CHEM 3610 Lecture Notes

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COURSE ADMINISTRATIVE DETAILS

- My office hours

- Intro to my research

- Introductory Quiz

- Grading details

    · Exams - 40, Final - 15, Quizzes - 15, Homework - 30
    · Homework
    · Quizzes

- Importance of reading and learning on your own

- Learning resources

    · My Office Hours
    · Tutoring services - https://www.suu.edu/academicsuccess/tutoring/

- Show how to access Canvas

    · Calendar, Grades, Modules, etc.
    · Zoom, etc.

TEXTBOOK ERRATA

Chapter 1

- p. 42 – In Brief illustration 1B.2 the v_{rms} is used where v_{mean} should be

- p. 46 – $Z = \dfrac{RT}{pV_m^\circ}$ in the paragraph between equations 1C.1 and 1C.2 is wrong. The expression for the molar volume of an ideal gas was erroneously substituted into the real gas molar volume

Chapter 2

- p.86 – Equations 2C.6 and 2C.7a both should have "...$= H(T_1)$..." instead of "...$= H(T_2)$..."

Chapter 5

- p.203 – Equation 5C.4 should be: $y_A = \dfrac{\chi_A p_A^\star}{p_B^\star + (p_A^\star - p_B^\star)\chi_A} = 1 - y_B$

THE PROPERTIES OF GASES

1A   The Perfect Gas

Variables of State

- Gases are composed of particles moving freely through space

- Gas particles interact only weakly, and only near the point of collision

- Collisions can explain all of the observed gas properties (such as temperature and pressure)

- Variables of state:

    - Pressure (p)
        - Pressure is the force a gas exerts on its surroundings (chamber walls)
        - Pressure can be measured by a barometer, manometer, or other gauge
        - Volume will change unless the pressure is in mechanical equilibrium with another force
    - Temperature (T)
        - Temperature is a measure of the kinetic energy of the gas particles
        - A perfect gas can be used to determine the *thermodynamic temperature scale*
        - This scale (called "Kelvin") relates to Celsius by: $T_K = T_{\circ C} - 273.15$ (exact)
    - Volume (V)
    - Moles (n) – The number of moles of gas particles in a particular gas sample

Equations of State

- An equation of state relates all of the state variables for a gas

- Developing the perfect gas equation of state:

    - By keeping one variable (plus n) fixed, the relationship between the other two can be determined (isotherms, isochores, and isobars)
    - Boyle's Law: $p \propto \dfrac{1}{V}$ at constant n, T
    - Charles's Law: $V \propto T$ at constant n, p
    - Avogardro's Principle: $V \propto n$ at constant T, p

- The same proportionality constant consistently appears: The gas constant R

- The gas constant can also be related to the Boltzmann constant: $R = N_A k_B$

- Combining these relations gives the perfect gas law: $pV = nRT$

- For mixtures of perfect gases, each gas exerts a partial pressure as if the others were not present

- This is Dalton's law of partial pressures: $p_{Total} = \sum \chi_i p_i$

1B   The Kinetic Model

Pressure and Molecular Speeds

- The kinetic-molecular theory of gases explains gas properties solely through elastic collisions of gas particles

- Despite being remarkably simple, kinetic theory accurately describes almost all physical properties and processes a gas can exhibit.

- This theory has three main assumptions:

  · A gas is composed of molecules in random ceaseless motion

  · The size of the molecules is negligible

  · All molecular collisions are elastic (translational kinetic energy is conserved)

- Pressure can be determined by analyzing the momentum transferred to the walls of a container through molecular collisions

- This approach also leads to the perfect gas law in a different form: $pV = \dfrac{1}{3} n M v_{rms}^2$

- Here, M is the molar molecular mass and $v_{rms} = \langle v^2 \rangle^{1/2}$

- Comparing this to the perfect gas law gives the relation: $v_{rms} = \left(\dfrac{3RT}{M} \right)^{1/2}$

The Maxwell-Boltzmann Distribution of Speeds

- In a ensemble of molecules, not all of them will have the average velocity

- Determining the distribution of speeds was a tour-de-force for Boltzmann and Maxwell, and one of the first applications of statistical mechanics

- For a perfect gas: $f(v) = 4\pi \left(\dfrac{M}{2\pi RT} \right)^{3/2} v^2 e^{\frac{-Mv^2}{2RT}}$

- Figure 1B.4 compares the velocity distributions of molecules of different sizes and at different temperatures

Mean Values

- Mean Speed: $v_{mean} = \left(\dfrac{8RT}{\pi M}\right)^{1/2} = \left(\dfrac{8}{3\pi}\right)^{1/2} v_{rms}$

- Most Probable Speed: $v_{mp} = \left(\dfrac{2RT}{M}\right)^{1/2} = \left(\dfrac{2}{3}\right)^{1/2} v_{rms}$

- Mean Relative Speed (Similar Particles): $v_{rel} = \sqrt{2}\, v_{mean}$

- Mean Relative Speed (Different Particles): $v_{rel} = \left(\dfrac{8RT}{\pi \mu}\right)^{1/2} \qquad \mu = \dfrac{M_A M_B}{M_A + M_B}$

Collisions

- Figure 1B.8 provides a framework for evaluating collisions

- σ, the collision cross-section, for some common gases is given in Table 1B.2 (For N_2, $\sigma = 0.43\, nm^2$)

- This gives the collision frequency as: $z = \sigma v_{rel} \mathcal{N} \qquad \mathcal{N} = \dfrac{N}{V} = \dfrac{pN_A}{RT} = \dfrac{p}{k_B T}$

- The mean free path (λ) is the average distance a particle travels between collisions

- $\lambda = \dfrac{v_{rel}}{z} = \dfrac{k_B T}{\sigma p} \qquad$ Note that for unit cancellation, p should be in Pa

1C   Real Gases

Deviations from Perfect Behavior

- Real gases interact with each other through both attractions and repulsions

- Under different circumstances, either of the two effects can dominate

- Attractions give a lower pressure than a perfect gas, while repulsions give a higher pressure than a perfect gas

- Figure 1C.1 shows the potential curve which is relevant as particles approach and collide

- At low pressures, the attractive portion of the potential dominates and the gases are more easily compressed

- At high pressures, the repulsive portion of the potential dominates and gases are more difficult to compress

- The potential curve will come up again soon in an unusual way, with respect to the Joule-Thompson coefficient

○ Examine the path from A → F in Figure 1C.2

· For A → B, the gas behaves like a perfect gas

· For B → C, the gas deviates from a perfect gas, requiring more pressure to compress the gas

· For C → E, the gas compresses with no additional pressure increase. During this period, the gas is actually condensing out as a liquid. The gas phase remains the same, but through the compression it comprises a smaller and smaller fraction of the whole, with the liquid phase growing

· For E → F, only liquid phase remains, and liquids are very incompressible

○ Figure 1C.2 contains a few more interesting points:

· Low temperature isotherms intersect with the blue region at the vapor pressure for that temperature

· $31.1°C$ is the *critical* isotherm, the warmest isotherm which can exhibit liquid and gas co-existing in equilibrium

· Supercritical fluids are shown above the critical pressure and critical temperature

○ The *compression factor* (Z) is a convenient way to characterize a gases deviation from perfect gas behavior

· $Z = \dfrac{V_m}{V_m^\circ}$

· $pV_m = RTZ$

· Figure 1C.3 shows hows how Z varies with pressure for different gases

· This behavior $(Z > 1 \text{ vs } Z < 1)$ can be explained by the relative importance of the repulsive and attractive portions of the potential curve

· Table 1C.2 shows how different gases have a similar compression factor at the critical point, even if their critical constants vary widely

The Virial Equation

○ A mathematical model for the compression factor could give us a reliable equation of state

○ One approach is to expand Z as a power series with respect to one of the state variables:

· $pV_m = RT\left(1 + B'p + C'p^2 + \cdots\right)$

· $pV_m = RT\left(1 + \dfrac{B}{V_m} + \dfrac{C}{V_m^2} + \cdots\right)$ (More Common)

○ These are different forms of the *Virial Equation*

○ The expansion could in principle be expanded indefinitely but in practice is limited to only the B or sometimes also the C terms

○ Table 1C.1 gives the B virial coefficient for several gases and two temperatures

○ The *Boyle temperature* is the temperature at which the second Virial coefficient (B) is zero

○ This temperature exhibits behavior closest to that of a perfect gas over the widest ranges of pressure

The Van der Waals Equation of State

○ The Virial equation makes sense mathematically, but is not easily related to specific properties of real gases

○ Van der Waals (in 1873) proposed an equation which explicitly considered both the attractive forces and finite volume of real gas particles

○ The van der Waals equation: $p = \dfrac{nRT}{V - nb} - a\dfrac{n^2}{V^2}$

○ In this equation, b accounts for the size of the gas particles, and a accounts for the attractive forces

○ To be clear, a and b are strictly empirical constants, but they very closely map on to these physical properties

○ Table 1C.3 shows van der Waals coefficients for a variety of gases

○ There are other equations of state, each with strengths and weaknesses

The Principle of Corresponding States

○ The compression factor of different gases is similar at the critical point

○ Using reduced state variables, gases give similar compression factors at all states

     · $V_r = \dfrac{V_m}{V_c}$

     · $p_r = \dfrac{p}{p_c}$

     · $T_r = \dfrac{T}{T_c}$

○ The van der Waals equation can be expressed in terms of reduced variables, and represent all gases simultaneously

○ Reduced van der Waals equation: $p_r = \dfrac{8T_r}{3V_r - 1} - \dfrac{3}{V_r^2}$

THE FIRST LAW

○ The first law of thermodynamics states that energy can be neither created nor destroyed, but only change form or transfer between systems

2A   Internal Energy

Terms and Definitions

○ When considering thermodynamic potentials, the universe is split into *system* and *surroundings*

○ We must further define the interactions which can occur between the system and surroundings

Open System: Energy and matter can transfer between system and surroundings

Closed System: Only energy can transfer between system and surroundings

Isolated System: Neither energy nor matter can transfer between system and surroudnings

○ Energy can transfer as either heat or work, so boundaries can come in two different varieties as well

Diathermic: Boundaries which can transfer heat

Adiabatic: Boundaries which do not transfew heat

○ And lastly, processes come in two varieties

Exothermic: A process which releases heat into the surroundings

Endothermic: A process which takes heat in from the surroundings

Developing the First Law

○ *Internal Energy* is the total energy of a system

○ Internal energy is a state function, which depends only on state variables of a system and not on its past processes or the state of the surroundings

○ Internal energy can be reported either as a total (extensive property) or molar (intensive property) amount

○ Generally, internal energy can include both kinetic and potential energy

○ The *equipartition theory* states that at equilibrium the kinetic energy will be shared equally between all degrees of freedom

- Each degree of freedom will hold $\frac{1}{2}RT$ units of energy per mole

- For a monoatomic perfect gas, internal energy can be easily analyzed

    - With no interactions, the perfect gas has no potential energy

    - There are also no vibrations or rotations, so tranlation is the only component of kinetic energy

    - The average translational kinetic energy in an ensemble of gas molecules is: $\frac{3}{2}k_BT$ for an individual molecule, or $\frac{3}{2}RT$ per mole

    - Note that the internal energy is independent of both p and V

- For a linear diatomic at room temperature (2 rotations added), $U_m = \frac{5}{2}RT$

- Mathematically, the first law can be stated as: $\Delta U = q + w$

- Considering infinitesimal changes gives: $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$

Work

- Generally, we can express work as force times distance: $\mathrm{d}w = -|F|\,\mathrm{d}z$

- Table 2A.1 shows the equations for several forms of work

- For gas expansion work this becomes: $\mathrm{d}w = -p_{ex}\mathrm{d}V$

- The total work is: $w = -\displaystyle\int_{V_i}^{V_f} p_{ex}\mathrm{d}V$

- It is important to note that the pressure here is the *external* pressure. This is true whether $\Delta V < 0$ or $\Delta V > 0$

- Indicator diagrams (p vs V) are useful when analyzing changes in gas states

- Free expansions have no external pressure, and so involve no work

- Infinitesimal changes in the state variables make any change *reversible*, but mostly we are concerned with two particular reversible processes

- Isothermal Reversible Expansion:

    - For the process to be reversible, $p_{ex} = p$
    - This allows us to replace $w = -\displaystyle\int_{V_i}^{V_f} p_{ex}\mathrm{d}V$ with $w = -nRT \displaystyle\int_{V_i}^{V_f} \frac{\mathrm{d}V}{V} = -nRT \ln \frac{V_f}{V_i}$

- Adiabatic Reversible Expansion: These are a little more complex to analyze and are covered in section 2E

Heat

○ On the molecular level, work can be seen as coordinate motion of the gas particles. Heat, on the other hand, represents a change in the velocities of *random*, undirected particle motion

○ In the absence of work (isochoric gas processes), $\int_i^f \mathrm{d}U = \int_i^f \mathrm{d}q_V$

○ Constant volume calorimeters ("bomb calorimeters") take advantage of this fact to relate internal energy changes to measured temperature changes

○ For a bomb calorimeter: $q = -C\Delta T$, where C is a calibrated heat capacity

○ Heat capacity at constant volume is defined as $C_V = \left(\dfrac{\partial U}{\partial T}\right)_V$

○ For a monoatomic perfect gas this gives: $C_{V,m} = \dfrac{\partial}{\partial T}\left(\dfrac{3}{2}RT\right)_V = \dfrac{3}{2}R = 12.47\dfrac{J}{mol\ K}$

○ And the heat at constant volume is: $q_V = C_V\Delta T = \Delta U_V$

2B   Enthalpy

○ When the volume is no longer constant, internal energy is no longer easy to measure or useful in determining spontaneity

○ Under constant pressure conditions, *enthalpy* takes the place of internal energy in both respects

○ Enthalpy is also a state function, and makes our second *Thermodynamic Potential*

○ $H = U + pV$

○ $\mathrm{d}H = \mathrm{d}U + \mathrm{d}(pV)$ can be simplified in constant pressure to $\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V$

○ Since $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$, if only expansion work is involved then it can be further simplified to $\mathrm{d}H = \mathrm{d}q_p$

○ Enthalpy can be measured with an *isobaric* (coffee-cup) calorimeter

○ $\Delta H = -C\Delta T$, where C is a calibrated heat capacity

○ ΔH can also be related to ΔU

   · For solids and liquids, $p\Delta V_m$ is often very small so $\Delta H \approx \Delta U$

   · For gases, $\Delta H \approx \Delta U + \Delta n_{gas}RT$

○ Constant pressure heat capacity: $C_p = \left(\dfrac{\partial H}{\partial T}\right)_p$ and $\Delta H_p = C_p\Delta T$

○ Isobaric heat capacity is a function of temperature, as different energetic degrees of freedom become available at higher temperature

○ An common empirical equation for C_p is: $C_{p,m} = a + bT + \dfrac{c}{T^2}$

○ For a perfect gas, $C_p = C_V + nR$ and $C_{p,m} = C_{V,m} + R$

2C   Thermochemistry

Standard Enthalpy Changes

○ Studying the flow of energy through the course of a reaction is called thermochemistry

○ Values in thermochemistry are often referenced to a *standard state*, defined as $p = 1 \, bar$ for gases

○ Other phases, mixtures, etc. have different standard state definitions, but they are all notated with the symbol: $^{\ominus}$

○ For example, the standard enthalpy of vaporization for water would be:

$\text{H}_2\text{O(l)} \longrightarrow \text{H}_2\text{O(g)} \qquad \Delta_{vap}H^{\ominus}(373 \, K) = 40.55 \, {kJ}/{mol}$

○ Because enthalpy is a state function, Hess's law applies

○ e.g. $\Delta_{sub}H^{\ominus} = \Delta_{fus}H^{\ominus} + \Delta_{vap}H^{\ominus}$

○ For a reaction, standard enthalpy change can be generally calculated as:

$$\Delta H^{\ominus} = \sum_{Products} \nu H_m^{\ominus} - \sum_{Reactants} \nu H_m^{\ominus}$$

○ Usually, however, finding molar enthalpies is not as convenient as using enthalpies related to some defined elemental state (enthalpies of formation)

Standard Enthalpies of Formation

○ For convenience, we define a reference state as an element at its most stable state and a pressure of $1 \, bar$

○ Compounds can be formed from that reference state, with a enthalpy of reaction called the standard enthalpy of formation: $\Delta_f H^{\ominus}$

○ One special exception is that for ionic solutions the hydrogen ion is also defined as a reference state $(\Delta_f H^{\ominus}(\text{H}^+, aq) = 0)$

○ We can imagine a reaction as breaking the reactants apart into their elements, then using them to form the products

○ Because enthalpy is a state function, it doesn't matter that this process is completely hypothetical

○ $\Delta_r H^{\ominus} = \sum_{Products} \nu \Delta_f H^{\ominus} - \sum_{Reactants} \nu \Delta_f H^{\ominus}$

Temperature Dependence of Reaction Enthalpies

- ○ When we have dealt with reaction enthalpies before, we have assumed that they are independent of temperature (e.g. $\Delta G = \Delta H - T\Delta S$)

- ○ The enthalpies of reactants and products will both increase with temperature, but not at the same rate

- ○ C_p describes how the enthalpy of a substance changes with temperature: $H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p \mathrm{d}T$

- ○ p.86 – Equations 2C.6 and 2C.7a both should have $= H(T_1)$ instead of $= H(T_2)$

- ○ Figure 2C.2 illustrates how the reaction enthalpy might change with temperature if C_p is different for reactants and products

- ○ This relation is summarized in Kirchoff's Law: $\Delta_r H^{\ominus}(T_2) = \Delta_r H^{\ominus}(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^{\ominus} \mathrm{d}T$

- ○ Note that this is the total change in heat capacity, taking into account the reaction stoichiometry:
$$\Delta_r C_p^{\ominus} = \sum_{Products} \nu C_p^{\ominus} - \sum_{Reactants} \nu C_p^{\ominus}$$

- ○ Even this approach is an approximation, as the heat capacities of individual substances can change with temperature

2D   State Functions and Exact Differentials

- ○ Changes in state functions can be found without dependance on the path from initial to final states

- ○ This is why the differential of a state function is called and *exact differential*: $\Delta U = \int_i^f \mathrm{d}U$

- ○ Other functions depend on the path and are called path functions

- ○ The differential of a path function is called an *inexact differential*: $q = \int_i^f đq$

- ○ The "đ" indicates that this is an inexact differential and a path integral

Changes in Internal Energy

- ○ Because internal energy is a function of both V and T: $\mathrm{d}U = \left(\dfrac{\partial U}{\partial V}\right)_T \mathrm{d}V + \left(\dfrac{\partial U}{\partial T}\right)_V \mathrm{d}T$

- ○ Note the natural variables of U, and reference the Wikipedia "Thermodynamic Potentials" page

○ Partial derivatives of natural variables yield state variables, but here we differentiate with respect to easily measurable V and T

○ Sometimes a partial derivative has a straightforward physical interpretation (such as C_p and C_V), and sometimes not

○ The *internal pressure* characterizes how internal energy changes with volume: $\pi_T = \left(\dfrac{\partial U}{\partial V}\right)_T$

○ So, the exact differntial is: $\mathrm{d}U = \pi_T \mathrm{d}V + C_V \mathrm{d}T$

○ Figures 2D.2 and 2D.3 illustrate what the exact and partial derivative mean

○ Note that while we use C_V in this expression, the differential is exact regardless of the conditions

○ At constant pressure we can get new equations which give us new physical constants:

○ The expansion coefficient: $\alpha = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_p$

○ The isothermal compressibility: $\kappa_T = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_T$

○ With some algebra, we finally arrive at: $\left(\dfrac{\partial U}{\partial T}\right)_p = \alpha \pi_T V + C_V$

○ And finally, we can (Justification 2D.1) get the general expression: $C_p - C_V = \dfrac{\alpha^2 T V}{\kappa_T}$

The Joule-Thompson Effect

○ We can examine the exact differential for enthalpy in a similar way:

$$\mathrm{d}H = \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T = -\mu C_p \mathrm{d}p + C_p \mathrm{d}T$$

○ μ is the Joule-Thompson coefficient, $\mu = \left(\dfrac{\partial T}{\partial p}\right)_H$

○ μ can be directly observed under *isenthalpic* conditions, as we will do next week in lab

○ $\mu > 0$ for most gases under standard conditions, but can become negative under certain conditions

○ Figures 2D.10 and 2D.11 show the heating and cooling regions in T/p space

○ The Joule-Thompson effect can be interpreted with respect to the exchange between potential and kinetic energy as gas molecules move farther apart in an expansion

2E   Adiabatic Changes

- We can find ΔU through a hypothetical two-step process shown in Figure 2E.1

    · First an isothermal expansion. For an ideal gas this process keeps U constant

    · Then an isochoric cooling. For any substance $\Delta U = C_V \Delta T$

- For an adiabatic process, there is no heat exhanged so $\delta U = w = C_V \Delta T$

- The temperature change can be found by: $V_i T_i^c = V_f T_f^c$ where $c = \dfrac{C_{V,m}}{R}$

- And the change in pressure is: $p_i V_i^\gamma = p_f V_f^\gamma$ where $\gamma = \dfrac{C_{p,m}}{C_{V,m}}$

THE SECOND AND THIRD LAWS

3A Entropy

Discovering and Defining Entropy

- The direction of spontaneous change is *not* always in the direction of lower energy

- Instead it relates to the distribution of energy, but understanding this concept will require the introduction f a new state variable, S

- You probably conceptualize S as a measure of disorder. This isn't wrong, but it is very different from how early physicists thought when discovering the second law

- Consider a bouncing ball (Figures 3A.1 and 3A.2):

    - Directed kinetic energy is converted into random thermal motion in the floor and air through friction and inelastic collisions

    - This process distributes the energy more widely, into more particles and more diverse energy modes

    - We wouldn't expect the random thermal motion of the floor to spontaneously transfer into a ball-at-rest as directed kinetic energy (i.e. the ball won't spontaneously bounce up from the floor)

    - Such a spontaneous coordination of the thermal energy would result in the floor getting colder, effectively converting thermal energy into work

- Kelvin's formulation of the second law (Figure 3A.3):

    No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

- This is actually synonymous with Clausius's formulation fo the second law (Figure 3A.4):

    Heat does not flow spontaneously from a cool body to a hotter body.

- To transfer heat in this way will always require an amount of work

- The thermodynamic definition of entropy is: $\mathrm{d}S = \dfrac{đq_{rev}}{T}$

- This definition came from studying heat engine cycles, and we will revisit it later, but for now suppose that it is true

- It is *essential* that you use the heat from an equivalent reversible process if the actual process is irreversible

○ For finding entropy change of the surroundings, you can use the actual heat since the surrounding are modeled as an infinite thermal reservoir

○ The statistical definition of entropy is: $S = k_B \ln \mathcal{W}$

○ $\mathcal{W}$ is the number of microstates available at a given temperature

○ Hard spheres gas simulation

Entropy as a State Function – Heat Engines

○ If entropy is truly a state function, then $\oint dS = \oint \frac{\text{đ}q_{rev}}{T} = 0$

○ Any arbitrary cycle can be approximated as a series of adiabats and isotherms (Figure 3A.10), so we need only consider those reversible processes

○ These reversible processes can combine in a heat engine cycle known as a *Carnot Cycle* (Figure 3A.7):

    · Walk through the heat engine process qualitatively

    · When considering the entropy of each step, the adiabats don't contribute because $q = 0$

    · The two isotherms take place at different temperatures, with heat entering the system during the isothermal expansion and leaving the system during the isothermal compression

    · $\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c}$

    · Assuming that the heat engine utilizes a perfect gas, we can prove the relation: $\frac{q_h}{q_c} = -\frac{T_h}{T_c}$

    · This proves that $\oint dS = 0$ and that entropy is therefore a state function

○ The next step is to prove that this result applies for any substance and not only for perfect gases

○ Define the engine efficiency: $\eta = \dfrac{\text{work performed}}{\text{heat absorbed from hot source}} = \dfrac{|w|}{|q_h|}$

○ Energy conservation dictates that $|w| = |q_h| - |q_c|$, so we can re-write the efficiency as: $\eta = 1 - \dfrac{T_c}{T_h}$

○ Now the efficiency of all reversible heat engines are equal, and greater than any non-reversible heat engines

○ This can be shown by using a heat engine to power a heat pump. If the efficiencies were different, then they could be configured to convert heat directly into work, contrary to the second law

○ This leads to the conclusion that the limits on efficiency apply regardless of configuration or working substance

- ○ By comparing the efficiency of a carnot heat engine with different temperatures, absolute zero can be extrapolated

  Let the hot source remain fixed, while decreasing the temperature of the cold sink, and extrapolate to the temperature which gives 100% efficiency

- ○ Ultimately, we can give the Clausius inequality: $dS \geq \dfrac{đq}{T}$

- ○ The equality holds only for reversible processes

Calculating Entropy Changes for Various Processes

- ○ Reversible Processes:

  - · For an isothermal process (on a perfect gas), $q = -w$ and $w = -nRT \ln \dfrac{V_f}{V_i}$, so $q = nRT \ln \dfrac{V_f}{V_i}$ and $\Delta S = nT \ln \dfrac{V_f}{V_i}$

  - · For a reversible adiabatic process, $q = 0$ so $\Delta S = 0$

  - · For a reversible isochoric process, $đq = C_V T$ so $\Delta S = \displaystyle\int \dfrac{đq}{T} = \int \dfrac{C_V}{T} dT$

  - · If C_V is independent of temperature over the relevant range it becomes $\Delta S = C_V \ln \dfrac{T_f}{T_i}$

  - · Reversible isobaric warming similarly gives $\Delta S = \int \dfrac{C_V}{T} dT = C_V \ln \dfrac{T_f}{T_i}$

  - · For arbitrary processes, since S is a state function we can model them as a combination of any two of the above

  - · Phase transitions *at the transition temperature* and constant pressure are: $\Delta_{trs} S = \dfrac{\Delta_{trs} H}{T_{trs}}$

  - · For reversible processes $\Delta_{surr} S = -\Delta_{sys} S$

- ○ Irreversible Processes:

  - · $\Delta_{surr} S = \displaystyle\int \dfrac{đ(-q_{sys})}{T_{surr}}$

  - · For ΔS_{sys}, model the change as reversible processes

  - · For example, an irreversible adiabatic free expansion can be modeled as an isotherm

  - · A phase change at a different temperature is modeled as an isobaric heating heating to T_{trs}, reversible phase change, and another isobaric heating to T_f

3B   The Measurement of Entropy

- ○ One way to find the absolute molar entropy of a substance is the calorimetric measurement of entropy

○ Essentially, you add up the integral of $\dfrac{C_p}{T}$ and the contribution from phase changes:

$$S_m(T) = S_m(0) + \int_0^T \frac{C_{P,m}(T)}{T}\mathrm{d}T + \sum_{transitions} \frac{\Delta_{trs}H}{T_{trs}}$$

○ Figure 3B.1 illustrates the integral in this expression

○ Heat capacities for solids near $T = 0$ are hard to directly measure, but can be modeled using the Debye approximation (extrapolating a cubic function)

○ The third law of thermodynamics states that $S_m(0) = 0$ for all perfect crystalline substances

○ We find $\Delta_{rxn}S$ entropies using Hess's law in the same way as $\Delta_{rxn}H$

3C   Concentrating on the System

○ Re-arranging the Claussius inequality gives us: $\mathrm{d}S - \dfrac{\mathrm{d}q}{T} \geq 0$

○ This is true for any spontaneous process, and it can be modified under specific conditions

  · For constant volume, $\mathrm{d}S - \dfrac{\mathrm{d}U}{T} \geq 0$ and $\mathrm{d}U - T\mathrm{d}S \leq 0$

  · For constant pressure, $\mathrm{d}S - \dfrac{\mathrm{d}H}{T} \geq 0$ and $\mathrm{d}H - T\mathrm{d}S \leq 0$

  · These expressions give a condition for spontanaety referring only to state variables!

○ We can now define new thermodynamic potentials:

  · Helmholtz energy: $A = U - TS$

  · Gibbs energy: $G = H - TS$

  · Conditions for spontanaety: $\mathrm{d}A_{T,V} \leq 0$ and $\mathrm{d}G_{T,p} \leq 0$

○ The tendency toward spontanaety for exothermic reactions has more to do with increasing the entropy of the surroundings than with the system seeking lower energy

○ The Helmholtz energy can also be shown to equal the maximum work possible for a process

○ Similarly, the Gibbs energy is the maximum non-expansion work possible for a process

○ In both cases, the maximum work is always less than the corresponding change in internal energy or enthalpy

○ When $\Delta A = 0$ or $\Delta G = 0$ for processes in equilibrium under the appropriate conditions

○ Like H and S, we use tables of $\Delta_f G$ but must be careful because these values are only applicable at $T = 298\ K$

3D   Combining the First and Second Laws

- ○ Recall that the exact differential of internal energy is: $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$

- ○ This expresses $\mathrm{d}U$ in terms of only state variables, and so is path independent

- ○ Mathematically, the exact differential of a state function gives rise to an important equality:

  - · For function $f(x, y)$, we can write $\mathrm{d}f = g\mathrm{d}x + h\mathrm{d}y$
  - · It can also be shown to be true that: $\left(\dfrac{\partial g}{\partial y}\right)_x = \left(\dfrac{\partial h}{\partial x}\right)_y$
  - · In the case of internal energy, this becomes: $\left(\dfrac{\partial T}{\partial V}\right)_S = -\left(\dfrac{\partial p}{\partial S}\right)_V$
  - · Table 3D.1 shows all the Maxwell relations

Properties of the Gibbs Energy

- ○ The differential form of Gibbs energy is: $\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T$ (From $G = H - TS$)

- ○ This gives us a few differentials: $\left(\dfrac{\partial G}{\partial T}\right)_p = -S$ and $\left(\dfrac{\partial G}{\partial p}\right)_T = V$

- ○ Figures 3D.2 and 3D.3 integrate these derivatives across T and p

- ○ The Gibbs-Helmholtz equation relates how entropy changes with temperature:

$$\left(\dfrac{\partial G/T}{\partial T}\right)_p = -\dfrac{H}{T^2}$$

- ○ This becomes particularly useful when relating energies of change: $\left(\dfrac{\partial \Delta G/T}{\partial T}\right)_p = -\dfrac{\Delta H}{T^2}$

- ○ Since the equilibrium composition depends on G, this equation tells how an equilibrium reaction might shift in response to a temperature change

- ○ By examining $\Delta G = \Delta H - T\Delta S$, it might seem strange that enthalpy, and not entropy determines the shift with a temperature change. The Gibbs-Helmholtz equation explains the experiments which prove this to be the case

- ○ As pressure increases, the Gibbs energy increases with a slope equal to the volume

- ○ For a perfect gas, we can calculate the molar Gibbs energy at different pressures:

$$G_m(p) = G_m^\ominus + RT \ln \dfrac{p}{p^\ominus}$$

fugacity

- For real gases, the Gibbs molar energy deviates from the ideal

- We replace the pressure with a new effective pressure called the *fugacity*:

$$G_m(p) = G_m^\ominus + RT \ln \frac{f}{p^\ominus}$$

- Here, $f = \phi p$ and $\ln \phi = \int_0^p \frac{Z - 1}{p} \mathrm{d}p$

- Fugacity can be compared to Activity: $\mathcal{A} = \gamma C$

- The fugacity of all van der Waals gases follow the same curve if reduced variables are used (Figure 3D.8)

PHYSICAL TRANSFORMATIONS OF PURE SUBSTANCES

○ A phase, generally, is any form of matter that is uniform throughout in chemical composition

○ This goes beyond just solid, liquid, and gas

○ Many substances have more than one solid phase, and solutions can have phases which vary by % composition

○ We call the number of components in a system C, and the number of phases in a system P

○ One component can have multiple phases, and multiple components can exist in a single phase

○ Phase transitions can be detected by thermal analysis (Figure 4A.2), even when the two phases are difficult to distinguish

○ Here, thermodynamics and kinetics must be distinguished. Metastable phases persist even when a phase change becomes thermodynamically spontaneous

○ Chemical potential (μ) is a new, strange state variable, along with n

· For phase changes and reactions, we will eventually talk about how the number of particles of each species may change (think leChâtelier's principle)

· Consider a chamber with a movable wall. We would determine how the volumes of the two sides might change by comparing their pressures

· Similarly, when there is a possible transition (phase change, reaction, etc.), we determine how the ns might change by comparing the μs

· At equilibrium, the chemical potential of all phases and species is the same

4A Phase Diagrams of Pure Substances

○ A phase diagram (Figure 4A.4) shows which phases are thermodynamically stable at various ps and Ts

○ At phase boundaries, multiple phases can coexist

○ Condensed phases have a vapor pressure at all temperatures. The phase boundary occurs when $p_{vap} = p_{ext}$

○ The phase rule describes the variance, or the number of variables which can be varied while maintaining equilibrium:

$$F = C - P + 2 \qquad \text{For pure substances, this is } F = 3 - P$$

- ○ So, 1-phase equilibria are areas, 2-phase equilibria are lines, and 3-phase equilibria are points

- ○ The solid/liquid line for water is sloped negatively because of the low density of ice

- ○ Discuss the phase diagrams in Figures 4A.7, 4A.9, and 4A.11

4B   Thermodynamic Aspects of Phase Transitions

- ○ μ, like G, changes with temperature according to molar entropy: $\left(\dfrac{\partial \mu}{\partial T} \right)_p = -S_m$

- ○ Figure 4B.1 shows how the stability of different phases compete at different temperatures

- ○ Applying pressure to chemical potential is again like G: $\left(\dfrac{\partial \mu}{\partial p} \right)_T = V_m$

- ○ Figure 4B.2 shows how the a substance's freezing point will respond to changes in pressure

Phase Boundaries

- ○ Phase boundaries occur where the chemical potentials of both phases are the same

- ○ As both phases respond to changes in temperature and pressure, the line of the phase boundary keeps the potentials equal to each other

- ○ The Clapeyron equation gives the slope of phase boundaries: $\dfrac{\mathrm{d}p}{\mathrm{d}T} = \dfrac{\Delta_{trs}S}{\Delta_{trs}V_m}$

- ○ Since phase changes along the boundary are reversible, we can replace $\Delta_{trs}S = \dfrac{\Delta_{trs}H}{T}$, giving $\dfrac{\mathrm{d}p}{\mathrm{d}T} = \dfrac{\Delta_{trs}H}{T\Delta_{trs}V_m}$

- ○ For vaporization, $\Delta_{vap}V_m = \dfrac{RT}{p}$, giving us $\dfrac{\mathrm{d}p}{\mathrm{d}T} = \dfrac{p\Delta_{vap}H}{RT^2}$

- ○ Put the pressures on the same side, and use the identity $\dfrac{\mathrm{d}p}{p} = \mathrm{d}\ln p$

- ○ This gives us the *Clausius-Clapeyron equation*: $\dfrac{\mathrm{d}\ln p}{\mathrm{d}T} = \dfrac{\Delta_{vap}H}{RT^2}$

- ○ Integrating across a temperature and assuming $\Delta_{vap}H$ is constant across the range gives:

$$p_{T_2} = p_{T_1}e^{-\chi} \qquad \chi = \dfrac{\Delta_{vap}H}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1} \right)$$

- ○ For the solid/gas boundary, merely substitute the enthalpy of sublimation: $\Delta_{sub}H = \Delta_{fus}H + \Delta_{vap}H$

Ehrenfest Classification of Phase Transitions

- ○ Phase transitions can be classified as first-order or second-order transitions

- ○ All of the phase transitions familiar to you are first-order

- ○ Figure 4B.9 shows the changes in V_m, H, μ, S, and C_p across phase transitions of both types

- ○ A third type, λ transitions, have C_p approach ∞ at the transition, but does so via asymptotes rather than discontinuously

- ○ Figure 4B.11 shows how a second-order transition might occur on a molecular level

SIMPLE MIXTURES

5A   The Thermodynamic Description of Mixtures

- In binary mixtures, the mole fractions are dependent according to: $\chi_A + \chi_B = 1$

- The volume change as one component is added depends on the interactions between components

- Partial molar volume: $V_j = \left(\dfrac{\partial V}{\partial n_j} \right)_{p,t,n'}$

- Figure 5A.1 shows the partial molar volumes of a water/ethanol mixture – Note the min/max at $\chi \approx 0.1$

- Adding $20\ ml$ of ethanol to $20\ ml$ water will give a final volume substantially lower than $40\ ml$

- The total change in volume is:

The Chemical Potential

- The mathematical definition of chemical potential is: $\mu_j = \left(\dfrac{\partial G}{\partial n_j} \right)_{p,T,n'}$

- This gives the exact differential of Gibbs energy as: $dG = V\,dp - S\,dT + \mu_A dn_A + \mu_B dn_B + \ldots$

- At constant pressure and temperature, $dG = \mu_A dn_A + \mu_B dn_B + \ldots$

- We can also state that the total Gibbs energy is: $G = n_A \mu_A + n_V \mu_B + \ldots$

- Now, this equation can be differentiated to give: $dG = \mu_A d_A + n_A d\mu_A + \mu_B dn_B + n_B d\mu_B + \ldots$

- Setting this equal to the constant T and p expression lets us remove the μdn terms

- This gives the Gibbs-Duhem equation: $\displaystyle\sum n_j d\mu_j = 0$

- The Gibbs-Duhem equation explicitly shows how the chemical potential of one component is dependent on the chemical potentials of all other components

Thermodynamics of Mixing

○ The dependence of μ with p is just like for G: $\mu = \mu^\ominus + RT \ln \dfrac{p}{p^\ominus}$

○ We can use this to find the Gibbs energy of mixing for perfect gases

  · Imagine a box split with one pure component on one side and another on the other

  · Mixing is analogous to expanding both components to fill the whole box (Figure 5A.6)

  · Because perfect gases don't interact, each gas expansion can be considered independently

  · $\Delta_{mix}G = \Delta\mu_A + \Delta\mu_B = n_A RT \ln \dfrac{p_A}{p} + n_B RT \ln \dfrac{p_B}{p}$

  · It is useful to simplify this and express it in terms of mole fractions:
  $\Delta_{mix}G = nRT \left(\chi_A \ln \chi_A + \chi_B \ln \chi_B \right)$

○ Entropy of mixing: $\Delta_{mix}S = - \left(\dfrac{\partial \Delta_{mix}G}{\partial T} \right)_{p,n_A,n_B} = -nR \left(\chi_A \ln \chi_A + \chi_B \ln \chi_B \right)$

○ For a perfect gas, the enthalpy of mixing is 0

Chemical Potentials of Liquids

○ We can use the fact that two phases in equilibrium have the same chemical potential

○ $\mu_A^\star = \mu_A^\ominus + RT \ln p_A^\star$ Where $\mu_A^\star$ is the chemical potential of a pure liquid

○ This can be rearranged into $\mu_A^\ominus = \mu_A^\star - RT \ln p_A^\star$

○ For a mixture, the liquid isn't pure: $\mu_A = \mu_A^\ominus + RT \ln p_A$

○ Combining the two gives: $\mu_A = \mu_A^\star + RT \ln \dfrac{p_A}{p_A^\star}$

○ Rault's law states that: $p_A = \chi_A p_A^\star$

○ We finally get: $\mu_A = \mu_A^\star + RT \ln \chi_A$

○ Rault's law works well for concentrated solutions, but dilute solutions follow Henry's law:
$p_B = \chi_B K_B$

○ Figures 5A.12-14 Show vapor pressures as a function of χ

5B   The Properties of Solutions

Colligative Properties

- Colligative properties depend only on the mole fraction of a substance, but not its identity

- Figure 5B.6 shows how dissolved solutes can affect the freezing and boiling points of a substance

- Boiling point elevation: $\Delta T_b = K_b \chi_B$ Where $K_b = \dfrac{RT^{\star 2}}{\Delta_{vap}H}$

- Freezing point depression: $\Delta T_f = K_f \chi_B$ Where $K_f = \dfrac{RT^{\star 2}}{\Delta_{freeze}H}$

- Table 5B.1 gives K_b and K_f for some common substances

- Solubility can be estimated, recognizing that when solute B is saturated in solvent A: $\mu_A(l) = \mu_A(g) = \mu_B^\star(s) = \mu_B^\star + RT \ln \chi_B$

- Osmotic pressure is the pressure of solvent across a semi-permeable membrane with a concentration gradient

- Osmotic pressure follows an equation just like the perfect gas law: $\Pi = \dfrac{n_B RT}{V}$

5C   Phase Diagrams of Binary Systems

- For a mixture of two substances, the total vapor pressure must include the vapor pressures for both components:

  $p = p_A + p_B = \chi_A p_A^\star + \chi_B p_B^\star = p_B^\star + (p_A^\star - p_B^\star) \chi_A$

- Figure 5C.1 shows the vapor pressure of a liquid following Rault's law

- When the pressure is less than the vapor pressure of either liquid, both are able to vaporize (The one makes head-space for the other)

- The two-dimensional region of coe-existant phases follows the rule $F = C - P + 2$

- The mole-fractions of the vapor phase (y_A and y_B) do not match the mole-fractions of the liquid phase

- p.203 – Equation 5C.4 should be: $y_A = \dfrac{\chi_A p_A^\star}{p_B^\star + (p_A^\star - p_B^\star) \chi_A} = 1 - y_B$

- We can express the total vapor pressure in terms of its composition as well:

  $p = \dfrac{p_A^\star p_B^\star}{P_A^\star + (p_B^\star - p_A^\star) y_A}$

- Figure 5C.4 shows a mole-fraction plot, combining χ and y

○ Figure 5C.5 shows how to draw tie-lines

    · Composition of the liquid and vapor phases are found by the intersections with the composition curves

    · The lever rule gives the fraction in vapor and liquid phases: $n_\alpha l_\alpha = n_\beta l_\beta$

○ Considering the system in Figure 5C.8, with $z_A = 0.4$ and $T = 80°C$, estimate:

    · χ_A and χ_B

    · y_A and y_B

    · The fraction of moles in the vapor and liquid phases

Distillation and Azeotropes

○ Because the composition of the vapor phase is enriched in one component, we can use this as a method of purification

○ Condensing the vapor and doing a second, third, etc. distillation can give very pure results

○ Figures 5C.10 and 5C.11 illustrate this process

○ Azeotropes have more complex composition curves with either a maximum or minimum boiling point

○ Distillations with azeotropes result in one pure phase, and one phase at the min/max composition

○ Figure 5C.12 shows a maximum boiling point azeotrope

○ Figure 5C.13 shows a minimum boiling point azeotrope

○ For these systems, which phase will have mixed composition, and what will be the composition?

Liquid-Liquid Phase Diagrams

○ Some liquids are only miscible in certain ratios and at certain temperatures

○ Demo with isopropyl alcohol/water mixture and beads

○ Figure 5C.15 shows one example

○ Like before, use tie-lines to determine the composition of the two phases (this time both are liquid)

○ There will be one or two *critical* temperatures, which mark the extremes where phase separation occur

○ Figure 5C.23 shows the water-nicotine phase diagram with upper and lower critical temperatures

○ When the temperature increases to the vapor pressure, we add the vapor composition curves

- ○ Figure 5C.24 is when the upper critical temperature is below the point where any vapor exists

- ○ Figure 5C.25 shows when the vapor composition curves collide with the liquid-liquid composition curves

Liquid-Solid Phase Diagrams

- ○ Figure 5C.27 shows a typical liquid-solid phase diagram

- ○ For most compositions, a pure solid will begin to freeze out first

- ○ The composition will change as the one component freezes, until the mixture reaches the *eutectic* composition

- ○ Then a eutectic solid freezes out

- ○ Eutectic mixtures can have dramatically lower melting points than the pure substances themselves

- ○ Lead/Tin solder or gold/silicon

5D Phase Diagrams of Ternary Systems

Skip this section.

5E Activities

- ○ Fugacity relates how a gas is more or less chemically active than its pressure might suggest

- ○ For solutions, *activity* plays the same role

- ○ For a solvent, $\mu_A = \mu_A^\star + RT \ln a_A$ where $a_A = \dfrac{p_A}{p_A^\star}$

- ○ Note that this expression is general, and does not necessarily follow Rault's law

- ○ For a solute we get an expression referenced to Henry's law:
  $\mu_B = \mu^\ominus + RT \ln a_B$ where $a_B = \dfrac{p_B}{K_B}$

- ○ In both cases we can give an activity coefficient γ where $a_A = \gamma_A \chi_A$

- ○ The parameter ξ compares the solvent-solute interactions to the pure substance interactions

  $\xi = 0$ Is an ideal mixture, where mixing is driven entirely by entropy

  $\xi < 0$ Gives exothermic mixing. Solvent-solute interactions are favorable, mixing is always spontaneous, and vapor pressures are depressed

$\xi > 0$ Gives endothermic mixing. Solvent-solute interactions are unfavorable, mixing is favorable at high temperatures, and vapor pressures are elevated

○ This parameter is used in the Margules equations: $\ln \gamma_A = \xi \chi_B^2$ and $\ln \gamma_B = \xi \chi_A^2$

○ Figure 5E.2 shows the vapor pressure of one component at various values of ξ, and Figure 5E.3 shows the total pressure of mixtures with two values of ξ

5F   The Activities of Ions

○ Activities for ions are much more complex than for neutral solutes

○ While we could assign a γ for each ion, in practice it is far easier to work with $\gamma_\pm$

○ Debye-Hückel limiting law:

· The Debye-Hückel limiting law states that: $\log \gamma_\pm = -A \left| z_+ z_- \right| \sqrt{I}$

· Here, A is a constant related to the solvent. $A = 0.509$ for water at $25°C$

· I is the ionic strength: $I = \frac{1}{2} \sum z_i^2 \left(\frac{b_i}{b^\ominus} \right)$ where $b^\ominus = 1 \, molal$

· Table 5F.2 shows how even modestly concentrated solutions deviate significantly from ideality

· At higher ionic strengths, this law is less reliable

○ Extended Debye-Hückel law:

· The extended Debye-Hückel law: $\log \gamma_\pm = -\dfrac{A \left| z_+ z_- \right| \sqrt{I}}{1 + B\sqrt{I}}$

· The Davies Equation: $\log \gamma_\pm = -\dfrac{A \left| z_+ z_- \right| \sqrt{I}}{1 + B\sqrt{I}} + CI$

· Here, B and C are both dimensionless, empirical quantities

· B can be interpreted as the closest approach of two ions

○ At lower salt concentrations, $\gamma_\pm < 1$ and sparingly soluble solutes can be "salted in"

○ At higher salt concentrations, $\gamma_\pm > 1$ and even miscible solutes can be "salted out," as in the water-isopropanol system

○ Consider the solubility of a sparingly soluble salt in solutions of various ionic strengths:

· Solve iteratively for a pure water solution

· Assume that I is buffered by the other salt for a salt-buffered solution

· $K_{SP} = 9.8 \times 10^{-9}$ for PbI_2 and $K_{SP} = 1.9 \times 10^{-13}$ for $Mn(OH)_2$

CHEMICAL EQUILIBRIUM

○ In a chemical system, the system will evolve until it minimizes the total Gibbs energy

○ For an equilibrium reaction, this means consuming reactants and producing products, or vice-versa

○ We can call the extent of a reaction ξ, which is the number of moles of reaction which have occurred

○ The reaction Gibbs energy is $\Delta_{rxn}G = \left(\dfrac{\partial G}{\partial \xi}\right)_{p,T} = \sum_{Products} \nu_i \mu_i - \sum_{Reactants} \nu_j \mu_j$

○ Figure 6A.1 shows how $\Delta_r G$ might vary as a function of ξ

○ When $\Delta_{rxn}G = 0$ the reaction is at the equilibrium composition and will remain in a dynamic equilibrium

○ When $\Delta_{rxn}G < 0$, the forward reaction is spontaneous and the reaction is called *exergonic*

○ When $\Delta_{rxn}G > 0$, the reverse reaction is spontaneous and the reaction is called *endergonic*

○ An exergonic reaction can be made to do work, and an endergonic reaction can be made to proceed anyway if sufficient work is input

6A   The Equilibrium Constant

○ Consider a gas-phase reaction: A(g) $\longleftrightarrow$ B(g)

○ $\Delta_{rxn}G = \mu_B - \mu_A = \left(\mu_B^{\ominus} + RT \ln p_B\right) - \left(\mu_A^{\ominus} + RT \ln p_A\right) = \Delta_{rxn}G^{\ominus} + RT \ln \dfrac{p_B}{p_A}$

○ Note that if $\Delta_{rxn}G^{\ominus} < 0$ the reaction is not necessarily spontaneous under any but standard conditions

○ This ratio of partial pressures is called the reaction quotient: $Q = \dfrac{p_B}{p_A}$

○ Generally, $Q = \prod \mathcal{A}_i^{\nu_i}$ where ν_i are the signed stoichiometric coefficients

○ For any reaction $\Delta_{rxn}G = \Delta_{rxn}G^{\ominus} + RT \ln Q$

○ When the system is at equilibrium, $\Delta_{rxn}G = 0$, and Q becomes K

○ We can rearrange the above equation to give: $RT \ln K = -\Delta_{rxn}G^{\ominus}$

- ○ In fact, the existence of equilibrium reactions is quite surprising:

  - · The Gibbs energy of the pure reactants or the pure products will be lower, so you should always be able to minimize the Gibbs energy by going to one extreme

  - · What is missed is the Gibbs energy of mixing for mixed composition in the middle

  - · Figure 6A.3 shows how the total system Gibbs energy would vary with ξ both neglecting and considering the Gibbs energy of mixing

  - · The presence of a minimum is only possible when mixing is considered

- ○ The equilibrium constant can be expressed in terms of concentrations (K_c) or of pressure (K_p)

- ○ $K_p = K_c \left(\dfrac{c^{\ominus} RT}{p^{\ominus}} \right)^{\Delta \nu}$

- ○ Figure 6A.4 shows the molecular interpretation of equilibrium. It maximizes the distribution of energy

6B   The Response of Equilibria to the Conditions

- ○ Any perturbation from equilibrium will cause a response, or change in the extent of reaction (ξ)

- ○ This response will act to restore equilibrium, and will often be in direct opposition to the perturbation

The Response to Pressure

- ○ This is really the response to the *partial* pressures of the reacting gases (As by a change in volume)

- ○ I.e., adding an inert gas to increase the total pressure will not affect the value of K_p

- ○ Changes in the partial pressures will result in a shift based on $\Delta_{rxn} n_g$

- ○ Increases in pressure will shift ξ toward the side with fewer moles of gas

The Response to Temperature

- ○ Unlike with p, changes in T affect the actual value of K

- ○ The direction of the shift depends on $\Delta_{rxn} H$

- ○ As a rule of thumb, we can treat "heat" as either a product or a reactant

- ○ The van't Hoff equation, derived from Gibbs energy equations, gives the change in $\ln K$:

  $$\frac{\mathrm{d} \ln K}{\mathrm{d}^1/_T} = -\frac{\Delta_{rxn} H^{\ominus}}{R}$$

○ If $\ln K$ is plotted against $1/T$, the slope of the curve will be: $-\dfrac{\Delta_{rxn}H^{\ominus}}{R}$

○ Integrating the van't Hoff equation gives: $\ln K_2 - \ln K_1 = -\dfrac{\Delta_{rxn}H^{\ominus}}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$

○ Note that here we use $\Delta_{rxn}H^{\ominus}$ even though standard conditions are not necessarily at equilibrium. This is because we are relying on the earlier equation: $RT\ln K = -\Delta_{rxn}G^{\ominus}$

6C   Electrochemical Cells

○ Electrochemical cell construction and operation:

· The cathode is the electrode where reduction occurs (cathode and reduction both begin with consonants)

· The anode is the electrode where oxidation occurs (anode and oxidation both begin with vowels)

· This is true for both electrolytic and voltaic cells

· The salt bridge completes the circuit, with anions flowing toward the anode, and cations flowing toward the cathode

○ The half-reactions can be notated like this: $Zn(s)|ZnSO_4(aq)||CuSO_4(aq)|Cu(s)$

○ For a cell at standard conditions, we can use the half-cell reduction potentials and

$E_{cell} = E_{r,\,cathode} - E_{r,\,anode}$ (no consideration of ν is necessary)

○ Under non-standard conditions, we use the Nernst equation: $-\nu F E_{cell} = \Delta_{rxn}G$

○ F is Faraday's constant, and ν is the moles of electrons transferred in the reaction

○ We can also relate $\Delta_{rxn}G$ to the reaction quotient, as seen above. Done here gives:

$E_{cell} = E_{cell}^{\ominus} - \dfrac{RT}{\nu F}\ln Q$

○ This equation also demonstrates why potential is, in one sense, independent of ν. Double the reaction to double ν, and you will also square Q which cancels out the effect and gives the same E_{cell}

○ Similarly, we can apply the relation between G and K to get: $E_{cell}^{\ominus} = \dfrac{RT}{\nu F}\ln K$

○ Since $\left(\dfrac{\partial G}{\partial T}\right)_p = -S$, we can also say that $\dfrac{dE_{cell}^{\ominus}}{dT} = \dfrac{\Delta_{rxn}S^{\ominus}}{\nu F}$

○ And finally, we find that $\Delta_{rxn}H^{\ominus} = -\nu F\left(E_{cell}^{\ominus} - T\dfrac{dE_{cell}^{\ominus}}{dT}\right)$

○ Consider an electrochemical cell constructed with a $AgCl(s)/Ag(s) + Cl^-(aq)$ electrode and a $Zn(s)/Zn^{2+}(aq)$ electrode

- Under standard conditions, what will be the cell potential?

- Under standard conditions, which electrode will be the cathode and which will be the anode?

- Draw the cell with a salt bridge, and indicate how charge will flow through every stage of the circuit

- How would the addition of NaCl into the $AgCl(s)/Ag(s) + Cl^-(aq)$ half-cell affect the cell potential (note that NaCl will not participate in direct redox chemistry at all)

- If a cell begins under standard conditions and is run until it "dies," what will be the final concentrations of Cl^- and Zn^{2+}?

6D   Electrode Potentials

○ Electric potential must be referenced to some standard. For cells, we reference the reduction of hydrogen

○ We could find reduction potentials by measuring half-reactions against a standard hydrogen electrode

○ In practice, we can also chain known redox reactions together to get an unknown half-cell potential (kind of like Hess's law)

○ For example, if you know the potential of the redox couples $Fe(s)/Fe^{2+}(aq)$ and $Fe^{2+}(aq)/Fe^{3+}(aq)$, you can calculate the potential for $Fe(s)/Fe^{3+}(aq)$

○ In this instance, the number of electrons matters! $\nu_C E^{\ominus}(C) = \nu_A E^{\ominus}(A) + \nu_B E^{\ominus}(B)$

○ So, $3E^{std}(Fe(s)/Fe^{3+}) = 2E^{\ominus}(Fe(s)/Fe^{2+}(aq)) + 1E^{\ominus}[Fe^{2+}(aq)/Fe^{3+}(aq)]$

MOLECULES IN MOTION

16A Transport in Gases

- ○ When a gas is not homogeneous, there will be a net flow of gas particles

- ○ The flow of heat and viscosity behave similarly, so all will have similar equations

- ○ Fick's first law of diffusion: $J_{\text{Matter}} = -D\dfrac{\mathrm{d}\mathcal{N}}{\mathrm{d}z}$

- ○ D is called the "Diffusion Coefficient"

- ○ For heat: $J_{\text{Energy}} = -\kappa\dfrac{\mathrm{d}T}{\mathrm{d}z}$

- ○ κ is the coefficient of thermal conductivity

- ○ $J_{\text{x}-\text{Momentum}} = -\eta\dfrac{\mathrm{d}v_x}{\mathrm{d}z}$

- ○ η is the coefficient of viscosity

- ○ We can understand transport by considering the collision flux through a slice along the gradient (Figure 19A.3)

  - · Collision frequency depends on the number density, temperature, and mass of a gas

  - · With different densities across a gradient, the number of collisions from the dilute side is lower than the number of collisions from the concentrated side

  - · Of course, particles don't actually collide since the slice is not a real barrier

  - · The collisions represent particles traveling across the slice

  - · The diffusion coefficient can be expressed as: $D = \frac{1}{3}\lambda v_{mean} = \frac{1}{3}\left(\dfrac{k_B T}{\sigma p}\right)\left(\dfrac{8RT}{\pi M}\right)^{1/2}$

  - · Higher pressures give slower diffusion

  - · Hotter temperatures give faster diffusion

  - · Smaller particles (both mass and size) give faster diffusion

- ○ Things are a bit different for thermal conductivity

  - · $\kappa = \frac{1}{3}\nu v_{mean}\lambda\mathcal{N}k_B = \frac{1}{3}\lambda v_{mean}[J]C_{V,\,m} = \dfrac{\nu p D}{T}$

  - · Here, $\nu = \frac{1}{2}N_{D.o.F}$ (Degrees of freedom divided by 2)

- $[J]$ is the molar concentration of the carrier particles J
- Thermal conductivity is *independent* of pressure
- The heat capacity scales the energy gradient for a given temperature gradient

○ And for viscosity

- $\eta = \frac{1}{3}v_{mean}\lambda m\mathcal{N} = MD[J] = \dfrac{pMD}{RT}$
- m is the particle mass, M is the molar mass, and λ is the mean free path
- $[J]$ is the molar concentration of the momentum-carrying particles
- Viscosity is also independent of pressure
- Hotter temperatures increase the viscosity of gases (This is the reverse of liquids, which must overcome intermolecular forces)

○ Effusion is also a transport phenomenon

- Again, consider "collisions" - this time collisions with the hole
- $Rate = Z_W A_0 = \dfrac{pA_0}{\sqrt{2\pi m k_B T}} = \dfrac{pA_0 N_A}{\sqrt{2\pi MRT}}$
- A_0 is the area of the hole, and Z_W is the collision rate
- Note that p is a function of T, so the final dependence is $Rate \propto \sqrt{T}$
- $Rate \propto M^{-1/2}$

16B   Motion in Liquids

○ For liquids to flow, intermolecular forces must be overcome

○ This gives a temperature dependence at constant volume of: $\eta = \eta_0 e^{E_a/RT}$

○ Under constant pressure, the thermal expansion is a more important factor than the activation energy

Conductivity in Electrolytes

○ For any electrical conductor, the conductance G is the inverse resistance: $G = \dfrac{1}{R}$

○ Conductance can also be expressed in terms of conductivity (κ), cross-sectional area (A), and length (l)

$G = \kappa\dfrac{A}{l}$

○ For a solution, we can expect that more ions would lead to higher conductivity

○ This leads to the *molar conductivity*: $\Lambda_m = \dfrac{\kappa}{c}$

○ It is even worse, however, since the molar conductivity is not constant, but varies with concentration too: $\Lambda_m = \Lambda_m^\circ - \mathcal{K}\sqrt{c}$ ($\mathcal{K}$ is an empirical constant)

○ On the microscopic level, we see that electrolyte conductivity has to do with ion mobility

· Ions in solution are met with a coefficient of friction: $f = 6\pi\eta a$

· Here, a is the hydrodynamic radius (or Stokes radius)

· The ion mobility is: $u = \dfrac{ze}{f}$ (z is the ion charge and e is the elementary charge)

· The ion drift speed is: $s = uE$

· Molar ion conductivity is: $\lambda = zuF$

· Table 19B.2 shows a few ion mobilities. Note the Grotthuss mechanism for H⁺ and OH⁻

○ Skip the Einstein relations, even though they are very cool

16C   Diffusion

○ Fick's first law, $J_{\text{Matter}} = -D\dfrac{\mathrm{d}\mathcal{N}}{\mathrm{d}z}$, only addresses an instantaneous flux

○ Fick's second law, or the diffusion equation, tells how concentrations change over time:
$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

○ We see that the concentration over time will change according to the curvature of the concentration gradient

○ Note that this is a partial derivative with respect to x. In 3-D space, you would have to include the partials along y and z as well

○ Integrating Fick's second law gives the time-dependence of the concentration:
$$c(x,t) = \frac{n_0}{A\sqrt{\pi Dt}}e^{-x^2/4Dt} \qquad \text{for 1 dimension}$$
$$c(r,t) = \frac{n_0}{8\left(\pi Dt\right)^{3/2}}e^{-r^2/4Dt} \qquad \text{for 3 dimensions}$$

○ A is the cross-sectional area and n_0 is the initial number of moles which start at point $x, r = 0$

○ We can quantify the extent of diffusion by the rms displacement: $x_{rms} = \sqrt{2Dt}$

○ Generally, diffusion can be very slow. Mixtures must be well stirred for efficient reaction

Practice and Application

○ Gas diffusion

- YouTube videos on Bromine diffusion by channel Isaac Physics
- Calculate the diffusion coefficient for Bromine in $1\ atm$ and in $0.01\ atm$ of pressure
- Predict the $x_r ms$ after 10 minutes, and compare to the video
- Use the diffusion spreadsheet

○ Viscosity and electrical conductance

- A fluorescent lamp is filled with $0.003\ atm$ of mercury vapor
- Find η for the mercury vapor at $315\ K$
- Assume that while the lamp is lit all mercury is in the Hg^{2+} state
- What is the ion mobility? (assume $a \approx 1.00 Å$)
- What is the ion drift speed at $120\ V$?
- What is the molar ion conductivity?
- What is the resistance, and current through the lamp (assume Hg^{2+} is the sole charge-carrier)?
- Note that in reality the plasma in a fluorescent lamp has free electrons, unlike in an electrolyte solution. Those electrons actually carry the charge in these lamps

CHEMICAL KINETICS

17A   The Rates of Chemical Reactions

○ For a reaction: aA + bB=cD + dD, $v = -\dfrac{\mathrm{d}[A]}{a\mathrm{d}t} = -\dfrac{\mathrm{d}[B]}{b\mathrm{d}t} = \dfrac{\mathrm{d}[C]}{c\mathrm{d}t} = \dfrac{\mathrm{d}[D]}{d\mathrm{d}t}$

○ The extent of the reaction can be expressed as: $\xi = \dfrac{n_J - n_{J,0}}{\nu_J}$

○ This gives the rate as: $v = \dfrac{1}{V}\dfrac{\mathrm{d}\xi}{\mathrm{d}t}$

○ If the concentration of a species can be monitored over time (e.g. spectrophotometrically) then the tangent slope will give the rate at any given time (Figure 20A.3)

○ The rate is ultimately governed by the opportunities for reactants to encounter and react together

○ Therefore, the rate can also be expressed in terms of the reactant concentrations: $v = k_r[A]^m[B]^n$

○ This form is called the rate law, and the exponents must be found experimentally

○ The exponents give the reaction order with respect to each reactant, and overall

○ The units of k_r must correspond to the overall reaction order to give final units of $v = {}^{mol}\!/_{ls}$

○ Method of initial rates to determine the reaction order:

   · The effect of a single reactant can be isolated by using all other reactants in large excess

   · This creates a psudo-reaction order that depends only on the limited reactant

   · A method must be used to determine the average initial rate v_0 (color indicator, spectrophotometrically, electrochemically, etc.)

   · Varying the concentration of the limiting reactant and comparing the rates can give the reaction order

   · $\log v_0 = \log k_r' + a\log[A]_0$

   · This method will not reveal complex kinetics, such as product-catalyzed reactions

○ Sample data for initial rate method with reaction A + B $\longrightarrow$ C:

Run	$[A]_0$	$[B]_0$	Rate M/s
1	$1.0\ M$	$0.010\ M$	1.5×10^{-4}
2	$1.0\ M$	$0.030\ M$	4.5×10^{-4}
3	$0.010\ M$	$1.0\ M$	1.5×10^{-6}
4	$0.030\ M$	$1.0\ M$	1.4×10^{-5}

○ Give the rate law, including k_r with proper units

17B   Integrated Rate Laws

○ We can equate the two forms of the rate to get: $\dfrac{d[A]}{a\,dt} = -k_r[A]^m$

○ This differential equation can be solved for different cases of the exponent m

○ First Order:

  · If $m = 1$, then the integrated form is: $\ln\dfrac{[A]}{[A]_0} = -k_r t \qquad [A] = [A]_0 e^{-k_r t}$

  · If $\ln[A]$ is plotted against time, then the data will fit a line with $slope = -k_r$

  · We can also consider the special case where $[A] = \frac{1}{2}[A]_0$ and $t_{1/2} = \dfrac{\ln 2}{k_r}$

  · For first-order reactions, there is a characteristic time constant: $\tau = \dfrac{1}{k_r}$

○ Second-Order:

  · If $m = 2$, then the integrated form is: $\dfrac{1}{[A]} - \dfrac{1}{[A]_0} = k_r t \qquad [A] = \dfrac{[A]_0}{1 + k_r t[A]_0}$

  · If $\dfrac{1}{[A]}$ is plotted against time, then the data will fit a line with $slope = k_r$

  · For 2nd-order reactions, the half-life is not constant: $t_{1/2} = \dfrac{1}{k_r[A]_0}$

17C   Reactions Approaching Equilibrium

○ As reactions approach dynamic equilibrium, the rate law must take into account the reverse reaction too

○ For the reaction A $\longrightarrow$ B, the master rate equation is: $\dfrac{d[A]}{dt} = -k_r[A] + k_r'[B]$

○ At equilibrium, the forward and reverse rates will be the same, so $k_r[A] = k_r'[B]$

○ This means we can relate the rate constants to the equilibrium constant: $K = \dfrac{k_r}{k_r'}$

○ If the system is perturbed away from equilibrium (say, by a sudden increase in temperature or pressure) it will relax into the new equilibrium according to: $\chi = \chi_0 e^{-t/\tau}$ and $\tau = \dfrac{1}{k_r + k_r'}$

17D   The Arrhenius Equation

○ So far we have talked about k_r as simply an empirical constant (found by fitting data)

○ Arrhenius found the dependence of k_r on temperature, and proposed a theory to describe this behavior

○ $\ln k_r = \ln A - \dfrac{E_a}{RT}$ or $k_r = Ae^{-\frac{E_a}{RT}}$

○ The activation energy can be plotting $\ln k_r$ vs $1/T$: $slope = -\dfrac{E_a}{R}$

○ A is the pre-exponential factor, or frequency factor

○ The frequency factor can be interpreted as the rate of "reaction attempts," or collisions with the proper orientation for a reaction to occur

○ A reaction coordinate diagram (Figure 20D.3) shows how a reaction might proceed

   · The E_a and ΔH_{rxn} are found on the diagram
   · The maximum energy point is called an activated complex or transition state
   · Catalysts change the pathway taken in the reaction coordinate diagram
   · What is the physical interpretation for the x-axis in this diagram?

17E   Reaction Mechanisms

○ Many reactions actually take place in a series of steps

○ Each step (and any one-step reactions) are called "elementary reactions"

○ Elementary reactions can have different molecularity

   · Molecularity is the number of molecules that come together for the elementary reaction
   · Molecularity is also like reaction order in the rate law for an elementary reaction
   · Unimolecular elementary reactions: A $\longrightarrow$ P $rate = k_r[A]$
   · Bimolecular elementary reactions: A+B $\longrightarrow$ P $rate = k_r[A][B]$

- Trimolecular elementary reactions...don't exist!
- It is important to remember that the reaction order of an overall reaction is not necessarily related to the molecularity of the elementary steps

○ Multi-step reactions:

- Multi-step reactions proceed through reaction intermediates
- Intermediates are not the same as activated complexes (transition states)
- Figure 20E.1 shows how the concentrations of

○ The steady-state approximation:

- The steady-state approximation assumes that any intermediates maintain a low, steady concentration after an initial induction period
- A steady state is distinct from equilibrium
- This is the case when the second step is much faster than the first step ($k_b \gg k_a$)
- Figure 20E.2 shows the reactant, product, and intermediate concentrations under this model
- The concentration of the intermediate can be found by setting its master rate equation equal to 0
- Solve the rate equation for the reaction A $\longrightarrow$ I $\longrightarrow$ B
- The overall rate law can be predicted by the "slow step"
- Figure 20E.5 shows a reaction coordinate diagram for this case

○ Pre-equilibria

- Consider the reaction: A+B $\longleftrightarrow$ I->P
- In this case, the second step is much slower than the first step, allowing equilibrium to be reached
- Solve the rate law

○ If more than one product can be formed, kinetics and thermodynamics are both relevant

○ In the long time limit, the thermodynamic product is produced

○ In the short time limit, the kinetic product is produced

17F   Examples of Reaction Mechanisms

○ Lindemann-Hinshelwood mechanism

- Some gas-phase reactions exhibit first-order kinetics, but they must occur via bimolecular collisions

- The Lindemann-Hinshelwood mechanism solves this question

  A+A $\longrightarrow$ A*+A

  A+A* $\longrightarrow$ A+A

  A* $\longrightarrow$ P

- $\dfrac{d[P]}{dt} = k_b[A^*]$ and $\dfrac{d[A^*]}{dt} = k_a[A]^2 - k_a'[A][A^*] - k_b[A^*]$

- $[A^*] = \dfrac{k_a[A]^2}{k_b + k_a'[A]}$

- $rate = \dfrac{k_a k_b [A]^2}{k_b + k_a'[A]}$

- This is only first-order if $k_a'[A] \gg k_b$, so going to lower pressures reveals the more complex kinetics

○ Skip polymerization except to say that we can talk statistically about how long an average polymer chain will be based on the reaction kinetics

17G Photochemistry

○ Photochemical processes are chemical reactions which require a photoexcited reactant (Table 20G.1)

○ Photophysical processes are processes which involve changes in electronic states, but not the breaking or forming of bonds (Table 20G.2)

○ Timescales are in femtoseconds for electronic transitions, picoseconds for fluorescence (excited state lifetime), and milliseconds to seconds for phosphorescence

○ Quantum yield (ϕ) is the fraction of absorption events which lead to the product or process of interest

○ Excited state decay

- The rate of absorption is merely the intensity of absorption
- Fluorescence (k_{IC}), internal conversion (k_{IC}), and intersystem crossing (k_{ISC}) are unimolecular decay processes
- $\tau = \dfrac{1}{k_F + k_{IC} + k_{ISC}}$
- $\phi_F = \dfrac{k_F}{k_F + k_{IC} + k_{ISC}}$

○ Quenching

- Any side-reactions which reduce the quantum yield contribute to quenching
- By varying the concentration of quencher, we can find the rate of the quenching reaction

- A quenching reaction is: $S^* + Q \longrightarrow S + Q$ $\qquad v_Q = k_Q[Q][S^*]$
- Stern-Volmer Equation: $\dfrac{\phi_0}{\phi} = 1 + \tau_0 k_Q[Q]$
- Self-quenching and the paradox: Aren't photoexcited molecules constantly bumping into solvent molecules?
- The answer lies in the requirement for resonance in collisional energy transfer as well as for photon absorption

○ Förster Theory

- Another quenching reaction is resonance energy transfer: $S^* + Q \longrightarrow S + Q^*$
- Usually we are interested in the fluorescence of the acceptor molecule (Q)
- Efficiency of transfer is: $\eta_T = 1 - \dfrac{\phi_F}{\phi_{F,0}}$
- Transfer is efficient when:
    * Donor and acceptor are able to get close to each other
    * Donor fluorescence and acceptor absorbance spectra overlap (resonance)
- Förster theory describes the distance relationship: $\eta_T = \dfrac{R_0^6}{R_0^6 + R^6}$
- R_0 is a parameter defined as the distance where transfer is 50% efficient
- FRET spectroscopy is used to measure molecular distances in proteins and other biomolecules

17H   Enzymes

○ Enzymes are biomolecules which act as catalysts for essential biochemical reactions

○ The substrates dock into the active sites of enzymes

○ The "lock-and-key" model has been largely supplanted by the "induced fit" model

○ The Michaelis-Menten Mechanism

- $E + S \longleftrightarrow ES$
- $ES \longrightarrow P + E$
- The rate equation will be: $\dfrac{k_b[E]_0}{1 + K_M/[S]_0}$
- Here, $K_M = \dfrac{k_a' + k_b}{k_a}$
- Lineweaver-Burk Plots (Figure 20H.4)
    * $\dfrac{1}{[S]}$ vs $\dfrac{1}{v}$
    * Slope is $\dfrac{K_M}{v_{max}}$, y-intercept is $\dfrac{1}{v_{max}}$, and x-intercept is $\dfrac{-1}{K_M}$

○ The turnover rate is a measure of how quickly an enzyme can do its work: $k_{cat} = k_b = \dfrac{v_{max}}{[E]_0}$

○ The catalytic efficiency can be interpreted as an effective rate constant, but it is also related to the fraction of substrate docking events which eventually lead to product: $\eta = \dfrac{k_{cat}}{K_M} = \dfrac{k_a k_b}{k_a' + k_b}$

○ Enzyme inhibition:

  · Inhibition is when a different, inactive substrate can also bind with the enzyme and prevent or delay production of products

  EIn $\longleftrightarrow$ E + In

  ESIn $\longleftrightarrow$ ES + In

  · Don't worry about the complex rate equation for inhibited enzymes

  · Figure 20H.6 shows the effects of different types of inhibition

  · Competitive inhibition: An inhibitor binds to the active site, blocking access for the substrate

  · Uncompetitive inhibition: An inhibitor binds to some other site, but only if the substrate is already present at the active site, and prevents product formation

  · Non-competitive inhibition: An inhibitor binds to some other site and reduces the binding activity of the active site

REACTION DYNAMICS

18A   Collision Theory

○ Here we will analyze the exponential pre-factor

○ Recall from chapter 1 that the collision frequency is: $z = \sigma v_{rel} \mathcal{N}$ $\mathcal{N} = \dfrac{N}{V} = \dfrac{pN_A}{RT} = \dfrac{p}{k_B T}$

○ This number is the collision rate from the perspective of a single particle

○ To find the rate of collisions throughout a substance, we use: $Z_{AB} = \sigma v_{rel} N_A^2 [A][B]$

○ For dissimilar molecules, $v_{rel} = \left(\dfrac{8kT}{\pi \mu} \right)^{1/2}$

○ Not all collisions lead to a reaction due to an activation energy requirement: $e^{-\frac{E_a}{RT}}$

○ Not all collisions lead to a reaction due to a steric factor (P)

  · The steric factor is usually less than 1 because improper orientation will stop a reaction

  · The steric factor can be greater than 1 if molecules need not actually collide to react

  · For example in the harpoon mechanism of K + Br$_2$ $\longrightarrow$ KBr + Br

  · The RRK model accounts for collisions which have enough energy, but distribute that energy into modes which are not conducive to reaction

  · RRK theory gives $P = \left(1 - \dfrac{E^\star}{E} \right)^{s-1}$ for the Lindemann mechanism

  · s is the number of energetic modes

  · E is the kinetic energy transferred in the collision and $E^\star$ is the energy needed to sufficiently activate the reactive molecule

○ Taken together, the rate is: $v = PZ_{AB} e^{-\frac{E_a}{RT}} = P\sigma v_{rel} N_A^2 [A][B] e^{-\frac{E_a}{RT}}$

○ This means that for collision theory, $k_r = P\sigma v_{rel} N_A^2 e^{-\frac{E_a}{RT}}$

○ $P\sigma$ can be interpreted to mean the reactive cross-section (rather than the van der Waals collisional cross-section alone). This is particularly appropriate for the harpoon mechanism

18B Diffusion-Controlled Reactions

○ In liquids, reactants and products encounter each other far less frequently, but the encounters last much longer

○ This "cage effect" gives an encounter pair the opportunity to acquire enough energy to overcome the activation energy barrier, even if they didn't have it initially

○ Many solvent reactions can be described by the following mechanism:

A + B $\longrightarrow$ AB $\qquad v = k_d[A][B]$

AB $\longrightarrow$ A + B $\qquad v = k_d'[AB]$

AB $\longrightarrow$ P $\qquad v = k_a[AB]$
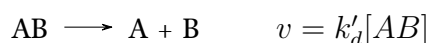
○ Applying a steady-state approximation gives $v = \dfrac{k_a k_d}{k_a + k_d'}[A][B]$

○ There are two extreme limits: Diffusion controlled and activation-controlled

○ Diffusion controlled ($k_d' \ll k_a$): $k_r \approx k_d$

○ Activation controlled ($k_a \ll k_d'$): $k_r \approx \dfrac{k_a k_d}{k_d'} \approx k_a K$

○ k_d is the rate at which molecules diffuse together: $k_d = 4\pi R^\star D N_A$

○ Here, D is the sum of the diffusion coefficients for both reactants and $R^\star$ is the reaction distance

○ Using the Stokes-Einstein equation and a convenient approximation of $R^\star$ simplifies this to: $k_d = \dfrac{8RT}{3\eta}$

○ Note that R here is the gas constant, and this expression is now general for all reactions in a given solvent

18C Transition-State Theory

○ Transition state theory (or activated complex theory) attempts to refine our estimates of the value of k_r based on statistical mechanics and the structure of the transition state

○ Assume that there is an equilibrium established between reactants and the activated complex A+B $\longleftrightarrow$ C‡ with equilibrium constant $K^{\ddagger}$

○ The activated complex can dissociate to products with rate constant $k^{\ddagger}$

○ In the end, the effective rate constant is: $k_r = RT k^{\ddagger} K^{\ddagger}$

○ Around the transition state, bonds are forming and breaking with an oscillatory frequency of $\nu^{\ddagger}$

○ $k^{\ddagger} = \kappa \nu^{\ddagger}$ where κ is assumed to be 1

○ We will cover vibrational structure, etc. next year, but

18D   The Dynamics of Molecular Collisions

18E   Electron Transfer in Homogeneous Systems

18F   Processes at Electrodes

CHAPTER 19

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PROCESSES ON SOLID SURFACES

19A   An Introduction to Solid Surfaces

19B   Adsorption and Desorption

19C   Heterogeneous Catalysis