

General Chemistry C, Fall 2023 Problem Set 4

- Due date: 2023/11/15 10:00 AM.
 - Write down how you calculate the answer step-by-step (don't forget about the units).
 - Please upload a PDF file containing your answers to NTU COOL.
1. (4 pt) Find the temperature ranges ($T > \text{__K}$ or $T < \text{__K}$) in which the following two reactions would become spontaneous.

Reaction A: $\Delta H_A = 126.0 \text{ kJ/mol}$ $\Delta S_A = 84 \text{ J/mol}\cdot\text{K}$

Reaction B: $\Delta H_B = -11.7 \text{ kJ/mol}$ $\Delta S_B = -105 \text{ J/mol}\cdot\text{K}$

Spontaneity is determined by the sign of Gibbs free energy difference:

Spontaneous: $\Delta G < 0$

The definition of Gibbs free energy is: $\Delta G = \Delta H - T\Delta S$

For reaction A to be spontaneous:

$$\Delta G_A = \Delta H_A - T\Delta S_A = 126.0 \cdot 1000 - 84T < 0$$

$$T > 1.5 \cdot 10^3 \text{ K}$$

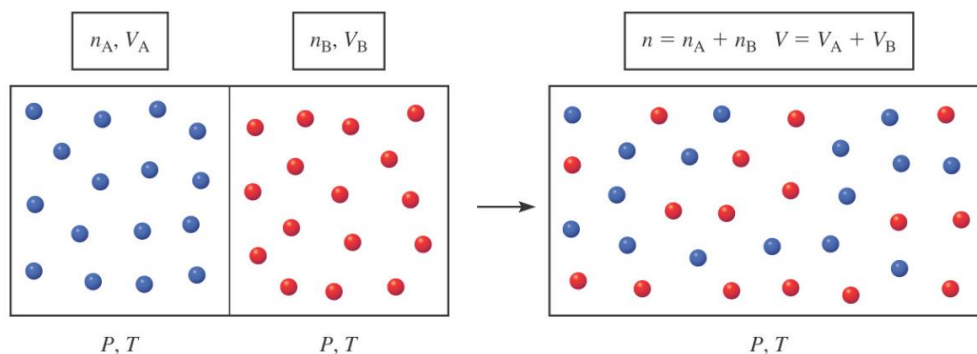
For reaction B to be spontaneous:

$$\Delta G_B = \Delta H_B - T\Delta S_B = -11.7 \cdot 1000 + 105T < 0$$

$$T < 111 \text{ K}$$

2. (5 pt) What is the Gibbs free energy change for a process in which a mixture of 1.00 mole of N_2 and 1.00 mole of O_2 is separated into two containers, each with a volume equal to half the original volume – one containing a mixture of 0.30 mole of N_2 and 0.70 mole of O_2 , and the other containing 0.70 mole of N_2 and 0.30 mole of O_2 ?
Assuming ideal gas behavior at 25°C .

Before delving into the solution for this problem, let's begin by providing a detailed derivation of how entropy and the change in Gibbs' free energy occur during the mixing of two ideal gases. This aspect may not have been thoroughly covered in your class.



This process is an isothermal expansion for both gases because they won't react while mixing and because the process is said to be constant pressure and temperature. The internal energy change should be zero, which leads to the heat equal to the work they did. That is:

$$\Delta U = 0 \rightarrow dq = -dw = -PdV$$

The entropy change of mixing can be thought of as the entropy change of Nitrogen and oxygen, respectively.

$$\Delta S_{mix} = \Delta S(A) + \Delta S(B) = \int_{V_A}^{V_A+V_B} \frac{dq_{rev}}{T} + \int_{V_B}^{V_A+V_B} \frac{dq_{rev}}{T}$$

Due to the isothermal expansion process, we can further arrange this equation like this:

$$\Delta S_{mix} = \int_{V_A}^{V_A+V_B} \frac{dq_{rev}}{T} + \int_{V_B}^{V_A+V_B} \frac{dq_{rev}}{T} = \int_{V_A}^{V_A+V_B} \frac{PdV}{T} + \int_{V_B}^{V_A+V_B} \frac{PdV}{T}$$

We can further arrange the equation by the ideal gas formula:

$$\Delta S_{mix} = \int_{V_A}^{V_A+V_B} \frac{n_A R dV}{T} + \int_{V_B}^{V_A+V_B} \frac{n_B R dV}{T} = n_A R \times \ln\left(\frac{V_A+V_B}{V_A}\right) + n_B R \times \ln\left(\frac{V_A+V_B}{V_B}\right)$$

$$X_A = \frac{V_A}{V_A+V_B}; X_B = \frac{V_B}{V_A+V_B}$$

$$\Delta S_{mix} = -n_A R \ln(X_A) - n_B R \ln(X_B)$$

Where X_A and X_B denote the molar ratio of gas-A and gas-B.

This is the reason why we can get the equation of entropy change in the slide.

The Gibbs free energy change of mixing is not related to the enthalpy because two gas won't react with each other, which makes the mixing process only dominated by the entropy and temperature.

$$\Delta G_{mix} = -T\Delta S_{mix} = \Delta S_{mix} = -n_A RT \ln(X_A) - n_B RT \ln(X_B)$$

From here, we can know that any mixing of two different gas would cause increased entropy and decreased Gibb's energy.

Now, let's begin addressing this problem. Based on our previous discussion, we understand that even mixing two ideal gases in the same container leads to changes in both entropy and Gibbs' energy.

Consequently, we can break down this question into three distinct parts.

(1) mixture of 1.00 mol N₂ and 1.00 mol O₂

The molar ratio of Nitrogen gas and Oxygen gas can be obtained:

$$X_{N_2} = \frac{1.00}{1.00+1.00} = 0.500 ; X_{O_2} = \frac{1.00}{1.00+1.00} = 0.500$$

$$\Delta S_{mix(1)} = -n_{N_2} R \ln(X_{N_2}) - n_{O_2} R \ln(X_{O_2}) =$$

$$= -1.00 * 8.314 * \ln(0.500) - 1.00 * 8.314 * \ln(0.500) = 11.53(JK^{-1})$$

$$\Delta G_{mix(1)} = -T \Delta S_{mix(1)} = -3436 (J)$$

(2) mixture of 0.30 mole of N₂ and 0.70 mole of O₂ on half of the volume

The molar ratio of Nitrogen gas and Oxygen gas can be obtained:

$$X_{N_2} = \frac{0.30}{1.00} = 0.30 ; X_{O_2} = \frac{0.70}{1.00} = 0.70$$

$$\Delta S_{mix(2)} = -n_{N_2} R \ln(X_{N_2}) - n_{O_2} R \ln(X_{O_2}) =$$

$$= -0.30 * 8.314 * \ln(0.30) - 0.70 * 8.314 * \ln(0.70) = 5.079(JK^{-1})$$

$$\Delta G_{mix(2)} = -T \Delta S_{mix(2)} = -1514 (J)$$

(3) mixture of 0.70 mole of N₂ and 0.30 mole of O₂ on another half of the volume

The molar ratio of Nitrogen gas and Oxygen gas can be obtained:

$$X_{N_2} = \frac{0.70}{1.00} = 0.70 ; X_{O_2} = \frac{0.30}{1.00} = 0.30$$

$$\Delta S_{mix(3)} = -n_{N_2} R \ln(X_{N_2}) - n_{O_2} R \ln(X_{O_2}) =$$

$$= -0.70 * 8.314 * \ln(0.70) - 0.30 * 8.314 * \ln(0.30) = 5.079(JK^{-1})$$

$$\Delta G_{mix(3)} = -T \Delta S_{mix(3)} = -1514 (J)$$

The Entropy change after the valve open can be think of as the difference of entropy and Gibb's energy change separately, that's is

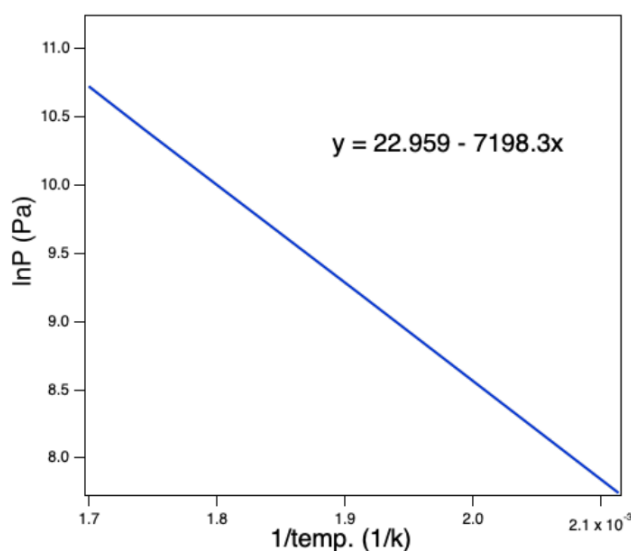
$$\Delta S_{process} = (\Delta S_{mix(3)} + \Delta S_{mix(2)}) - \Delta S_{mix(1)} = 5.079 + 5.079 - 11.53 = -1.37(JK^{-1})$$

$$\Delta G_{process} = (\Delta G_{mix(3)} + \Delta G_{mix(2)}) - \Delta G_{mix(1)} = -(1514 + 1514) + 3436 = 408 \text{ (J)}$$

3. (5 pt) The measured vapor pressures of mercury (Hg) at several different temperatures are shown below. (a) Calculate the molar heat of vaporization ΔH_{vap} (in kJ/mol) of mercury. Please include a figure showing your regression analysis results. (Hint: use Microsoft Excel or similar software) (b) Predict the normal boiling point (in °C) of mercury.

T (°C)	200	250	300	320	340
P (mmHg)	17.3	74.4	246.8	376.3	557.9

Point	'Temp (°C)'	'Temp (K)'	'1/T (1/K)'	'P (mmHg)'	'P (Pa)'	'lnP (Pa)'
0	200	473.15	0.00211349	17.3	2306.47	7.74347
1	250	523.15	0.00191115	74.4	9919.16	9.20222
2	300	573.15	0.00174474	246.8	32903.9	10.4013
3	320	593.15	0.00168591	376.3	50169.1	10.8232
4	340	613.15	0.00163092	557.9	74380.3	11.2169



- a. From the Clausius-Clapeyron equation, we can plot the natural logarithm of pressure (in Pa) against reciprocal temperature (in K), and the slope of this line is the molar heat of evaporation over R. (2pt for the graph, -0.5 if each unit is incorrect)

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (1\text{pt})$$

$$-\frac{\Delta H_{vap}}{R} = -7198.3, \Delta H_{vap} = 7198.3 \times 8.314 = 59.8 \text{ kJ/mol}$$

1pt for the correct answer (-0.5 if the unit is incorrect, no deduction for the s.f.)

- b. Using the equation we derive, the pressure of normal boiling point is 101325 Pa.

$$\ln 101325 = 7198.3(1/T_b).$$

$$T_b = 624.5 \text{ K} = 351.4 \text{ }^\circ\text{C} \text{ (1pt, -0.5 if the unit is incorrect, no deduction for the s.f.)}$$

4. (5 pt) Pheromones are compounds secreted by the females of many insect species to attract males. One of these compounds contains 80.78% C, 13.56% H, and 5.66% O. A solution of 1.00 g of this pheromone in 8.50 g of benzene freezes at 3.37°C (the normal freezing point of pure benzene is 5.50°C). If the molal freezing-point depression constant K_f of benzene is 5.12 K·kg/mol, calculate the molar mass and molecular formula of this compound.

From the colligative properties, we know that the vapor pressure of the solution depends on the number of solutes, instead of the other identities of solute molecules. Pheromones are compounds that won't dimerize or dissociate in benzene, therefore, it's trivial that the colligative constant $i = 1$. The impurities will drive the freezing point depression of the benzene solution, which relates to the depression constant and molality of the solute as indicated below.

Assuming that the molar mass of pheromones M .

$$\Delta T_f = k_f \times C_m \text{ (1pt)}$$

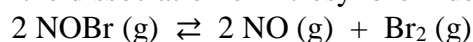
$$C_m = \frac{1.00/M \text{ (mol)}}{8.50 \times 10^{-3} \text{ (Kg)}} = \frac{117.65}{M} \text{ (m)} \text{ (1pt)}$$

$$5.50 - 3.37 = 5.12 \times \frac{117.65}{M}, M = 283 \text{ g/mol} \text{ (1pt)}$$

$$C:H:O = \frac{283 \times 0.8087}{12} : \frac{283 \times 0.1356}{1} : \frac{283 \times 0.0566}{16} \approx 19:38:1 \text{ (1pt)}$$

$$\text{So the molecular formula is } C_{19}H_{38}O_1 \text{ (1pt)}$$

5. (4 pt) Consider the dissociation of nitrosyl bromide (NOBr):



After equilibrium was established at 40°C, it was found that 34.0% of the NOBr had dissociated, and the total pressure was 0.25 bar. Calculate the equilibrium constants K_p and K_c for the reaction.

Assume the initial pressure of NOBr is x bar

After equilibrium, the pressure of NOBr, NO, and Br_2 is $0.66x$, $0.34x$, and $0.17x$, respectively. The equilibrium has a difference of 1 in the gas coefficient sum, which leads to an RT fold of difference in K_p and K_c . By substituting the fractional pressure in K_p to P/RT , we can derive K_c .

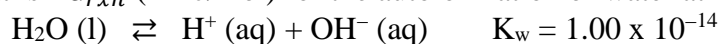
$$0.66x + 0.34x + 0.17x = 0.25 \text{ bar}, x = 0.214 \text{ bar (1pt)}$$

$$K_p = \frac{P_{\text{NO}}^2 \times P_{\text{Br}_2}}{P_{\text{NOBr}}^2} = 9.7 \times 10^{-3} \text{ (1pt)}$$

$$K_p = (RT)^{\Delta n} \times K_c \text{ (1pt)}$$

$$9.7 \times 10^{-3} = (0.083145 \times 313.25)^1 \times K_c, K_c = 3.72 \times 10^{-4}$$

6. (7 pt) (a) What is ΔG_{rxn}^0 (in kJ/mol) for the autoionization of water at 25°C?



- (b) At 60°C, the autoionization constant K_w is determined to be 9.61×10^{-14} . Calculate the values of ΔH_{rxn}^0 and ΔS_{rxn}^0 (assuming they are both temperature-independent).

- (c) Explain why ΔS_{rxn}^0 is negative for the autoionization of water.

(a)

$$\Delta G = -RT \ln(K) = -8.314 \times 298.15 \times \ln(1.0 \times 10^{-14}) = 8.004 \times 10^1 \text{ kJ/mol (1pt, no deduction for s.f.)}$$

(b)

The standard enthalpy of autoionization of water can be calculated by using the van't Hoff equation:

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H_{\text{rxn}}^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \text{ (1 pt)}$$

$$\ln\left(\frac{9.61 \times 10^{-14}}{1.00 \times 10^{-14}}\right) = \frac{\Delta H_{\text{rxn}}^0}{8.314 \text{ (J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})} \left(\frac{1}{298 \text{ (K)}} - \frac{1}{333 \text{ (K)}}\right)$$

$$\Delta H_{\text{rxn}}^0 = 53.4 \text{ kJ/mol (1 pt, no deduction for s.f.)}$$

The change of the equilibrium constant with temperature is determined by the standard enthalpy change, ΔH_{rxn}^0 , and the standard entropy change, ΔS_{rxn}^0 :

$$\Delta G = -RT \ln(K) = \Delta H_{\text{rxn}}^0 - T \Delta S_{\text{rxn}}^0$$

$$-8.314 \text{ (J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \times 333 \text{ (K)} \times \ln(9.61 \times 10^{-14}) = 53.4 \left(\frac{\text{kJ}}{\text{mol}}\right) \times$$

$$1000 \left(\frac{\text{J}}{\text{kJ}}\right) - 333 \times \Delta S_{\text{rxn}}^0$$

$$\Delta S_{\text{rxn}}^0 = -88.8 \text{ J/K} \cdot \text{mol (1pt, no deduction for s.f.)}$$

(c)

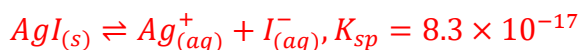
In autoionization of H_2O , a water molecule deprotonates (loses the nucleus of one of its hydrogen atoms) to become a hydroxide ion, OH^- . The hydrogen nucleus, H^+ , immediately protonates another water molecule to form hydronium, H_3O^+ .



The water molecules encircle the formed ions in a spherical manner (1pt), so they would get one order indirectly and decrease the disorder of water (1pt). Therefore, $\Delta S_{\text{H}_2\text{O}}$ is negative for the autoionization of water.

KEY POINT: "the disorder of the solvent decreases!"

7. (6 pt) The solubility product of AgI is 8.3×10^{-17} , whilst the formation constant of $\text{Ag}(\text{CN})_2^-$ is 1.0×10^{21} . Determine the molar solubility of AgI (in M) (a) in pure water, (b) in 0.20 M KI solution, and (c) in 0.20 M KCN solution.



Assume that the solubility of AgI is S.

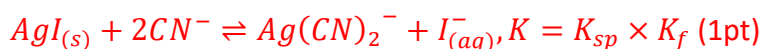
(a)

$$K_{sp} = 8.3 \times 10^{-17} = S^2 \text{ (1pt)}, S = 9.1 \times 10^{-9} \text{ (M)} \text{ (1pt)}$$

(b)

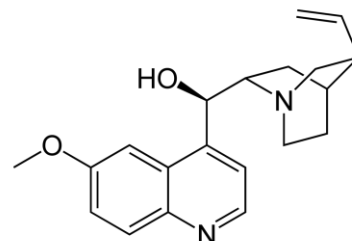
$$K_{sp} = 8.3 \times 10^{-17} = S(0.2 + S) \text{ (1pt)}, S = 4.2 \times 10^{-16} \text{ (M)} \text{ (1pt)}$$

(c)



$$K = 8.3 \times 10^4 = \frac{S^2}{(0.2 - 2S)^2}, S = 0.10 \text{ (M)} \text{ (1pt)}$$

8. (5 pt) Quinine (structure shown to the right) is a natural product commonly used as an anti-malarial drug. (a) Determine which nitrogen atom in quinine has stronger basicity (Explain your reasoning). (b) If a 1.5×10^{-3} M quinine solution has pH = 9.84, calculate the K_b value for quinine.



(a)

The quinoline N is sp^2 hybridization while the 3° amine N is sp^3 hybridization. They both possess one lone pair in the hybridization mentioned above. Basicity can be perceived as the ability to the donation of electron density no matter in Brønsted-Lowry's (electron density donated to the proton) or Lewis's theory. sp^2 hybridization has more s-orbital factor than sp^3 hybridization, which implies the lone pair is closer to the nucleus in space, resulting in a stronger attractive force to the lone pair. (1pt) Hence, sp^3 hybridized lone pair (3° amine N) is easier donated, in other words, stronger in basicity. (1pt)

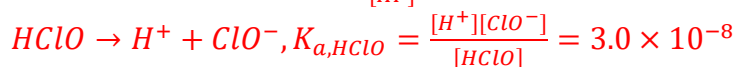
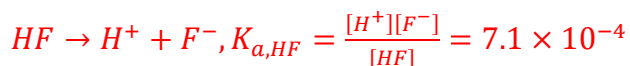
(b)

The equilibrium constant of hydrolyzation of quinine is given by:

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \text{ (1pt)}$$

$$K_b = \frac{10^{-2 \times (14 - 9.84)}}{0.0015 - 10^{-(14 - 9.84)}} = 3.4 \times 10^{-6} \text{ (1pt)}$$

9. (5 pt) (a) Calculate the pH value of a solution consisting of 0.15 M HF ($K_a = 7.1 \times 10^{-4}$) and 0.1 M HClO ($K_a = 3.0 \times 10^{-8}$). (b) Calculate $[F^-]$, $[ClO^-]$, and $[OH^-]$ in this solution.



Assume that the dissociation of HF is x (M) and that of HClO is y (M). Because the dissociation constant of HF is 1000 times greater than HClO, it means that the solution is dominated by the dissociation of HF molecule. Note that the dissociation constant is relatively big to approximate $0.15 - x$ as 0.15 , so we should solve the quadratic equation using the calculator (1pt). On the other hand, owing to the small dissociation constant of HClO, we can approximate $0.1 - y$ as 0.1 and $x + y$ as x .

$$\text{for weak acid HF, } \alpha \approx \sqrt{\frac{K_a}{C_0}} = 0.069 > 5\%$$

$$K_{a, HF} = \frac{[H^+][F^-]}{[HF]} = \frac{(x+y)x}{0.15-x} \approx \frac{x^2}{0.15-x} = 7.1 \times 10^{-4} \text{ (1pt)}, x = 0.00997 = 0.010 \text{ (M)}$$

$$K_{a, HClO} = \frac{[H^+][ClO^-]}{[HClO]} = \frac{(x+y)y}{0.1-y} \approx \frac{xy}{0.1} = 3.0 \times 10^{-8} \text{ (1pt)}, y = 3.0 \times 10^{-7} = 3 \times 10^{-7} \text{ (M)}$$

$$pH = -\log(x + y) = 2.00 \text{ (0.5pt)}$$

$$[F^-] = x = 0.010 \text{ (M)} \text{ (0.5pt)}$$

$$[ClO^-] = y = 3 \times 10^{-7} \text{ (M)} \text{ (0.5pt)}$$

$$[OH^-] = \frac{10^{-14}}{[H^+]} = 1.0 \times 10^{-12} \text{ (M)} \text{ (0.5pt)}$$

10. (4 pt) A 0.1276-g sample of an unknown monoprotic acid was dissolved in 25.0 mL of water and titrated with 0.0633 M NaOH solution. The volume of base required to bring the solution to the equivalence point was 18.4 mL. (a) Calculate the molar mass of the acid. (b) After 10.0 mL of base had been added during the titration, the pH was determined to be 5.87. What is the K_a of this unknown acid?

(a)

When the titration reaches its equivalence point, moles of acid and base should be the same. Because the sample is a monoprotic acid, moles of the unknown sample should be equal to these of acids.

$$n_{H^+} = n_{OH^-} = 0.0633 \text{ (M)} \times 18.4 \text{ (mL)} = 1.165 \text{ mmol (1pt)}$$

$$n_{un} = n_{H^+} = \frac{0.1276}{M} = 1.165 \times 10^{-3} \text{ mol, } M = 110 \text{ (g/mol)} \text{ (1pt)}$$

(b)

We can apply the Henderson-Hasselbalch equation to get the pKa value.

$$\text{pH} = \text{pKa} + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad (1\text{pt})$$

$$5.87 = \text{pKa} + \log \frac{(0.633)/35}{(1.165 - 0.633)/35}, \text{pKa} = 5.87 - \log \frac{633}{532} = 5.80$$

$$\text{Ka} = 1.6 \times 10^{-6} \quad (1\text{pt})$$