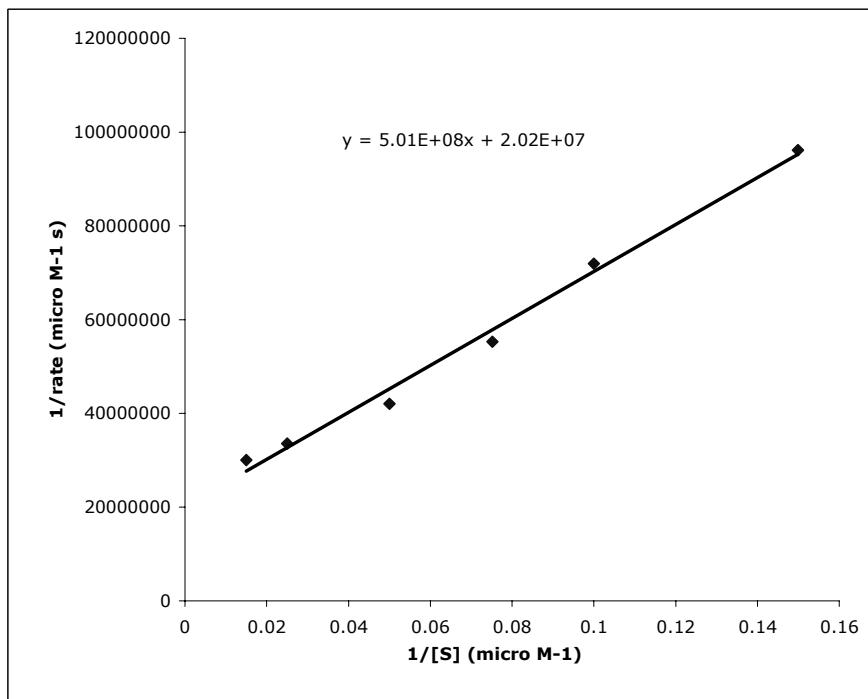
$$rate_{max} = 4.74 \times 10^{-8} \mu\text{M s}^{-1}$$

With the maximum rate and slope of the best-fit line, the Michaelis constant obtained as follows:

$$K_m = (\text{slope})(rate_{max}) = (1.39 \times 10^8 \text{ s})(4.74 \times 10^{-8} \mu\text{M s}^{-1})$$

$$K_m = 6.49 \mu\text{M}$$

Using the inhibited data, the Lineweaver-Burk plot is:



Best fit by a straight line to the data yields the following equation:

$$\frac{1}{\text{rate}_0} = 5.01 \times 10^8 \text{ s} \frac{1}{[S]}_0 + 2.01 \times 10^7 \mu\text{M}^{-1}\text{s}$$

The maximum rate with inhibitor is equal to the inverse of the y-intercept:

$$\begin{aligned} \text{rate}_{\max} &= \frac{1}{2.01 \times 10^7 \mu\text{M}^{-1}\text{s}} \\ &= 4.98 \times 10^{-8} \mu\text{M}^{-1}\text{s} \end{aligned}$$

The apparent Michaelis constant is given by:

$$\begin{aligned} K_m^* &= (\text{slope})(\text{rate}_{\max}) \\ &= (5.01 \times 10^8 \text{ s})(4.98 \times 10^{-8} \mu\text{M}^{-1}\text{s}) \end{aligned}$$

$$K_m^* = 24.9 \mu\text{M}$$

Finally, the K_I value is given by:

$$\begin{aligned} K_I &= \frac{[I]}{\frac{K_m^*}{K_m} - 1} = \frac{200 \mu\text{M}}{\left(\frac{24.9 \mu\text{M}}{6.49 \mu\text{M}}\right) - 1} \\ &= 70.4 \mu\text{M} \end{aligned}$$

P37.17) In the Michaelis–Menten mechanism, it is assumed that the formation of product from the enzyme–substrate complex is irreversible. However, consider the following modified version in which the product formation step is reversible:



mechanism in the limit where $[S]_0 \gg [E]_0$.

The reaction rate in terms of the differential rate expression for product formation is

$$\frac{d[P]}{dt} = k_2[ES] - k_{-2}[E][P]$$

Using the steady state for $[ES]$

$$\frac{d[ES]}{dt} = 0 = k_1[E][S] - (k_{-1} + k_2)[ES] + k_{-2}[E][P]$$

Now, noting that $[E]_0 = [E] + [ES]$, and $[S]_0 = [S] + [ES] + [P]$. As in the text, we confine ourselves to early times so that $[ES]$ and $[P]$ are small and $[S] = [S]_0$.

Using the preceding equation, $[ES]$ is given by:

$$0 = k_1[E]_0[S]_0 - k_1[ES][S]_0 - (k_{-1} + k_2)[ES] + k_{-2}[E]_0[P] - k_{-2}[ES][P]$$

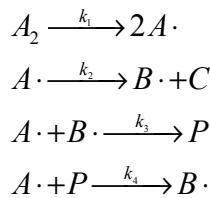
$$[ES] = \frac{k_1[E]_0[S]_0 + k_{-2}[E]_0[P]}{k_1[S]_0 + k_{-2}[P] + (k_{-1} + k_2)}$$

If $[S] \gg [P]$, $[E]_0$, we can neglect the term involving $[E]_0[P]$ in the preceding equation.

$$\begin{aligned} \frac{d[P]}{dt} &= k_2[ES] - k_{-2}[E][P] \\ &= \frac{k_2 k_1 [E]_0 [S]_0}{k_1 [S]_0 - k_{-2}[P] + (k_{-1} + k_2)} - k_{-2}([E]_0 - [ES])[P] \\ &= \frac{k_2 k_1 [E]_0 [S]_0}{k_1 [S]_0 - k_{-2}[P] + (k_{-1} + k_2)} - k_{-2}[ES][P] \\ &= \frac{k_2 k_1 [E]_0 [S]_0 - k_{-2} k_1 [E]_0 [S]_0 [P]}{k_1 [S]_0 - k_{-2}[P] + (k_{-1} + k_2)} \\ &\approx \frac{k_2 k_1 [E]_0 [S]_0 - k_{-2} k_1 [E]_0 [S]_0 [P]}{k_1 [S]_0 + (k_{-1} + k_2)} \\ &= \frac{k_1 [E]_0 (k_1 [S]_0 - k_{-2} [S]_0 [P])}{k_1 [S]_0 + (k_{-1} + k_2)} \\ &= \frac{k_2 [E]_0}{\frac{k_1 [S]_0}{(k_1 [S]_0 - k_{-2} [S]_0 [P])} + \frac{(k_{-1} + k_2)}{(k_1 [S]_0 - k_{-2} [S]_0 [P])}} \end{aligned}$$

If the term involving $[P]$ is ignored in the denominator of the preceding equation, then the original Michaelis expression is recovered.

P37.18) Determine the predicted rate law expression for the following radical-chain reaction:



The differential rate of P formation is

$$\frac{d[P]}{dt} = k_3[A\cdot][B\cdot] - k_4[A\cdot][P]$$

The rate expression for A· and B· are

$$\frac{d[A\cdot]}{dt} = 2k_1[A_2] - k_2[A\cdot] - k_3[A\cdot][B\cdot] - k_4[A\cdot][P]$$

$$\frac{d[B\cdot]}{dt} = k_2[A\cdot] - k_3[A\cdot][B\cdot] + k_4[A\cdot][P]$$

Applying the steady state approximation for [B]

$$k_3[A\cdot][B\cdot] - k_4[A\cdot][P] = k_2[A\cdot]$$

$$[B\cdot] = \frac{k_2 + k_4[P]}{k_3}$$

Substituting this result into the differential rate expression for P yields:

$$\begin{aligned} \frac{d[P]}{dt} &= k_3[A\cdot] \left(\frac{k_2 + k_4[P]}{k_3} \right) - k_4[A\cdot][P] \\ &= k_2[A\cdot] \end{aligned}$$

Now, adding the steady-state expressions for [A·] and [B·] yields:

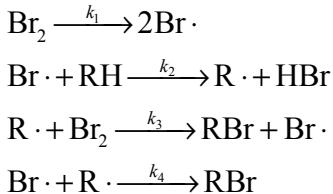
$$0 = 2k_2[A_2] - 2k_3[A\cdot][B\cdot]$$

$$[A\cdot] = \frac{k_2[A_2]}{k_3[B\cdot]} = \frac{k_2[A_2]}{k_2 + k_4[P]}$$

Substituting this expression into the differential rate expression for P yields the final result:

$$\frac{d[P]}{dt} = \frac{k_2 k_1[A_2]}{k_2 + k_4[P]}$$

P37.19) The overall reaction for the halogenation of a hydrocarbon (RH) using Br as the halogen is $\text{RH} + \text{Br}_2 \longrightarrow \text{RBr} + \text{HBr}$. The following mechanism has been proposed for this process:



Determine the rate law predicted by this mechanism.

$$\text{Rate} = \frac{d[\text{HBr}]}{dt} = k_2 [\text{Br}\cdot][\text{RH}]$$

Applying the steady-state approximation to the intermediate species Br and R yields:

$$\begin{aligned}
 \frac{d[\text{Br}\cdot]}{dt} &= 0 = 2k_1[\text{Br}_2] - k_2[\text{Br}\cdot][\text{RH}] + k_3[\text{R}\cdot][\text{Br}_2] - k_4[\text{Br}\cdot][\text{R}\cdot] \\
 \frac{d[\text{R}\cdot]}{dt} &= 0 = k_2[\text{Br}\cdot][\text{RH}] - k_3[\text{R}\cdot][\text{Br}_2] - k_4[\text{Br}\cdot][\text{R}\cdot]
 \end{aligned}$$

Adding the last two equations yields:

$$0 = 2k_1[\text{Br}_2] - 2k_4[\text{Br}\cdot][\text{R}\cdot]$$

or

$$[\text{Br}\cdot] = \frac{k_1[\text{Br}_2]}{k_4[\text{R}\cdot]}$$

Using the steady-state approximation for $d[\text{R}\cdot]/dt$ ignoring the term corresponding to the termination step yields:

$$0 = k_2[\text{Br}\cdot][\text{RH}] - k_3[\text{R}\cdot][\text{Br}_2]$$

$$k_2[\text{Br}\cdot][\text{RH}] = k_3[\text{R}\cdot][\text{Br}_2]$$

$$k_2 \left(\frac{k_1[\text{Br}_2]}{k_4[\text{R}\cdot]} \right) [\text{RH}] = k_3[\text{R}\cdot][\text{Br}_2]$$

$$\sqrt{\frac{k_2 k_1}{k_3 k_4}} [\text{RH}] = [\text{R}\cdot]$$

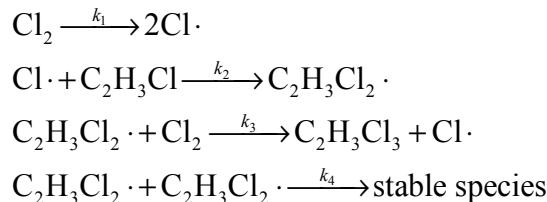
Substitution into the expression for $[\text{Br}\cdot]$ results in:

$$[\text{Br}\cdot] = \frac{k_1[\text{Br}_2]}{k_4[\text{R}\cdot]} = \frac{k_1}{k_4} \frac{[\text{Br}_2]}{\left(\sqrt{\frac{k_2 k_1}{k_3 k_4}} [\text{RH}] \right)} = \sqrt{\frac{k_1 k_3}{k_2 k_4}} \frac{[\text{Br}_2]}{[\text{RH}]^{\frac{1}{2}}}$$

Finally, the rate of reaction is then:

$$\begin{aligned}\text{Rate} &= k_2 [\text{Br}\cdot][\text{RH}] = k_2 \left(\sqrt{\frac{k_1 k_3}{k_2 k_4}} \frac{[\text{Br}_2]}{[\text{RH}]^{1/2}} \right) [\text{RH}] \\ &= \sqrt{\frac{k_1 k_2 k_3}{k_4}} [\text{Br}_2] [\text{RH}]^{1/2}\end{aligned}$$

P37.20) The chlorination of vinyl chloride, $\text{C}_2\text{H}_3\text{Cl} + \text{Cl}_2 \longrightarrow \text{C}_2\text{H}_3\text{Cl}_3$, is believed to proceed by the following mechanism:



Derive the rate law expression for the chlorination of vinyl chloride based on this mechanism.

The rate of vinyl chloride production is

$$\frac{d[\text{C}_2\text{H}_3\text{Cl}_3]}{dt} = k_3 [\text{C}_2\text{H}_3\text{Cl}_2\cdot][\text{Cl}_2]$$

The rate expressions of the intermediates are

$$\frac{d[\text{C}_2\text{H}_3\text{Cl}_2\cdot]}{dt} = k_2 [\text{Cl}\cdot][\text{C}_2\text{H}_3\text{Cl}] - k_3 [\text{C}_2\text{H}_3\text{Cl}_2\cdot][\text{Cl}_2] - 2k_4 [\text{C}_2\text{H}_3\text{Cl}_2\cdot]^2 = 0$$

$$\frac{d[\text{Cl}\cdot]}{dt} = 2k_1 [\text{Cl}_2] - k_2 [\text{Cl}\cdot][\text{C}_2\text{H}_3\text{Cl}] + k_3 [\text{C}_2\text{H}_3\text{Cl}_2\cdot][\text{Cl}_2] = 0$$

Adding the two preceding equations yields:

$$0 = 2k_1 [\text{Cl}_2] - 2k_4 [\text{C}_2\text{H}_3\text{Cl}_2\cdot]^2$$

$$[\text{C}_2\text{H}_3\text{Cl}_2\cdot] = \left(\frac{k_1}{k_4} \right)^{1/2} [\text{Cl}_2]^{1/2}$$

Substitution of this expression into the differential rate expression for vinyl chloride yields:

$$\begin{aligned}\frac{d[\text{C}_2\text{H}_3\text{Cl}_3]}{dt} &= k_3 \left(\left(\frac{k_1}{k_4} \right)^{1/2} [\text{Cl}_2]^{1/2} \right) [\text{Cl}_2] \\ &= k_3 \left(\frac{k_1}{k_4} \right)^{1/2} [\text{Cl}_2]^{3/2}\end{aligned}$$

P37.21) Determine the expression for fractional coverage as a function of pressure for the dissociative adsorption mechanism described in the text in which adsorption is

accompanied by dissociation: $R_2(g) + 2M(\text{surface}) \xrightleftharpoons[k_d]{k_a} 2RM(\text{surface})$

The rate of absorption is second order with respect to the particle and site concentrations:

$$\frac{d\theta}{dt} = k_a PN(1-\theta)^2$$

The desorption rate is also second order with respect to the number of occupied sites, thus:

$$\frac{d\theta}{dt} = -k_d N \theta^2$$

At equilibrium

$$k_a PN(1-\theta)^2 = k_d N \theta^2$$

$$KP(1-\theta)^2 = \theta^2 \Rightarrow \sqrt{KP} = \theta(1 + \sqrt{KP})$$

and

$$\theta = \frac{\sqrt{KP}}{1 + \sqrt{KP}} \quad \text{where} \quad K = \frac{k_a}{k_d}$$

P37.22) The adsorption of ethyl chloride on a sample of charcoal at 0°C measured at several different pressures is as follows:

$P_{C_2H_5Cl}$ (Torr)	V_{ads} (mL)
20	3.0
50	3.8
100	4.3
200	4.7
300	4.8

Using the Langmuir isotherm, determine the fractional coverage at each pressure and V_m .

The Langmuir equation can be written as

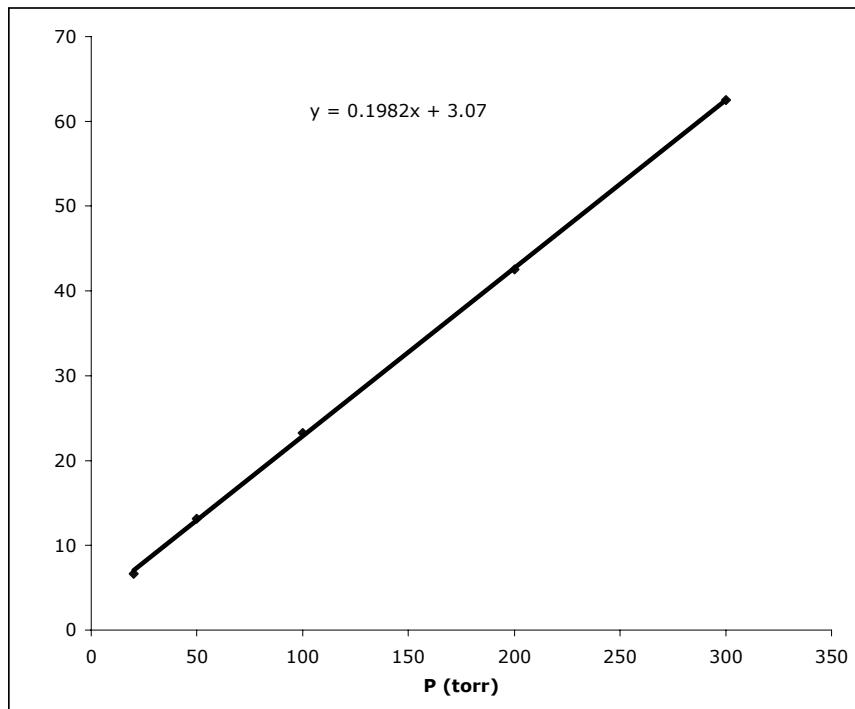
$$\frac{P}{V} = \frac{P}{V_m} + \frac{1}{KV_m}$$

And the fractional coverage, θ , is simply the ratio of adsorbed volume to the volume of maximum adsorption (V_m):

$$\theta = \frac{V}{V_m}$$

Therefore, V_m is required to determine the fractional coverage versus pressure.

The plot of $\frac{P}{V}$ vs. P should yield a straight line with slope equal to the inverse of V_m . This plot is as follows:



The equation for the best-fit line is: $\frac{P}{V} = 0.198 \text{ mL}^{-1}(P) + 3.07 \text{ torr mL}^{-1}$

Thus, the V_m value is

$$V_m = \frac{1}{slope}$$

$$V_m = 5.04 \text{ mL}$$

With V_m θ can be determined resulting in the following:

P (atm)	θ
20	0.595
50	0.754
100	0.853
200	0.932
300	0.952

P37.23) Given the limitations of the Langmuir model, many other empirical adsorption isotherms have been proposed to better reproduce observed adsorption behavior. One of these empirical isotherms is the Temkin isotherm: $V_{adsorbed} = r \ln sP$, where V is the volume of gas adsorbed, P is pressure, and r and s are empirical constants.

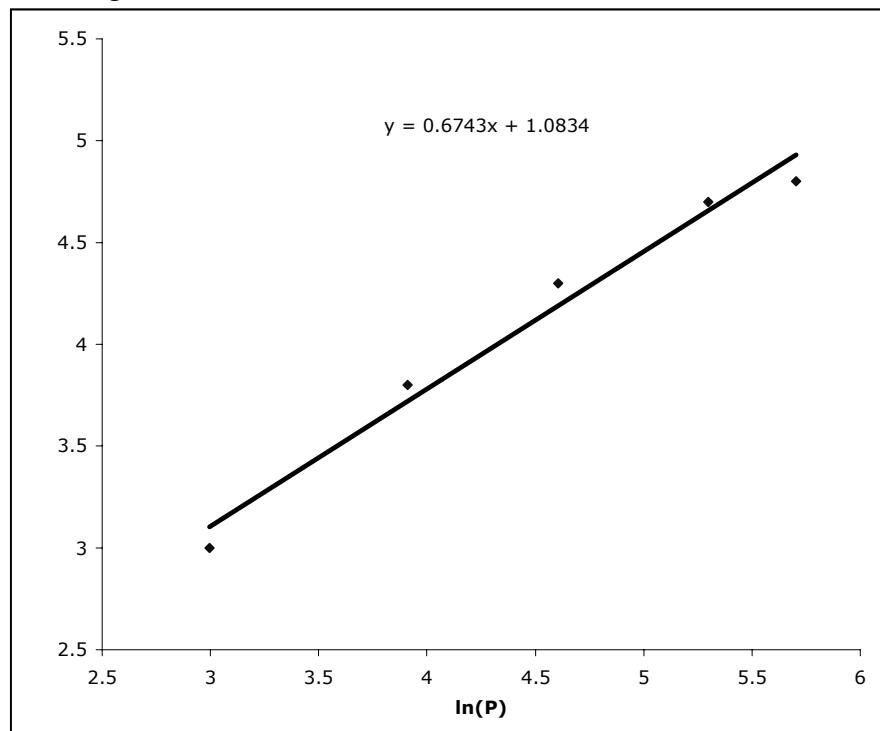
- Given the Temkin isotherm provided, what type of plot is expected to give a straight line?
- Use your answer from part (a) to determine r and s for the data presented in Problem P37.22.

a) The Temkin isotherm can be manipulated to the form

$$V_{\text{ads}} = r \ln(P) + r \ln(s)$$

Therefore, a plot of V_{ads} versus $\ln(P)$ is expected to yield a straight line.

b) The data in the preceding problem plotted as V_{ads} versus $\ln(P)$ results in the following:



Best fit to the data by a straight line yields the following equation:

$$V_{\text{ads}} = 0.674 \ln(P) + 1.083$$

The slope of the line is equal to r

$$r = 0.674 \text{ mL}$$

With r , s can be determined as follows:

$$s = e^{\frac{y-\text{int}}{r}} = e^{1.083/0.674}$$

$$s = 4.99 \text{ torr}^{-1}$$

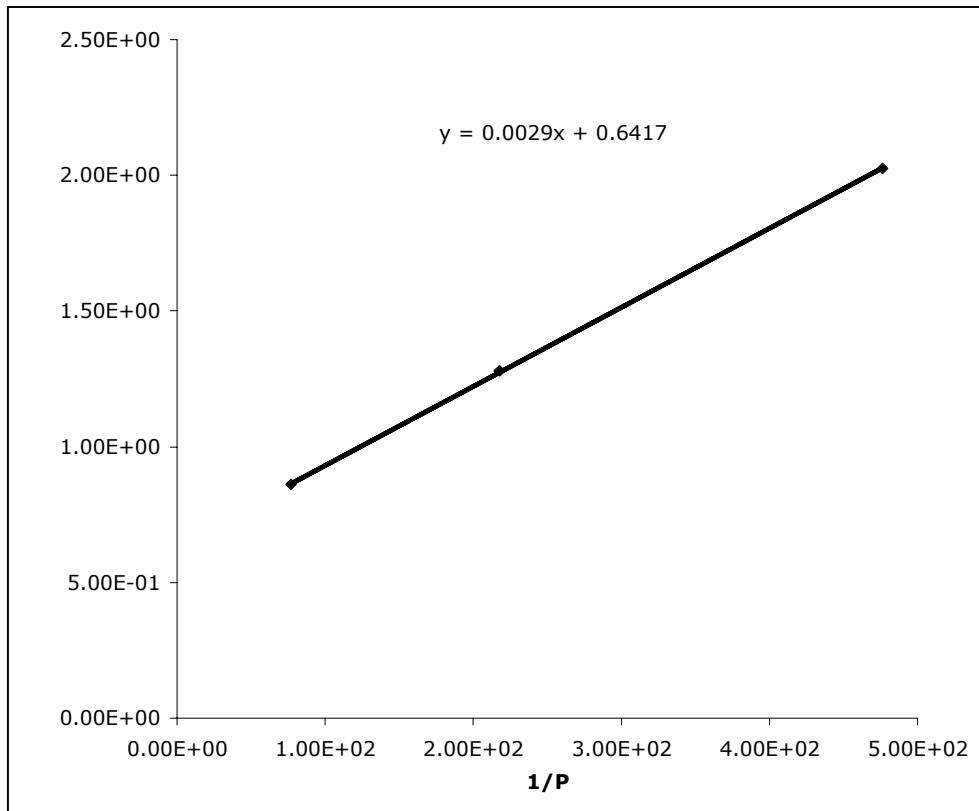
P37.24) Use the following data to determine the Langmuir adsorption parameters for nitrogen on mica:

V_{ads} ($\text{cm}^3 \text{ g}^{-1}$)	P (Torr)
0.494	2.1×10^{-3}
0.782	4.60×10^{-3}
1.16	1.30×10^{-2}

As illustrated in the example problem in the text, the following plot is used to compare the data to the prediction of the Langmuir model:

$$\frac{1}{V_{ads}} = \frac{1}{KV_m} \left(\frac{1}{P} \right) + \frac{1}{V_m}$$

A plot of $(V_{ads})^{-1}$ versus $(P)^{-1}$ is as follows:



Best fit to the data by a straight line yields the following equation:

$$\frac{1}{V} = 2.90 \times 10^{-3} \text{ torr g cm}^{-3} \left(\frac{1}{P} \right) + 0.642 \text{ g cm}^{-3}$$

The maximum adsorption volume is

$$\begin{aligned} V_m &= \frac{1}{y\text{-int}} \\ &= \frac{1}{0.642 \text{ g cm}^{-3}} \\ &= 1.56 \text{ cm}^3 \text{ g}^{-1} \end{aligned}$$

The K value is

$$\begin{aligned} K &= \frac{1}{slope(V_m)} \\ &= \frac{1}{(2.9 \times 10^{-3} \text{ torr g cm}^{-3})(1.56 \text{ cm}^3 \text{ g})} \\ &= 221 \text{ torr}^{-1} \end{aligned}$$

P37.25) Many surface reactions require the adsorption of two or more different gases. For the case of two gases, assuming that the adsorption of a gas simply limits the number of surface sites available for adsorption, and derive expressions for the fractional coverage of each gas.

If we assume that the only effect of the gases is to limit the number of sites available for adsorption, then the Langmuir model yields the two following relationships:

$$k_{d1}\theta_1 = k_{a1}P_1(1-\theta_1-\theta_2)$$

$$k_{d2}\theta_2 = k_{a2}P_2(1-\theta_1-\theta_2)$$

Where k_a , k_d , and θ are the rate of adsorption, desorption, and fractional coverage, respectively. In addition, the subscript denotes either gas 1 or 2 in the two gas mixture. The two equations can be solved to yield θ_1 and θ_2 as follows:

$$\theta_1 = \frac{K_1 P_1}{1 + K_1 P_1 + K_2 P_2}$$

$$\theta_2 = \frac{K_2 P_2}{1 + K_1 P_1 + K_2 P_2}$$

P37.26) Sunburn is caused primarily by sunlight in what is known as the UVB band, or the wavelength range from 290 to 320 nm. The minimum dose of radiation needed to create a sunburn (erythema) is known as an MED (minimum erythema dose). The MED for a person of average resistance to burning is 50 mJ cm^{-2} .

- a) Determine the number of 290-nm photons corresponding to the MED assuming each photon is absorbed. Repeat this calculation for 320-nm photons.
- b) At 20° latitude, the solar flux in the UVB band at the surface of the earth is 1.45 mW cm^{-2} . Assuming that each photon is absorbed, how long would a person with unprotected skin be able to stand in the sun before acquiring one MED?

a) The energy released by n photons is given as

$$E = \frac{nhc}{\lambda}$$

$$n = \frac{E\lambda}{hc}$$

For $\lambda = 290 \text{ nm}$

$$n = \frac{(50 \times 10^{-3} \text{ J}) (290 \times 10^{-9} \text{ m})}{(6.626 \times 10^{-34} \text{ J s}) (3.00 \times 10^8 \text{ m s}^{-1})}$$

$$= 7.29 \times 10^{16} \text{ photons cm}^{-2}$$

For $\lambda = 320 \text{ nm}$

$$n = \frac{(50 \times 10^{-3} \text{ J})(320 \times 10^{-9} \text{ m})}{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m s}^{-1})}$$

$$= 8.05 \times 10^{16} \text{ photons cm}^{-2}$$

b) Assuming an average person – 1 MED = 50 mJ cm⁻², the MED is equal to the solar flux times a unit of time

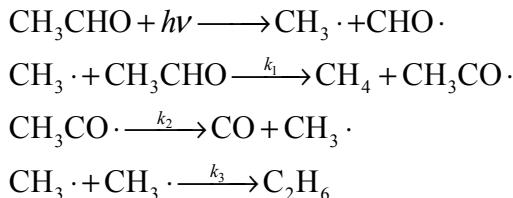
$$\text{MED} = \Phi \cdot t$$

$$t = \frac{\text{MED}}{\Phi}$$

$$= \frac{50 \text{ mJ cm}^{-2}}{1.45 \text{ mJ s}^{-1} \text{cm}^{-2}}$$

$$= 34.5 \text{ s}$$

P37.27) A likely mechanism for the photolysis of acetaldehyde is



Derive the rate law expression for the formation of CO based on this mechanism.

$$\text{The rate is } \frac{d[\text{CO}]}{dt} = k_2 [\text{CH}_3\text{CO}]$$

Applying the steady-state approximation to [CH₃] and [CH₃CO]

$$\frac{d[\text{CH}_3]}{dt} = 0 = I\sigma_{\text{CH}_3\text{CHO}} [\text{CH}_3\text{CHO}] - k_1 [\text{CH}_3][\text{CH}_3\text{CHO}] + k_2 [\text{CH}_3\text{CO}] - 2k_3 [\text{CH}_3]^2$$

$$\frac{d[\text{CH}_3\text{CO}]}{dt} = 0 = k_1 [\text{CH}_3][\text{CH}_3\text{CHO}] - k_2 [\text{CH}_3\text{CO}]$$

Adding the last two equations yields:

$$I\sigma_{\text{CH}_3\text{CHO}} [\text{CH}_3\text{CHO}] = 2k_3 [\text{CH}_3]^2$$

$$\left(\frac{I\sigma_{\text{CH}_3\text{CHO}} [\text{CH}_3\text{CHO}]}{2k_3} \right)^{1/2} = [\text{CH}_3]$$

And using the steady-state expression for [CH₃CO] in the rate expression for CO production results in the following:

$$\begin{aligned}
 \frac{d[\text{CO}]}{dt} &= k_2 [\text{CH}_3\text{CO}] \\
 &= k_1 [\text{CH}_3][\text{CH}_3\text{CHO}] \\
 &= k_1 \left(\frac{I\sigma_{\text{CH}_3\text{CHO}} [\text{CH}_3\text{CHO}]}{2k_3} \right)^{1/2} [\text{CH}_3\text{CHO}] \\
 &= k_1 \left(\frac{I\sigma_{\text{CH}_3\text{CHO}}}{2k_3} \right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}
 \end{aligned}$$

P37.28) If $\tau_f = 1 \times 10^{-10}$ s and $k_{ic} = 5 \times 10^8$ s⁻¹, what is ϕ_f ? Assume that the rate constants for intersystem crossing and quenching are sufficiently small that these processes can be neglected.

Φ_f is related to k_f and τ_f by the expression

$$\Phi_f = k_f \tau_f$$

and k_f is related to τ_f by

$$\frac{1}{\tau_f} = k_f + k_{ic} \quad (\text{assuming } k_{isc}^3, k_7 \approx 0)$$

$$\tau_f = 1 \times 10^{-10} \text{ s} \quad \text{and} \quad k_{ic} = 5 \times 10^8 \text{ s}^{-1}$$

Thus

$$\frac{1}{1 \times 10^{-10} \text{ s}} = k_f + 5 \times 10^8 \text{ s}^{-1}$$

and

$$k_f = 1 \times 10^{10} \text{ s}^{-1} - 5 \times 10^8 \text{ s}^{-1}$$

$$k_f = 9.5 \times 10^9 \text{ s}^{-1}$$

And finally,

$$\begin{aligned}
 \Phi_f &= k_f \tau_f \\
 &= 9.5 \times 10^9 \text{ s}^{-1} \cdot 1 \times 10^{-10} \\
 &= 0.95
 \end{aligned}$$

P37.29) The quantum yield for CO production in the photolysis of gaseous acetone is unity for wavelengths between 250 and 320 nm. After 20 min of irradiation at 313 nm, 18.4 cm³ of CO (measured at 1008 Pa and 22°C) is produced. Calculate the number of photons absorbed, and the absorbed intensity in J s⁻¹.

The number of moles of CO is calculated using the ideal gas law:

$$n = \frac{(1008 \text{ Pa}) \left(\frac{1 \text{ atm}}{1.013 \times 10^5 \text{ Pa}} \right) (0.0184 \text{ L})}{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(295 \text{ K})}$$

$$= 7.50 \times 10^{-6} \text{ mol}$$

This corresponds to 4.55×10^{18} molecules or 4.55×10^{18} photons that have resulted in reaction.

The intensity is then determined by:

$$I = \frac{E}{t} = \frac{nhc}{\lambda t} = \frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m s}^{-1})(4.55 \times 10^{18})}{(393 \times 10^{-9} \text{ m})(20 \text{ min})} \left(\frac{1 \text{ min}}{60 \text{ sec}} \right)$$

$$I = 2.41 \times 10^{-3} \text{ J s}^{-1}$$

P37.30) If 10% of the energy of a 100-W incandescent bulb is in the form of visible light having an average wavelength of 600 nm, how many quanta of light are emitted per second from the light bulb?

Assuming that 10% of energy from the bulb is in the form of visible light, the power of the light is given by:

$$P_e = 0.1(P)$$

$$= 0.1(100 \text{ W})$$

$$= 10 \text{ J s}^{-1}$$

The energy per photon at 600 nm is:

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m s}^{-1})}{600 \times 10^{-9} \text{ m}} = 3.31 \times 10^{-19} \text{ J}$$

Therefore, the number of photons per second is given by:

$$n = \frac{10 \text{ J s}^{-1}}{3.31 \times 10^{-19} \text{ J photon}^{-1}} = 3.02 \times 10^{19} \text{ photon s}^{-1}$$

P37.31) For phenanthrene, the measured lifetime of the triplet state (τ_p) is 3.3 s, the fluorescence quantum yield is 0.12, and the phosphorescence quantum yield is 0.13 in an alcohol-ether class at 77 K. Assume that no quenching and no internal conversion from the singlet state occurs. Determine k_p , k_{isc}^T , and k_{isc}^S/k_r .

Assuming no quenching or internal conversion, then

$$\Phi_p = \frac{k_p}{k_p + k_{ISC}^T} \quad \text{and} \quad k_p \tau_p = \Phi_p$$

$$\Phi_f = \frac{k_f}{k_f + k_{ISC}^S} = \frac{1}{1 + \frac{k_{ISC}^S}{k_f}}$$

Since $\Phi_f = 0.12$, then

$$\frac{k_{ISC}^S}{k_f} = \frac{1}{\Phi_f} - 1$$

$$= \frac{1}{0.12} - 1$$

$$= 7.33$$

Since $\Phi_p = 0.13$ and $\tau_p = 3.35$, then

$$k_p = \frac{\Phi_p}{\tau_p} = \frac{0.13}{3.35 \text{ s}}$$

$$k_p = 3.88 \times 10^{-2} \text{ s}^{-1}$$

Now

$$k_{ICS}^T = \frac{k_p}{\Phi_p} - k_p$$

$$= \frac{3.88 \times 10^{-2} \text{ s}^{-1}}{0.13} - 3.88 \times 10^{-2} \text{ s}^{-1}$$

$$k_{ics}^T = 0.260 \text{ s}^{-1}$$

P37.32) In this problem you will investigate the parameters involved in a single-molecule fluorescence experiment. Specifically, the incident photon power needed to see a single molecule with a reasonable signal-to-noise ratio will be determined.

- a) Rhodamine dye molecules are typically employed in such experiments because their fluorescence quantum yields are large. What is the fluorescence quantum yield for Rhodamine B (a specific rhodamine dye) where $kr = 1 \times 10^9 \text{ s}^{-1}$ and $k_{ic} = 1 \times 108 \text{ s}^{-1}$? You can ignore intersystem crossing and quenching in deriving this answer.
- b) If care is taken in selecting the collection optics and detector for the experiment, a detection efficiency of 10% can be readily achieved. Furthermore, detector dark noise usually limits these experiments, and dark noise on the order of 10 counts s^{-1} is typical. If we require a signal-to-noise ratio of 10:1, then we will need to detect 100 counts s^{-1} . Given the detection efficiency, a total emission rate of 1000 fluorescence photons s^{-1} is required. Using the fluorescence quantum yield and a molar extinction coefficient for Rhodamine B of $\sim 40,000 \text{ M}^{-1} \text{ cm}^{-1}$, what is the intensity of light needed in this experiment in terms of photons $\text{cm}^{-2} \text{ s}^{-1}$?
- c) The smallest diameter focused spot one can obtain in a microscope using conventional refractive optics is one-half the wavelength of incident light. Studies of Rhodamine B generally employ 532-nm light such that the focused-spot diameter is $\sim 270 \text{ nm}$. Using this diameter, what incident power in watts is required for this experiment? Don't be surprised if this value is relatively modest.

a) $k_f = 1 \times 10^9 \text{ s}^{-1}$ and $k_K = 1 \times 10^8 \text{ s}^{-1}$

Assuming no intersystem crossing and quenching, then

$$\begin{aligned}\Phi_f &= \frac{k_f}{k_f + k_{ic}} \\ &= \frac{1 \times 10^9 \text{ s}^{-1}}{1 \times 10^9 \text{ s}^{-1} + 1 \times 10^8 \text{ s}^{-1}} \\ &= 0.91\end{aligned}$$

b) Excitation rate constant required given the signal to noise constraints and the fluorescence quantum yield is:

$$\begin{aligned}k_{abs} &= \frac{1000 \text{ photons s}^{-1}}{0.91} \\ &= 1100 \text{ photons s}^{-1}\end{aligned}$$

The excitation rate constant is equal to the product of light intensity and the absorption cross section with the later determined using the molar extinction coefficient:

$$k_{abs} = I \sigma_A$$

$$1100 \text{ photons s}^{-1} = I \left(\frac{2303(40,000) \text{ cm}^2 \text{ mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \right)$$

$$1100 \text{ photons s}^{-1} = I(1.53 \times 10^{-16} \text{ cm}^2)$$

$$7.19 \times 10^{18} \text{ photons cm}^{-2} \text{ s}^{-1} = I$$

c) The focused spot size is:

$$area = \pi \left(\frac{2.70 \times 10^{-5} \text{ cm}}{2} \right)^2 = 5.72 \times 10^{-10} \text{ cm}^2$$

Multiplying the required intensity by this area yields the required power in terms of photons s^{-1} :

$$\begin{aligned}P &= I(area) = 7.19 \times 10^{18} \text{ photons cm}^{-2} \text{ s}^{-1} (5.72 \times 10^{-10} \text{ cm}^2) \\ &= 4.11 \times 10^9 \text{ photons s}^{-1}\end{aligned}$$

At 532 nm, the energy per photon is:

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m s}^{-1})}{532 \times 10^{-9} \text{ m}} = 3.74 \times 10^{-19} \text{ J photon}^{-1}$$

Therefore, the power in Watts is:

$$\begin{aligned}P &= 4.11 \times 10^9 \text{ photons s}^{-1} (3.74 \times 10^{-19} \text{ J photon}^{-1}) \\ &= 1.53 \times 10^{-9} \text{ W} = 1.53 \text{ nW}\end{aligned}$$

P37.33) A central issue in the design of aircraft is improving the lift of aircraft wings. To assist in the design of more efficient wings, wind-tunnel tests are performed in which the pressures at various parts of the wing are measured generally using only a few localized pressure sensors. Recently, pressure-sensitive paints have been developed to provide a more detailed view of wing pressure. In these paints, a luminescent molecule is dispersed into a oxygen-permeable paint and the aircraft wing is painted. The wing is placed into an airfoil, and luminescence from the paint is measured. The variation in O₂ pressure is measured by monitoring the luminescence intensity, with lower intensity demonstrating areas of higher O₂ pressure due to quenching.

a) The use of platinum octaethylporphyrin (PtOEP) as an oxygen sensor in pressure-sensitive paints was described by Gouterman and coworkers [*Review of Scientific Instruments* 61 (1990), 3340]. In this work, the following relationship between

luminescence intensity and pressure was derived: $\frac{I_0}{I} = A + B\left(\frac{P}{P_0}\right)$, where I_0 is the fluorescence intensity at ambient pressure P_0 , and I is the fluorescence intensity at an arbitrary pressure P . Determine coefficients A and B in the preceding expression using the Stern–Volmer equation: $k_{total} = \frac{1}{\tau_l} = k_l + k_q [Q]$. In this equation τ_l is the

luminescence lifetime, k_l is the luminescent rate constant, and k_q is the quenching rate constant. In addition, the luminescent intensity ratio is equal to the ratio of luminescence quantum yields at ambient pressure, Φ_0 , and an arbitrary pressure, Φ : $\frac{\Phi_0}{\Phi} = \frac{I_0}{I}$.

b) Using the following calibration data of the intensity ratio versus pressure observed for PtOEP, determine A and B :

I_0/I	P/P_0	I_0/I	P/P_0
1.0	1.0	0.65	0.46
0.9	0.86	0.61	0.40
0.87	0.80	0.55	0.34
0.83	0.75	0.50	0.28
0.77	0.65	0.46	0.20
0.70	0.53	0.35	0.10

c) At an ambient pressure of 1 atm, $I_0 = 50,000$ (arbitrary units) and 40,000 at the front and back of the wing. The wind tunnel is turned on to a speed of Mach 0.36 and the measured luminescence intensity is 65,000 and 45,000 at the respective locations. What is the pressure differential between the front and back of the wing?

a) Starting with the version of the Stern-Volmer Eq. provided in the problem:

$$k_{tot} = k_l + k_q [Q]$$

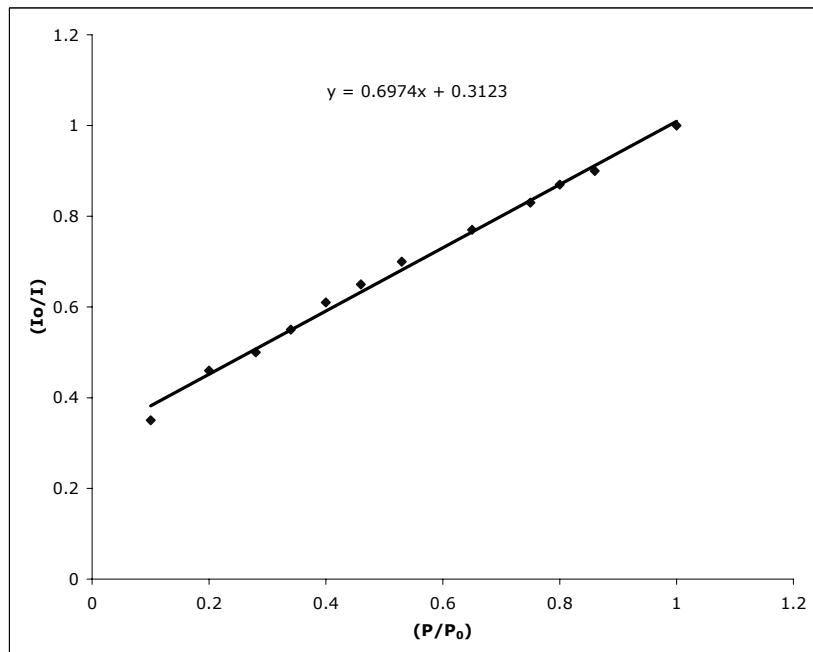
The luminescence quantum yield can be expressed in terms of k_l and k_{total} as:

$$\Phi = \frac{k_l}{k_{total}}$$

Therefore:

$$\begin{aligned}\frac{\Phi_0}{\Phi} &= \frac{k_{total}}{k_{total_0}} \\ &= \frac{k_l + k_q P}{k_l + k_q P_0} \\ &= \frac{k_l}{k_l + k_q P_0} + \frac{k_q P_0}{k_l + k_q P_0} \left(\frac{P}{P_0} \right) \\ &= A + B \left(\frac{P}{P_0} \right)\end{aligned}$$

b) The plot of (I_0/I) versus (P/P_0) is as follows:



Best fit by a straight line to the data yields the following equation:

$$\frac{I_0}{I} = 0.697 \left(\frac{P}{P_0} \right) + 0.312$$

Thus, $A = 0.312$ and $B = 0.697$.

c)

$$\begin{aligned} \left(\left(\frac{I_0}{I} \right)_{front} - \left(\frac{I_0}{I} \right)_{back} \right) &= 0.697 \left(\frac{P_{front} - P_{back}}{P_0} \right) \\ \left(\frac{50,000}{65,000} - \frac{40,000}{45,000} \right) &= 0.697 \left(\frac{P_{front} - P_{back}}{1 \text{ atm}} \right) \\ -0.120 &= 0.697 \left(\frac{P_{front} - P_{back}}{1 \text{ atm}} \right) \\ -0.172 \text{ atm} &= P_{front} - P_{back} \end{aligned}$$

P37.34) Oxygen sensing is important in biological studies of many systems. The variation in oxygen content of sapwood trees was measured by del Hierro and coworkers [*J. Experimental Biology* 53 (2002), 559] by monitoring the luminescence intensity of $[\text{Ru(dpp)}_3]^{2+}$ immobilized in a sol-gel that coats the end of an optical fiber implanted into the tree. As the oxygen content of the tree increases, the luminescence from the ruthenium complex is quenched. The quenching of $[\text{Ru(dpp)}_3]^{2+}$ by O_2 was measured by Bright and coworkers [*Applied Spectroscopy* 52 (1998), 750] and the following data were obtained:

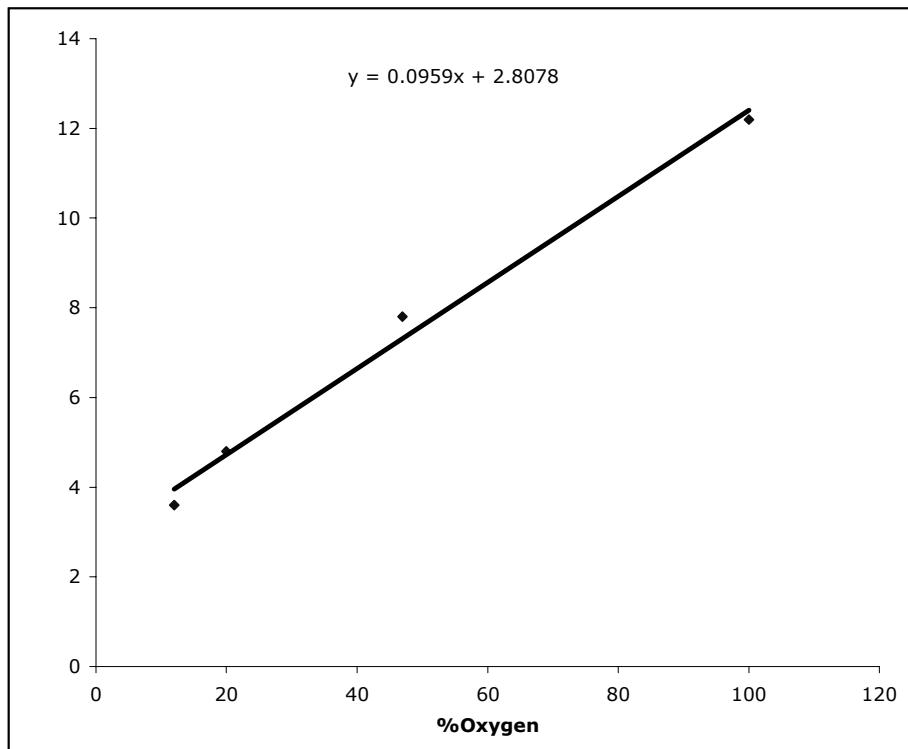
I_0/I	% O_2
3.6	12
4.8	20
7.8	47
12.2	100

- Construct a Stern–Volmer plot using the data supplied in the table. For $[\text{Ru(dpp)}_3]^{2+}$, $k_r = 1.77 \times 10^5 \text{ s}^{-1}$, what is k_q ?
- Comparison of the Stern–Volmer prediction to the quenching data led the authors to suggest that some of the $[\text{Ru(dpp)}_3]^{2+}$ molecules are located in sol-gel environments that are not equally accessible to O_2 . What led the authors to this suggestion?

The Stern–Volmer plot of interest is of the form:

$$\frac{I_0}{I} = k_l + k_q [\text{O}_2]$$

Therefore, a plot of the intensity ratio versus % O_2 should yield a straight line:



Although the data are fairly well fit by a straight line, there is noticeable curvature of the data. This curvature led the authors to suggest that more than one environment may be present.