

## Physical Chemistry II - Homework 5

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February 27<sup>th</sup> 2019

**1. Acetone and water are miscible liquids. Ice is added to liquid acetone until solid ice remains. Give the number of components, phases, and degree of freedom of this system.**

There are two components (water and acetone)

There are three phases (liquid, solid, and vapor above the substances)

There is one degree of freedom (because this is on the phase boundary of liquid and solid)

**2. The boiling point of hexane at 1 atm is 68.7°C. What is the boiling point at 1 bar? Given: The vapor pressure of hexane at 49.6°C is 53.32 kPa. State any assumptions made.**

Assumptions: Vapor pressures behave as in ideal gas and  $V_m(l) \ll V_m(g)$ .

$$T_{b, \text{ at } 1 \text{ atm}} = T_1 = 68.7^\circ\text{C} = 341.88\text{K}, \quad P_1 = 1 \text{ atm} = 101.325\text{kPa}.$$

$$T_2 = 49.6^\circ\text{C} = 322.75\text{K}, \quad P_2 = 53.32\text{kPa}$$

$$T_{b, \text{ at } 1 \text{ bar}} = T_3 = ?, \quad P_3 = 1\text{bar} = 100\text{kPa}$$

Apply the Clausius-Clapeyron equation to  $T_1$ ,  $P_1$  and  $T_2$ ,  $P_2$ :

$$(1) \quad \ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_{\text{vap}}H_{\text{hexane}} \times (T_2 - T_1)}{RT_1T_2}$$

$$(2) \quad \Delta_{\text{vap}}H_{\text{hexane}} = \ln\left(\frac{P_2}{P_1}\right) \times \frac{RT_1T_2}{T_2 - T_1}$$

$$(3) \quad = \ln\left(\frac{53.32}{101.325}\right) \times \frac{(8.3145)(341.88)(322.75)}{322.75 - 341.88} = 30.8\text{kJmol}^{-1}$$

Apply the Clausius-Clapeyron equation to  $T_2$ ,  $P_2$  and  $T_3$ ,  $P_3$

$$(4) \quad \ln\left(\frac{P_3}{P_2}\right) = \frac{\Delta_{\text{vap}}H_{\text{hexane}}}{R} \left(\frac{1}{T_3} - \frac{1}{T_2}\right)$$

$$(5) \quad T_3 = \left(\frac{\ln \frac{P_3}{P_2} \times R}{-\Delta_{\text{vap}}H_{\text{hexane}}} + \frac{1}{T_2}\right)^{-1}$$

$$(6) \quad T_3 = \left(\frac{\ln \frac{100}{53.32} \times 8.3145}{-30.8 \times 10^3} + \frac{1}{322.75}\right)^{-1} = \boxed{341.5\text{K}}$$

**3. Liquid mercury has a density of  $13.690\text{ g cm}^{-3}$  and solid mercury  $14.193\text{ g cm}^{-3}$ , both measured at the melting point ( $-38.87^\circ\text{C}$ ) and 1 bar pressure. The heat of fusion is  $9.75\text{ J g}^{-1}$ . Calculate the melting points of mercury under a pressure of (a) 10 bar and (b) 3540 bar. The experimentally observed melting point under 3540 bar is  $-19.9^\circ\text{C}$**

$$\Delta_{fus}H = 9.75 J g^{-1}, \quad T = -38.87^{\circ}C = 234.28K$$

$$V_{liq} = \frac{1}{\rho} = \frac{1}{13.609 gcm^{-3}} = 7.305 \times 10^{-8} m^3 g^{-1}, \quad V_{sol} = \frac{1}{14.193 gcm^{-3}} = 7.046 \times 10^{-8} m^3 g^{-1}$$

$$\Delta V = V_l - V_s = 2.59 \times 10^{-9} m^3 g^{-1}$$

$$P_1 = 1 atm = 10^5 Pa, \quad P_2 = 10 atm = 10^6 Pa, \quad , \quad , \quad P_3 = 3540 bar = 3540 \times 10^5 Pa$$

Using Clapeyron equation:

$$(7) \quad \frac{dT}{dP} = \frac{\Delta_{trs}V}{\Delta_{trs}S} = \frac{T\Delta_{trs}V}{\Delta_{fus}H}$$

$$(8) \quad \rightarrow \frac{\Delta T}{\Delta P} \simeq \frac{T\Delta V}{\Delta_{fus}H}$$

$$(9) \quad \Delta T = \frac{T\Delta V\Delta P}{\Delta_{fus}H}$$

$$(10) \quad \text{for a) } \Delta T = \frac{(234.28K)(2.59 \times 10^{-9} m^3 g^{-1})(9 \times 10^5 Pa)}{9.75 J g^{-1}} = 0.056K$$

$$(11) \quad T = T_i + \Delta T = 234.28 + 0.056 = 234.336K = \boxed{-38.81^{\circ}C}$$

$$(12) \quad \text{for b) } \Delta T = \frac{(234.28K)(2.59 \times 10^{-9} m^3 g^{-1})(3539 \times 10^5 Pa)}{9.75 J g^{-1}} = 22.02K$$

$$(13) \quad T = T_i + \Delta T = 234.28 + 22.02 = 256.30K = \boxed{-16.85^{\circ}C}$$

**4. Vapor pressures of n-butane are given. Use them to calculate the enthalpy of vaporization, assuming that the enthalpy is constant over the temperature range.**

P/torr	T/K
5	187.45
10	195.35
20	204.25
40	214.05
60	220.35
100	228.95
200	241.95
400	256.85

Use the Clausius-Clapeyron, with the assumptions that the vapor is ideal and the vaporization enthalpy is constant over the temperature range given.

$$(14) \quad \frac{d \ln P}{dT} = \frac{\Delta_{vap}H}{RT^2}$$

$$(15) \quad \ln P = \left( \frac{-\Delta_{vap}H}{R} \right) \left( \frac{1}{T} \right) + C$$

$\frac{-\Delta_{vap}H}{R}$  is the slope of the line  $y = mx + b$  where  $y = \ln P$  and  $x = 1/T$

Hence:

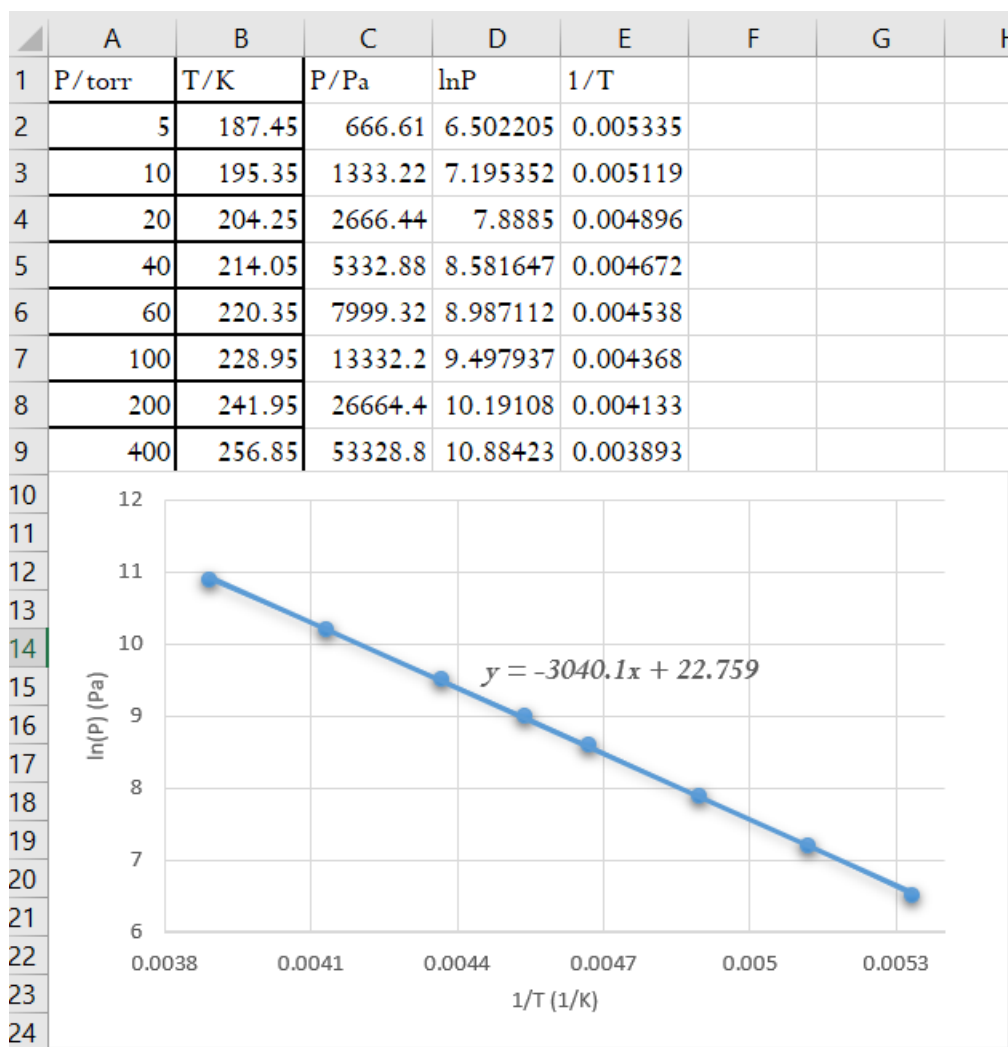
$$(16) \quad \frac{-\Delta_{vap}H}{R} = \frac{\ln P_2 - \ln P_1}{\frac{1}{T_2} - \frac{1}{T_1}}$$

$$(17) \quad \Delta_{vap}H = -R \frac{\ln P_2 - \ln P_1}{\frac{1}{T_2} - \frac{1}{T_1}}$$

$$(18) \quad = (-8.3145) \left( \frac{\ln 60 - \ln 20}{\frac{1}{220.35} - \frac{1}{204.25}} \right) = \boxed{25.5 kJ/mol}$$

An alternative method to find the slope is using Excel to plot the line. The work shown below includes the slope of -3040.1. Hence:

$$\Delta_{vap}H = (-3040.1)(-8.3145) = 25277 J/mol = \boxed{25.3 kJ/mol}$$



**5. The vapor pressure of ethane between 100 and 200 K is given by  $\ln(\frac{P}{MPa}) = 45.8006 + 2681.5/T + 0.012366T - 6.8688 \ln T$ .**

**(a) Calculate the normal boiling point.**

**(b) Calculate the enthalpy of vaporization at 125, 150, and 175 K.**

a)

For normal boiling point:  $P = 1 \text{ atm} = 0.101325 \text{ MPa}$

$$(19) \quad \ln(0.101325) = 45.8006 - \frac{2681.5}{T} + 0.012366T - 6.8688 \ln T$$

$$(20) \quad \text{Solve for } T \rightarrow T = \boxed{184.52 \text{ K}}$$

b)

$$(21) \quad \frac{d \ln(P)}{d \frac{1}{T}} = \frac{-\Delta H}{R}$$

$$(22) \quad \frac{d \ln P}{dT} = \frac{\Delta H}{RT^2}$$

$$(23) \quad \frac{d(45.8006 + 2681.5/T + 0.012366T - 6.8688 \ln T)}{dT} = \frac{\Delta H}{8.3145 T^2}$$

$$(24) \quad \Delta H = \left( \frac{2681.5}{T^2} + 0.012366 - \frac{6.8688}{T} \right) (8.3145) (T^2)$$

$$(25) \quad T = 125 \text{ K} \rightarrow \Delta H = \boxed{16763 \text{ J/mol}}$$

$$(26) \quad T = 150 \text{ K} \rightarrow \Delta H = \boxed{16042 \text{ J/mol}}$$

$$(27) \quad T = 175 \text{ K} \rightarrow \Delta H = \boxed{15450 \text{ J/mol}}$$

**6. Estimate the location of the triple point for cyanogen ( $C_2N_2$ ) from the vapor pressure data. Also estimate the enthalpies for sublimation, vaporization, and fusion.**

	t/K	P/torr
solid	210.45	40
solid	221.35	100
liquid	240.15	400
liquid	252.15	760

$$(28) \quad \ln \frac{P_2}{P_1} = \frac{-\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$(29) \quad \Delta H = \ln \frac{P_2}{P_1} \left( \frac{T_1 T_2}{T_2 - T_1} \right) R$$

Using  $T_1 = 240.15 \text{ K}$ ,  $T_2 = 252.15 \text{ K}$ ,  $P_1 = 400 \text{ torr}$ , and  $P_2 = 760 \text{ torr}$

$$(30) \quad \Delta_{vap} H = \boxed{26.93 \text{ kJ/mol}}$$

Using  $T_1 = 210.45 \text{ K}$ ,  $T_2 = 221.35 \text{ K}$ ,  $P_1 = 40 \text{ torr}$ , and  $P_2 = 100 \text{ torr}$

$$(31) \quad \Delta_{sub}H = \boxed{32.56 kJ/mol}$$

$$(32) \quad \Delta_{fus}H = \Delta_{sub}H - \Delta_{vap}H = 32.56 - 26.93 = \boxed{5.63 kJ/mol}$$

For finding the triple point ( $P_{tp}$  and  $T_{tp}$ ):

$$(33) \quad \ln\left(\frac{P_{tp}}{P_{solid}}\right) = \frac{\Delta_{sub}H}{R}\left(\frac{1}{T_{solid}} - \frac{1}{T_{tp}}\right)$$

$$(34) \quad \ln\left(\frac{P_{tp}}{P_{liquid}}\right) = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T_{liquid}} - \frac{1}{T_{tp}}\right)$$

From equations (33) and (34)

$$(35) \quad \frac{\Delta_{sub}H}{R}\left(\frac{1}{T_{solid}} - \frac{1}{T_{tp}}\right) + \ln P_{tp} = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T_{liq}} - \frac{1}{T_{tp}}\right) + \ln P_{tp}$$

$$(36) \quad \frac{1}{T_{tp}} = \frac{1}{\Delta_{sub}H - \Delta_{vap}H}\left(\frac{\Delta_{sub}H}{T_{solid}} - \frac{\Delta_{vap}H}{T_{liq}}\right) + R \ln P_{solid} - R \ln P_{liq}$$

Using  $T_{solid} = 210.45K$ ,  $P_{solid} = 40\text{torr}$ ,  $T_{liq} = 240.15K$ , and  $P_{liq} = 400\text{torr}$

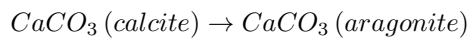
$$T_{tp} = 240.2586K = \boxed{-32.89^\circ C}$$

Using equations (33) or (34)

$$P_{tp} = P_{solid} \times \exp\left[\frac{\Delta_{sub}H}{R}\left(\frac{1}{T_{solid}} - \frac{1}{T_{tp}}\right)\right]$$

$$\rightarrow P_{tp} = \boxed{402.45 \text{ torr}}$$

**7. Calcium carbonate is found in two forms, calcite and aragonite. The following data apply to the transition**



$$\rho_{cal} = 2.71 g/cm^3 \quad \rho_{ara} = 2.93 g/cm^3$$

$$\Delta H^\theta = -0.21 kJ/mol, \quad \Delta G^\theta = 1.04 kJ/mol, \quad \Delta S^\theta = -4.2 J/K \text{ mol}, \quad T = 298.15 K$$

- (a) What is the stable form at  $25^\circ C$ ,  $1\text{bar}$ ? Explain how you know.  
 (b) At what pressure would these two forms be in equilibrium at  $25^\circ C$ ?  
 (c) At what pressure would they be in equilibrium at  $1000K$ ?

a)

Because  $\Delta G^\theta$  for the process is positive, the process is non-spontaneous. Hence, the calcite form is more stable at  $298K$ .

b)

$$V_{ara} - V_{cal} = 100 g/mol \left( \frac{1}{2.93 g/cm^3} - \frac{1}{2.71 g/cm^3} \right) \left( \frac{1 L}{1000 cm^3} \right) = -2.77 \times 10^{-3} L \text{ mol}^{-1}$$

$$\Delta G^\theta = 1.04 kJ/mol = 10.4 L \cdot bar \cdot mol^{-1}$$

At equilibrium  $\Delta G = 0$  or the chemical potentials are equal.

$$\begin{aligned}
 (37) \quad & \mu_{cal} = \mu_{ara} \\
 (38) \quad & \mu_{cal}^o + V_{cal}(p - p^o) = \mu_{ara}^o + V_{ara}(p - p^o) \\
 (39) \quad & (\mu_{ara}^o - \mu_{cal}^o) = (V_{cal} - V_{ara})(p - p^o) \\
 (40) \quad & \Delta G^o = (V_{cal} - V_{ara})(p - p^o) \\
 (41) \quad & p = \frac{\Delta G^o}{(V_{cal} - V_{ara})} + p^o \\
 (42) \quad & p = \frac{10.4 L \cdot bar \cdot mol^{-1}}{2.77 \times 10^{-3} L \cdot mol^{-1}} + 1 bar \\
 (43) \quad & p = 3756 bar = \boxed{375.6 MPa} \\
 & \text{c)}
 \end{aligned}$$

$$\begin{aligned}
 (44) \quad & \Delta G^o(at 1000K) = \Delta H^o - T\Delta S^o \\
 (45) \quad & \Delta G^o = -0.21 - (1000)(-0.0042) = 3.99 kJ \cdot mol^{-1} \\
 & \text{As in part b)}
 \end{aligned}$$

$$\begin{aligned}
 (46) \quad & p = \frac{\Delta G^o}{(V_{cal} - V_{ara})} + p^o \\
 (47) \quad & p = \frac{39.9 L \cdot bar \cdot mol^{-1}}{2.77 L \cdot mol^{-1} \times 10^3} + 1 bar \\
 (48) \quad & p = 14405 bar = \boxed{1440.5 MPa}
 \end{aligned}$$

**8. Assuming ideal solution, calculate  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  for mixing 0.25 moles of benzene with 0.5 moles of toluene at  $30^\circ C$**

$$\Sigma mol = 0.25 + 0.5 = 0.75 mol$$

$$\chi_{toluene} = 0.5/0.75 = 0.667, \quad \chi_{benzene} = 0.25/0.75 = 0.333$$

For ideal solutions:

$$\begin{aligned}
 (49) \quad & \boxed{\Delta_{mix} H = 0} \\
 (50) \quad & \Delta_{mix} S = -nR(\chi_{toluene} \ln \chi_{toluene} + \chi_{benzene} \ln \chi_{benzene}) \\
 (51) \quad & = -(0.75)(8.3145)(0.666 \ln 0.666 + 0.333 \ln 0.333) \\
 (52) \quad & = \boxed{3.97 J/K} \\
 (53) \quad & \Delta_{mix} G = \Delta_{mix} H - T\Delta_{mix} S \\
 (54) \quad & = 0 - (30 + 273.15)(3.97) = \boxed{-1.2 kJ}
 \end{aligned}$$

**9. Henry's Law constants for  $N_2$  and  $O_2$  in water at  $20.0^\circ C$  and 1 atm pressure are  $7.58 \times 10^4$  atm and  $3.88 \times 10^4$  atm, respectively. If the density of water at  $20.0^\circ C$**

is  $0.9982 \frac{g}{cm^3}$  calculate

(a) the equilibrium mole fraction and (b) the concentration of  $N_2$  and  $O_2$  in water exposed to air at  $20.0^\circ C$  and 1 atm total pressure. Assume that the air is 80 mole %  $N_2$  and 20 mole %  $O_2$ .

(55) a)

$$(56) \quad P_{N_2} = (80\%)(1atm) = 0.8atm, \quad P_{O_2} = (20\%)(1atm) = 0.2atm$$

$$(57) \quad \chi_{N_2} = \frac{P_{N_2}}{K_{N_2}}, \quad \chi_{O_2} = \frac{P_{O_2}}{K_{O_2}}$$

$$(58) \quad \chi_{N_2} = \frac{0.8atm}{7.58 \times 10^4 atm} = \boxed{1.06 \times 10^{-5}}, \quad \chi_{O_2} = \frac{0.2atm}{3.88 \times 10^4} = \boxed{5.15 \times 10^{-6}}$$

(59)

b)

$$V_m(H_2O) = \frac{18.01528g.mol^{-1}}{0.9982g.cm^{-3}} \times \frac{1L}{1000cm^3} = 0.018048L/mol$$

$$(60) \quad \text{Concentration of } N_2 = \frac{\chi_{N_2}}{V_m(H_2O)} = \frac{1.06 \times 10^{-5}}{0.018048L.mol^{-1}} = \boxed{5.87 \times 10^{-4}M}$$

$$(61) \quad \text{Concentration of } O_2 = \frac{\chi_{O_2}}{V_m(H_2O)} = \frac{5.15 \times 10^{-6}}{0.018048L.mol^{-1}} = \boxed{2.85 \times 10^{-4}M}$$

10. The following data are for mixtures of isopropanol in benzene at  $25^\circ C$ .

(a) Prepare a pressure-composition plot that includes both components and total pressure.

(b) Does the solution exhibit positive or negative deviations from Raoult's law? Explain the physical reasons for this.

(c) Use the graph to calculate the activities and activity coefficients for both isopropanol and benzene at  $\chi_{isopropanol} = 0.20, 0.50, \text{ and } 0.80$ .

(d) Calculate the excess Gibbs Free energy of mixing at the same concentrations as in part (c).

(a), (c), (d) are shown below using Excel to compute the values.

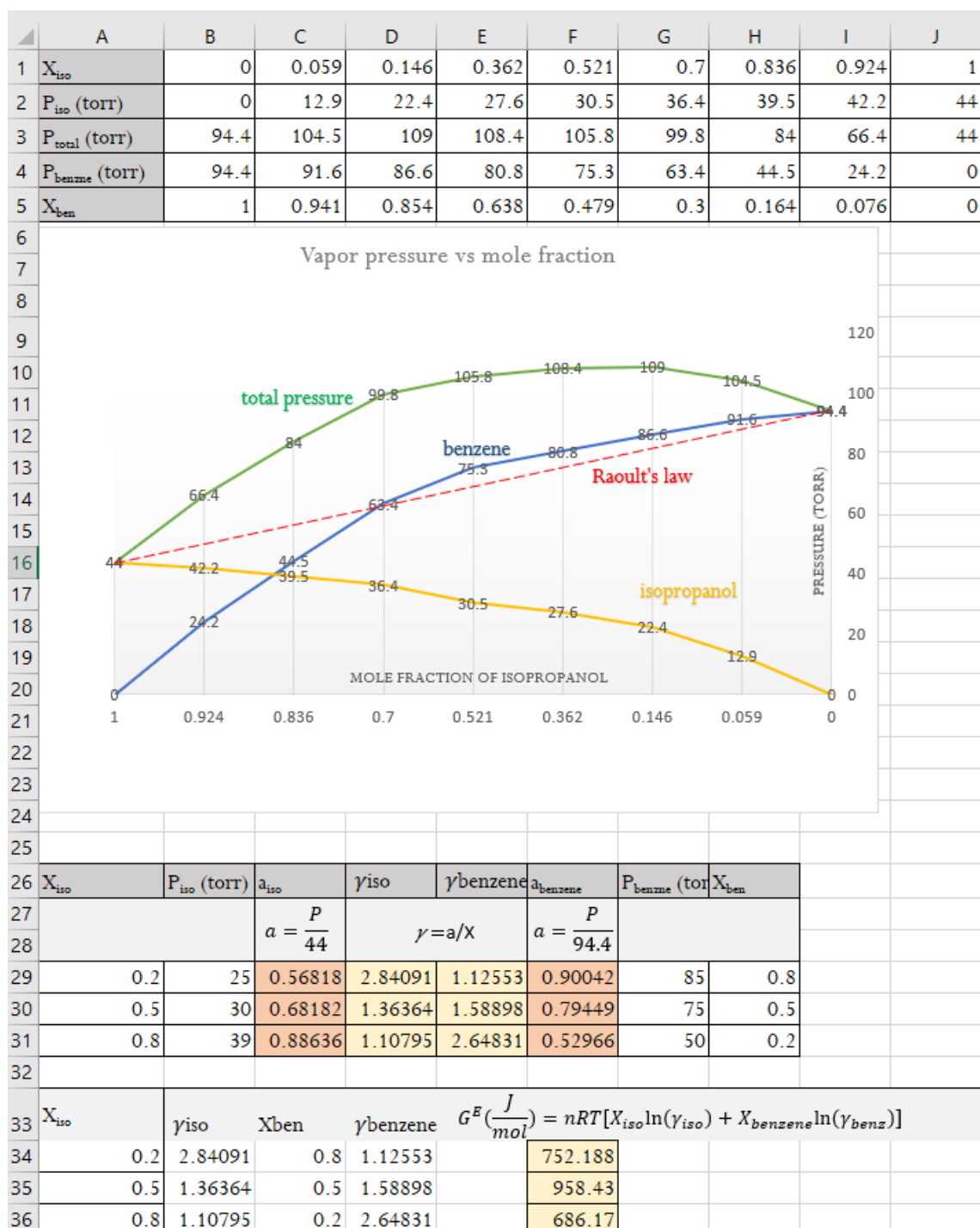
(b) As in the graph, the solution exhibits positive deviation from Raoult's law. This means that the vapor pressure of the mixture is always higher than you would expect from an ideal mixture. The interactions between benzene and isopropanol are weaker than those between benzene molecules or isopropanol molecules. This indicates that in the solution, molecules of benzene or isopropanol will find it easier to escape than in pure state.

(d) The excess Gibbs free energy can be calculated as below:

$$(62) \quad G^E = \Delta_{mix}G_{non-ideal} - \Delta_{mix}G_{ideal}$$

$$(63) \quad G^E = nRT[\chi_A \ln(a_A) + \chi_B \ln(a_B)] - nRT[\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B)]$$

$$(64) \quad G^E = nRT[\chi_A \ln \gamma_A + \chi_B \ln \gamma_B]$$





# Physical Chemistry II - Homework 5

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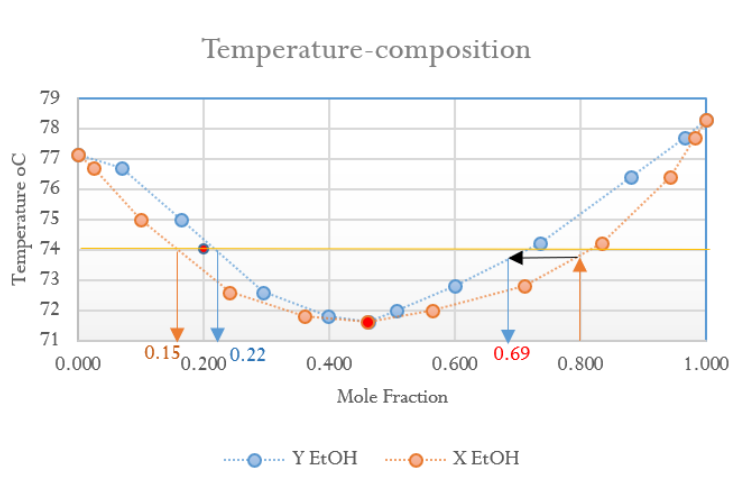
February 27<sup>th</sup> 2019

1. The protein human plasma albumin has a molar mass of  $69,000 \text{ g mol}^{-1}$ . Calculate the osmotic pressure of a solution of this protein containing  $2 \text{ g}$  per  $100 \text{ cm}^3$  at  $25^\circ \text{C}$  in (a) Pa and (b) mm  $\text{H}_2\text{O}$ . (The experiment is carried out using salt solution as the solvent and a membrane permeable to both salt and water.) (c) Neglecting the influence of the salt (i.e., assume the solvent is water), what is the freezing point depression of an albumin solution of the same molality?

$$\begin{aligned} & \text{a and b.} \\ & \text{mole of albumin: } n = 2 \text{ g} \times \frac{1 \text{ mol}}{69000 \text{ g}} = 2.89 \times 10^{-5} \text{ mol} \\ & \text{Osmotic pressure: } \pi = \frac{nRT}{v} = \frac{2.89 \times 10^{-5} \text{ mol} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times (25 + 273.15) \text{ K}}{0.0001 \text{ m}^3} = \boxed{718 \text{ Pa}} = \\ & \quad 718 \text{ Pa} \times \frac{0.10197 \text{ mm H}_2\text{O}}{\text{Pa}} = \boxed{73.3 \text{ mm H}_2\text{O}} \\ & \text{c.} \\ & \text{Freezing point depression: } \Delta T_f = K_f b = 1.86 \times \frac{2.89 \times 10^{-5} \text{ mol}}{0.1 \text{ kg water}} = \boxed{5.39 \times 10^{-4} \text{ }^\circ \text{C}} \end{aligned}$$

2. From the data given in the following table, (a) construct a complete temperature-composition diagram for the system ethanol-ethyl acetate for  $1.013 \text{ bar}$ . A solution containing  $X_{\text{EtOH}} = 0.8$  is distilled at  $1.013 \text{ bar}$ . (b) What is the composition of the first vapor to come off? (c) Can ethanol be completely separated from this mixture by simple distillation? Explain. (d) What is the sign of  $G^E$ ? Describe the interactions between ethanol and ethyl acetate. (e) At a total mole fraction  $Z_{\text{EtOH}} = 0.2$  and a temperature of  $74^\circ \text{C}$ , what are the amounts and composition of each phase present?

X EtOH	Y EtOH	BP, °C
0.000	0.000	77.15
0.025	0.070	76.7
0.100	0.164	75.0
0.240	0.295	72.6
0.360	0.398	71.8
0.462	0.462	71.6
0.563	0.507	72.0
0.710	0.600	72.8
0.833	0.735	74.2
0.942	0.880	76.4
0.982	0.965	77.7
1.000	1.000	78.3



b. The first vapor to come off should have the fraction of 0.69

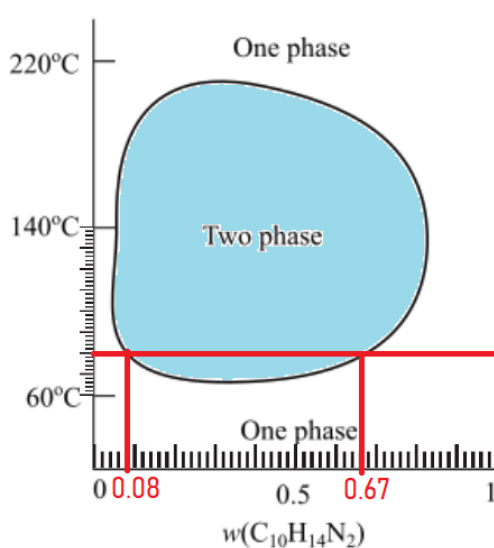
c. The ethanol can not be completely because at the azeotrope point, the vapor coming off has the exactly the same composition of the liquid boiling as shown in the graph.

d. The sign of  $G^E$  is positive because the boiling point is at the minimum of the graph. This means that the EtOH - Ethyl Acetate attraction is not favourable. Thus, the mixing of the two components less favourable leading the positive value of  $G^E$ .

e. %EtOH vapor =  $(0.2 - 0.15) / (0.22 - 0.15) \times 100\% = 71\%$

%EtOH liquid =  $(0.22 - 0.2) / (0.22 - 0.15) \times 100\% = 29\%$

3. Use the figure below to estimate the masses of nicotine and water present in each phase if the 10g of nicotine and 10 g of water are mixed at 80°C and 1atm



	Phase 1	Phase 2	
mass of nicotin	$n_1$	$n_2$	$n_1 + n_2 = 10g$
mass of water	$w_1$	$w_2$	$w_1 + w_2 = 10g$
mass fraction of nicotine	$\frac{n_1}{n_1 + w_1} = 0.08$	$\frac{n_2}{n_2 + w_2} = 0.67$	

Solving four equations in the table above:

$$\frac{10 - n_2}{20 - n_2 - w_2} = 0.08 \text{ and } n_2 = 0.67n_2 + 0.67w_2$$

$$n_2 = \frac{0.67}{0.33}w_2 \text{ and } 10 - n_2 = 1.6 - 0.08n_2 - 0.08w_2$$

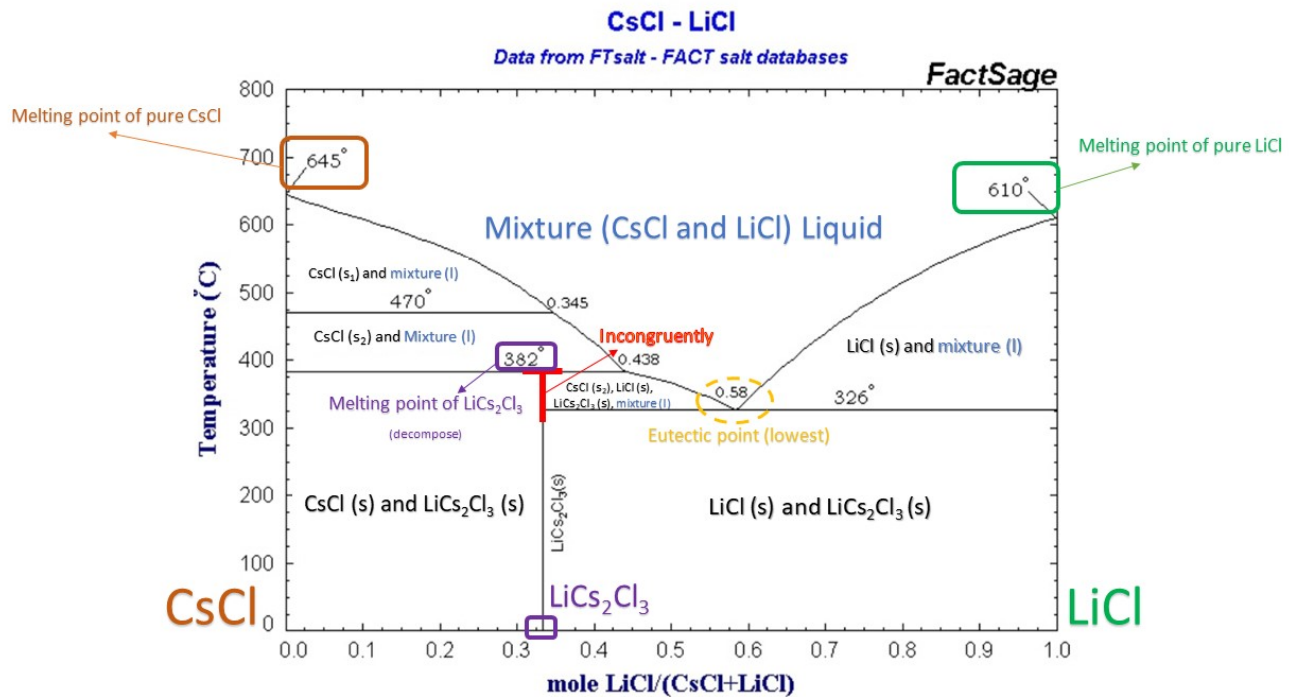
$$10 - \frac{67}{33}w_2 = 1.6 - 0.08 \times \frac{67}{33} \times w_2 - 0.08w_2$$

Thus

$$n_1 = 0.5g, \quad w_1 = 5.3g, \quad n_2 = 9.5g, \quad w_2 = 4.7g$$

4. Answer the following questions using the binary phase diagram of CsCl-LiCl.

- What is the melting point of pure LiCl? Of pure CsCl?
- What is the formula for the compound formed between LiCl and CsCl? At what temperature does this compound melt? Does this compound melt congruently or incongruently?
- What is the temperature and composition of the eutectic point formed?
- Give the phases and composition present in each labeled area (A)-(G).



5. The conversion of malate into fumarate (1)  $\text{malate (aq)} \rightleftharpoons \text{fumarate (aq)} + \text{H}_2\text{O (l)}$  is endergonic at body temperature, 37°C;  $\Delta G^\circ = 2.93 \text{ kJ mol}^{-1}$ . In metabolism,

the reaction is coupled with (2) fumarate (aq)  $\rightleftharpoons$  aspartate (aq) for which  $\Delta G^\circ = -15.5 \text{ kJ mol}^{-1}$  at  $37^\circ\text{C}$ . (a) Calculate  $K_c$  for reaction 1; (b) Calculate  $K_c$  for reaction 2. (c) Calculate  $K_c$  and  $\Delta G^\circ$  for the coupled reaction 1+2.

a)

For reaction 1

$$\frac{\Delta G^\circ}{T} = -R \ln K_c$$

$$\ln K_c = \frac{-\Delta G^\circ}{RT} = \frac{-2930 \text{ J/mol}}{(37 + 273.15) \text{ K} \times (8.3145 \text{ J/K mol})} = -1.136$$

$$K_c = e^{-1.136} = \boxed{0.321}$$

b)

For reaction 2

$$\frac{\Delta G^\circ}{T} = -R \ln K_c$$

$$\ln K_c = \frac{-\Delta G^\circ}{RT} = \frac{15500 \text{ J/mol}}{(37 + 273.15) \text{ K} \times (8.3145 \text{ J/K mol})} = 6.011$$

$$K_c = e^{-1.136} = \boxed{408}$$

c)

For reaction 1+2

$$\frac{\Delta G^\circ}{T} = -R \ln K_c$$

$$\ln K_c = -\frac{\Delta G_1^\circ + \Delta G_2^\circ}{RT} = -\frac{-15500 + 2930 \text{ J/mol}}{(37 + 273.15) \text{ K} \times (8.3145 \text{ J/K mol})} = 4.874$$

$$K_c = e^{-1.136} = \boxed{131}$$

6. The table below lists the standard free energies of formation (using the old standard state of  $P^\theta = 1 \text{ atm}$ ) of several hydrates of  $\text{MgCl}_2$  at  $25^\circ\text{C}$ . Which hydrate will be the stable form in air at  $25^\circ\text{C}$  if the relative humidity is 80%? State the source of your value for the free energy of formation of water. The vapor pressure of water is  $23.76 \text{ torr}$  at  $25^\circ\text{C}$ .

$$\Delta_{rxn} G = \Delta_f G^\theta + RT \ln(Q)$$

$$\Delta_{rxn} G^\theta = \Delta_f G_{\text{MgCl}_2 \cdot n\text{H}_2\text{O}}^\theta - \Delta_f G_{\text{MgCl}_2(s)}^\theta - n \Delta_f G_{\text{H}_2\text{O}(g)}^\theta$$

$$Q = \frac{a_{\text{MgCl}_2 \cdot n\text{H}_2\text{O}(s)}}{a_{\text{MgCl}_2(s)} \times a_{\text{H}_2\text{O}(g)}} = \frac{1}{1 \times \left(\frac{P_{\text{H}_2\text{O}}}{P^\theta}\right)^n}$$

According to Physical Chemistry, 10th Edition by Peter Atkins:

$$\Delta_f G_{\text{H}_2\text{O}(g)}^\theta = -228.57 \text{ kJ/mol} \text{ and } \Delta_f G_{\text{MgCl}_2(s)}^\theta = -592.33 \text{ kJ/mol}$$

Also,  $K = 8.3 \times 10^{-3} \text{ L atm K}^{-1} \text{ mol}^{-1}$ ,  $T = 298.15 \text{ K}$ ,  
 $P_{H_2O} = (0.8)(23.76 \text{ torr})\left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = 0.025 \text{ atm}$ , and  $P^\theta = 1 \text{ atm}$

	A	B	C	D	E	F	G	H
1		$\Delta_f G^\circ$ (kJ/mol)	n	$\Delta_{rxn} G^\circ$ (kJ/mol)	Q			$\Delta_{rxn} G$ (kJ/mol)
2	MgCl <sub>2</sub>	-592.33	0	0		1		0
3	MgCl <sub>2</sub> ·H <sub>2</sub> O	-862.36	1	-41.46		40		-32.32252973
4	MgCl <sub>2</sub> ·2H <sub>2</sub> O	-1118.5	2	-69.03		1600		-50.75505946
5	MgCl <sub>2</sub> ·4H <sub>2</sub> O	-1633.8	4	-127.19		2560000		90.64011892
6	MgCl <sub>2</sub> ·6H <sub>2</sub> O	-1278.8	6	684.95		4096000000		739.7748216

$MgCl_2 \cdot 4H_2O$  has the lowest  $\Delta_{rxn} G$ , hence this is the most stable form of this hydrate.

**7. The average molar mass M of equilibrium mixtures of  $NO_2$  and  $N_2O_4$  at 1.013bar total pressure is given in the table below at three temperatures.**

(a) Calculate the degree of dissociation of  $N_2O_4$  and the equilibrium constant at each of these temperatures.

(b) Graphically determine the enthalpy for the dissociation of  $N_2O_4$ .

(c) Calculate the equilibrium constant at  $35^\circ C$

(d) Calculate the degree of dissociation for  $N_2O_4$  at  $35^\circ C$  when the total pressure is 0.5bar. a.

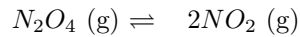
Molar mass of  $NO_2 = 46 \text{ g/mol}$

Molar mass of  $N_2O_4 = 92 \text{ g/mol}$

Let x is the mole fraction of  $NO_2$  so the mole fraction of  $N_2O_4$  is  $1 - x$

$$\text{average mass} = 46x + (1 - x)(92)$$

$$x = \frac{92 - \text{average mass}}{46}$$

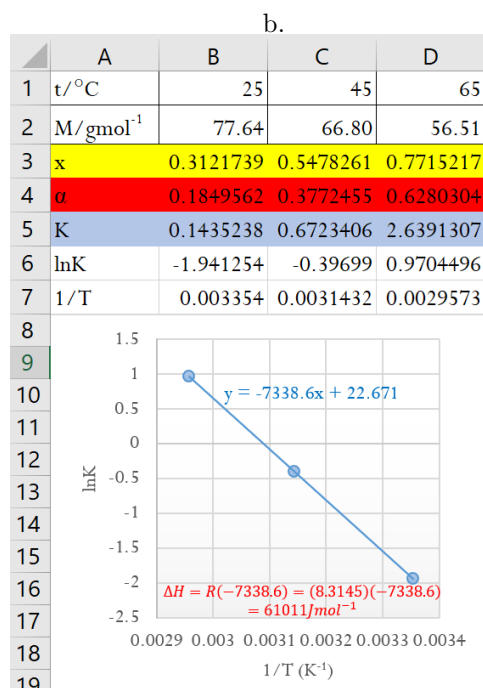


I	1			
C	$-\alpha$	$2\alpha$		
E	$1 - \alpha$	$2\alpha$	Total mole = $1 + \alpha$	
Mole Fraction	$1 - x = \frac{1 - \alpha}{1 + \alpha}$	$x = \frac{2\alpha}{1 + \alpha}$		

$$\alpha = \frac{x}{2 - x}$$

$$K = \frac{(\chi_{NO_2} \times P)^2}{\chi_{N_2O_4} \times P} = \frac{\chi_{NO_2}^2 \times P}{\chi_{N_2O_4}} = \frac{x^2 \times 1.013 \text{ bar}}{1 - x}$$

	A	B	C	D
1	t/ $^\circ C$	25	45	65
2	M/gmol <sup>-1</sup>	77.64	66.80	56.51
3	x	0.31217	0.54783	0.77152
4	$\alpha$	0.18496	0.37725	0.62803
5	K	0.14352	0.67234	2.63913



c. Using the equation from the graph in part b.

$$\ln K = (-7338.6) \times (35 + 273.15) + 22.671 = -1.144025$$

$$K = e^{-1.144025} = \boxed{0.32}$$

d.

$$K = \frac{(\chi_{NO_2} \times P)^2}{\chi_{N_2O_4} \times P} = \frac{(\chi_{NO_2} \times P)^2}{1 - \chi_{NO_2} \times P} = \frac{x^2 \times 0.5 \text{ bar}}{1 - x} = 0.32$$

$$0.5x^2 + 0.32x - 0.32 = 0$$

Solve the quadratic equation, the only positive solution is  $x = 0.542$ .

Using the equation in part a.

$$\alpha = \frac{x}{2 - x} = 0.372$$

8. At 2000°C water is 2% dissociated into oxygen and hydrogen at a total pressure of 1 bar.

(a) Calculate K for  $H_2O(g) \rightleftharpoons H_2(g) + 1/2O_2(g)$

(b) Will the extent of reaction increase or decrease if the pressure is reduced? Explain.

(c) Will the extent of reaction increase or decrease if argon gas is added, holding the total pressure to 1 bar? Explain.

(d) Will the extent of reaction change If the pressure is raised by addition of argon at constant volume to the closed system containing partially dissociated water vapor?

Explain.

(e) Will the extent of reaction increase or decrease if oxygen is added while holding the total pressure constant at 1 bar? Explain.

		$H_2O$ (g) $\rightleftharpoons$	a. $H_2$ (g)	$+ \frac{1}{2}O_2$ (g)	
I		1			
C		-x	+x	$+\frac{1}{2}x$	
E		1-x	x	$\frac{1}{2}x$	$n_{total} = 1 - x + x + \frac{1}{2}x = 1 + \frac{1}{2}x$
Mole fraction		$\frac{1-x}{1+\frac{1}{2}x}$	$\frac{x}{1+\frac{1}{2}x}$	$\frac{\frac{1}{2}x}{1+\frac{1}{2}x}$	
Partial Pressure	$P_{H_2O} = \frac{1-x}{1+\frac{1}{2}x} P_{total}$		$P_{H_2} = \frac{x}{1+\frac{1}{2}x} P_{total}$	$P_{O_2} = \frac{\frac{1}{2}x}{1+\frac{1}{2}x} P_{total}$	Dalton's law

$$K = \frac{(a_{H_2})(a_{O_2})^{1/2}}{a_{H_2O}} = \frac{(\frac{x}{1+\frac{1}{2}x} P_{total}/P^\theta)(\frac{\frac{1}{2}x}{1+\frac{1}{2}x} P_{total}/P^\theta)^{1/2}}{\frac{1-x}{1+\frac{1}{2}x} P_{total}/P^\theta}$$

$$K = \frac{\sqrt{0.5}x^{3/2}}{P^{\theta^{1/2}} P_T^{1/2} (1 + \frac{1}{2}x)^{1/2} (1 - x)}$$

With  $P^\theta = P_T = 1bar$  and  $x = 0.02$ ,  $K = 2.03 \times 10^{-3}$

Apply the Le Chatelier's Principle to b. , c. , d. , and e.

b. The extent of reaction increases since the equilibrium shifts to the right. When pressure is reduced, the equilibrium will shift to the side which has more moles of gases.

c. The extent of reaction increases since the equilibrium shifts to the right. When Argon is added with constant total pressure, the partial pressure of each component decreases.

Therefore, the effect will be the same in part b.

d. The extent of reaction will be unchanged since the equilibrium is stable. When Argon is added with constant volume, the total pressure and the partial pressure of each component increase relatively which makes no change in the equilibrium.

e. The extent of reaction decreases since the equilibrium shifts to the left. When Oxygen gas (the product) is added at constant pressure, the equilibrium will shift to the side which opposes the change.

These problems are typically more lengthy and difficult (and may require software) than those that will be presented on an exam.

For extra practice on simpler problems, work on the following exercises: 5A1.a; 5A4.a; 5A6.a; 5A8.a; 5A10.a; 5C: 2a, 3a, 4a; 5D: 1a, 4a, 6a; 5F1a; 5F2a; 5F4a

1. For a solution of ethanol and water at 20 °C that has a concentration of 0.2 mole fraction ethanol, the partial volume of water is  $17.9 \text{ cm}^3\text{mol}^{-1}$  and the partial molar volume of ethanol is  $55.0 \text{ cm}^3\text{mol}^{-1}$ . What volumes of pure ethanol and water are required to make one liter of this solution? What is  $\Delta_{\text{mix}}V$  under these conditions? At 20 °C the density of ethanol is  $0.789 \text{ g cm}^{-3}$  and the density of water is  $0.998 \text{ g cm}^{-3}$ . **(Ans. 570 cm<sup>3</sup> water, 461 cm<sup>3</sup> ethanol, -31 cm<sup>3</sup>)**

Solution: component 1 is water and component 2 is ethanol:

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2 = 4n_2 \bar{V}_1 + n_2 \bar{V}_2 = n_2 (4\bar{V}_1 + \bar{V}_2)$$

The substitution is made since  $X_2 = \frac{n_2}{n_1+n_2} = 0.2$   $n_2 = 0.2(n_1 + n_2)$   $0.8 n_2 = 0.2n_1$   $4 n_2 = n_1$  (Or, without the detailed math, since the solution is mole fraction= 1/5 ethanol and mole fraction=4/5 water, then there are 4 times as many moles of water as ethanol.)

Find how many moles of each component are in a liter of solution, where the

$$1000 = n_2(4 \cdot 17.9 + 55.0) \quad n_2 = 7.90 \text{ moles ethanol} \quad \text{mass ethanol: } w_2 = 46.07 \frac{\text{g}}{\text{moles}} 7.90 \text{ moles ethanol} = 364.0 \text{ g}$$

$$\text{The volume of ethanol needed to obtain this are } V = \frac{g}{\text{g/cm}^3} = \frac{364.0}{0.789} = 461 \text{ cm}^3$$

$$\text{Therefore, there are } n_1 = 4 n_2 = 4 \cdot 7.90 = 31.6 \text{ moles water}$$

$$\text{The mass of water is } w_1 = 18.01 \frac{\text{g}}{\text{moles}} 31.6 \text{ moles water} = 569.1 \text{ g}$$

$$\text{The volume of water needed is } V = \frac{g}{\text{g/cm}^3} = \frac{569.1}{0.998} = 570 \text{ cm}^3$$

This means that there is a shrinkage of  $(570 + 461) - 1000 = 31 \text{ cm}^3$  when these amounts of ethanol and water are mixed at 20°C.

2. What is the entropy change for mixing 1 liter of a monoatomic ideal gas (call it A) at 2 atm and 100 °C with 2 liters of a different monoatomic ideal gas (call it B) at 0.5 atm and 0 °C (the total volume is confined to 3 liters)? Assume  $C_V = 1.5R$  for both gases. (Hint: you need to include the entropy change for the change in volume, change in temperature, and for mixing) **(Ans. 0.763 J/K)**

Solution. We will expand/contract the gases so they will have the same moles per volume, so after the temperature is changed, each part will be at the same pressure. After calculating the entropy change for the volume changes, the temperature change, then we can calculate the entropy change for mixing A and B.



First, calculate the moles of each gas from the ideal gas law:  $n = \frac{PV}{RT} = \frac{2 \text{ atm} \cdot 1 \text{ L}}{0.082056 \frac{\text{Latm}}{\text{K mole}} \cdot 373 \text{ K}} = 0.0654 \text{ moles A}$   
 $n = \frac{PV}{RT} = \frac{0.5 \text{ atm} \cdot 2 \text{ L}}{0.082056 \frac{\text{Latm}}{\text{K mole}} \cdot 273 \text{ K}} = 0.0446 \text{ moles B}$

In mole fractions,  $X_A=0.594$  and  $X_B=0.406$ . Since in the end the gases will be at the same temperatures, we know that the volumes they would take up will be proportional to their number of moles. Since the total volume is 3 liters, we will expand A to  $0.594 \times 3 \text{ liters} = 1.78 \text{ liters}$  and B to  $1.22 \text{ liters}$ . The entropy changes for these two isothermal expansions are

$$\Delta S_A = n_A R \ln \frac{V_f}{V_i} = 0.0654 \cdot 8.314 \cdot \ln \frac{1.78}{1} = 0.314 \frac{\text{J}}{\text{mol}}$$

$$\Delta S_B = n_B R \ln \frac{V_f}{V_i} = 0.0446 \cdot 8.314 \cdot \ln \frac{1.22}{2} = -0.184 \frac{\text{J}}{\text{mol}}$$

Next, determine the final temperature:  $T_F(n_T C_V) = T_A(n_A C_V) + T_B(n_B C_V)$

Since the heat capacity is the same for both cases, that can be factored out to give

$$T_F = \frac{T_A(n_A) + T_B(n_B)}{(n_T)} = \frac{373(0.0654) + 273(0.0446)}{(0.0654 + 0.0446)} = 332 \text{ K}$$

Now calculate the entropy due to the temperature change for each gas  $\Delta S_A = n_A C_V \ln \frac{T_f}{T_i} = 0.0654 \cdot 1.5 \cdot 8.314 \ln \frac{332}{373} = -0.0939 \text{ J/K}$

$$\Delta S_B = n_B C_V \ln \frac{T_f}{T_i} = 0.0446 \cdot 1.5 \cdot 8.314 \ln \frac{332}{273} = 0.110 \text{ J/K}$$

Since the concentration  $n/V$  is the same on each side and the  $T$  is the same, the pressures will be the same, so we can use the regular formula for mixing gases at the same pressure.

$$\Delta S_{mix} = -R(n_A \ln(X_A) + n_B \ln(X_B)) = -8.314 [0.0654 \ln(0.549) + 0.0446 \ln(0.406)] = 0.618 \text{ J/K}$$

Add all the different components of entropy to get  $\Delta S_{mix} = 0.763 \text{ J/Kmole}$

3. Two components, A and B, were mixed forming a nonideal solution and their liquid and vapor phases were allowed to equilibrate at 298 K and a pressure of 1 atm. The mole fraction of A in the liquid phase was found to be 0.380. The mole fraction of A in the vapor phase was 0.490. Calculate the activities and activity coefficients of both A and B in the solution on the basis of Raoult's law. The vapor pressures of the pure liquids were  $P^*(A) = 790 \text{ Torr}$  and  $P^*(B) = 600 \text{ Torr}$ . Do these represent positive, negative, or no deviations from Raoult's Law? Describe the intermolecular interactions that take place between A and B. **(Ans: 0.471; 1241; 0.646; 1.042; positive)**

Solution:  $a_A = \frac{P_A}{P_A^*}$  and  $a_A = \gamma_A X_A$

The activity is determined by comparing the vapor pressure above the solution to the vapor pressure of the pure component. For A,  $a_A = \frac{P_A}{P_A^*} = \frac{0.490 \cdot 760}{790} = 0.471$ , where the vapor pressure above solution was determined through Dalton's Law.

For B,  $a_B = \frac{P_B}{P_B^*} = \frac{0.510 \cdot 760}{600} = 0.646$

The activity coefficients are determined by comparing the activity to the mole fraction in solution. For A,  $\gamma_A = \frac{a_A}{X_A} = \frac{0.471}{0.380} = 1.241$

For B,  $\gamma_B = \frac{a_B}{X_B} = \frac{0.646}{0.620} = 1.042$

These are positive deviations from Raoult's Law. The components have a higher vapor pressure above the solution than they predicted by Raoult's Law. This indicates that favorable interactions that exist between A-A and/or B-B are disrupted when the molecules are mixed together.

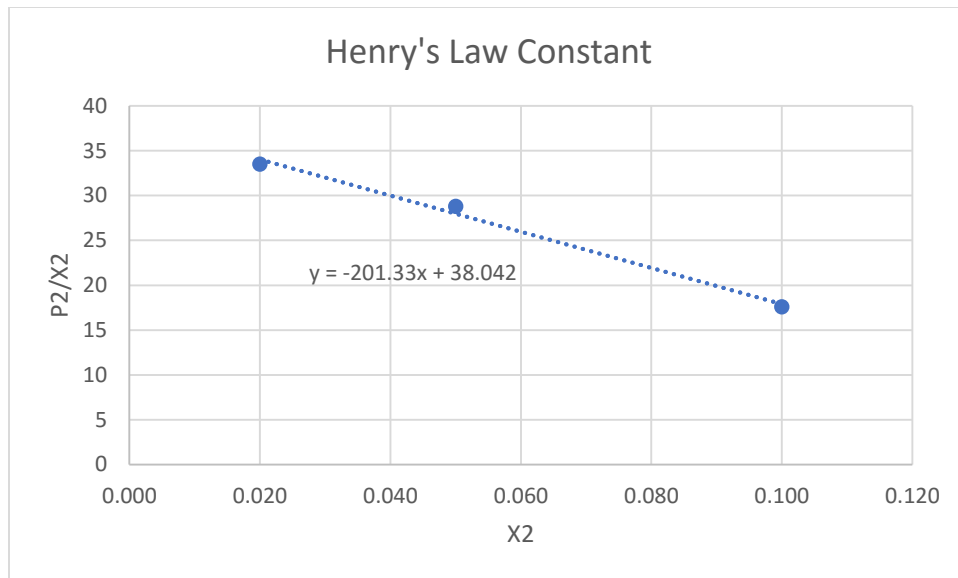
4) Using the data below of the vapor pressures in kPa for a solution of n-propanol and water, calculate the activity and activity coefficients of water (1) and n-propanol (2) at 0.20, 0.40, 0.60, and 0.80 mole fraction of n-propanol. Used Henry's Law standard state for the solute and Raoult's Law standard state for the solvent (water). **(Ans in table)**

Xn-propanol	PH <sub>2</sub> O	Pn-propanol	Activity n-prop	activity coefficient nprop	Activity H <sub>2</sub> O	activity coefficient H <sub>2</sub> O
0.000	3.168	0				
0.020	3.13	0.67				
0.050	3.09	1.44				
0.100	3.03	1.76				
0.200	2.91	1.81	<b>0.05</b>	<b>0.24</b>	<b>0.92</b>	<b>1.15</b>
0.400	2.89	1.89	<b>0.05</b>	<b>0.12</b>	<b>0.91</b>	<b>1.52</b>
0.600	2.65	2.07	<b>0.05</b>	<b>0.091</b>	<b>0.84</b>	<b>2.09</b>
0.800	1.79	2.37	<b>0.06</b>	<b>0.078</b>	<b>0.57</b>	<b>2.83</b>
0.900	1.08	2.59				
0.950	0.56	2.77				
1.000	0	2.901				

Solution:

For Henry's Law,  $a_B = P_B/K_B$  where  $K_X = \lim_{X_B \rightarrow 0} \left( \frac{P_B}{X_B} \right)$  and  $a_B = \gamma_B X_B$

First, the Henry's Law constant must be obtained by extrapolating the value of P/X to X=0. The value obtained from the graph is 38 kPa.



Now  $K=38$  can be used to determine activity  $a_B = P_B/38$ , and then activity can be used to determine activity coefficient for n-propanol,  $\gamma_B = a_B/X_B$ . For water, the vapor pressure will be used to determine the activity  $a_A = \frac{P_A}{3.18}$  and then the mole fraction to determine the activity coefficient  $\gamma_A = \frac{a_A}{1-X_B}$ .

5. A regular solution is defined as one where  $\mu_1 = \mu_1^\theta + RT \ln X_1 + \zeta X_2^2$  and  $\mu_2 = \mu_2^\theta + RT \ln X_2 + \zeta X_1^2$ . Derive the activity coefficients in terms of  $\zeta$ :  $\gamma_1 = \exp\left(\frac{\zeta X_2^2}{RT}\right)$  and  $\gamma_2 = \exp\left(\frac{\zeta X_1^2}{RT}\right)$ .

Solution: By definition  $\ln a_1 = \left(\frac{\mu_1 - \mu_1^\theta}{RT}\right) = \left\{ \ln X_1 + \frac{\zeta X_2^2}{RT} \right\} = \left\{ \ln X_1 + \ln \exp\left(\frac{\zeta X_2^2}{RT}\right) \right\} = \left\{ \ln \left[ X_1 \exp\left(\frac{\zeta X_2^2}{RT}\right) \right] \right\}$ , since  $\ln x + \ln y = \ln(xy)$

Therefore,  $a_1 = \gamma_1 X_1 = X_1 \exp\left(\frac{\zeta X_2^2}{RT}\right)$ . And  $\gamma_1 = \exp\left(\frac{\zeta X_2^2}{RT}\right)$ .

By a similar argument,  $\gamma_2 = \exp\left(\frac{\zeta X_1^2}{RT}\right)$

6. From the data given in the following table construct a complete temperature-composition diagram for the system ethanol-ethyl acetate for 1.013 bar. A solution containing 0.8 mole fraction of ethanol is distilled completely at 1.013 bar.

a) What is the composition of the first vapor to come off?

b) What is the composition that of the last drop of liquid to evaporate?

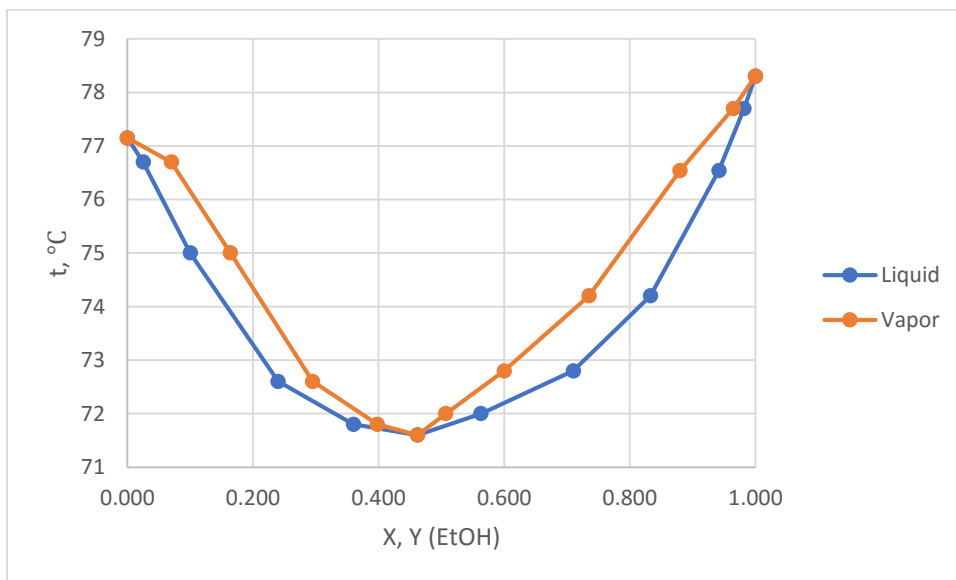
c) What would be the values of these quantities if the distillation were carried out in a cylinder with a piston so that none of the vapor escapes?

(Ans.  $Y=0.7$ ;  $X=1$ ;  $\&=0.7$  and  $X=0.9$ )

XEtOH	YEtOH	BP
0.000	0.000	77.15

0.025	0.070	76.7
0.100	0.164	75.0
0.240	0.295	72.6
0.360	0.398	71.8
0.462	0.462	71.6
0.563	0.507	72.0
0.710	0.600	72.8
0.833	0.735	74.2
0.942	0.880	76.5
0.982	0.965	77.7
1.000	1.000	78.3

Solution:



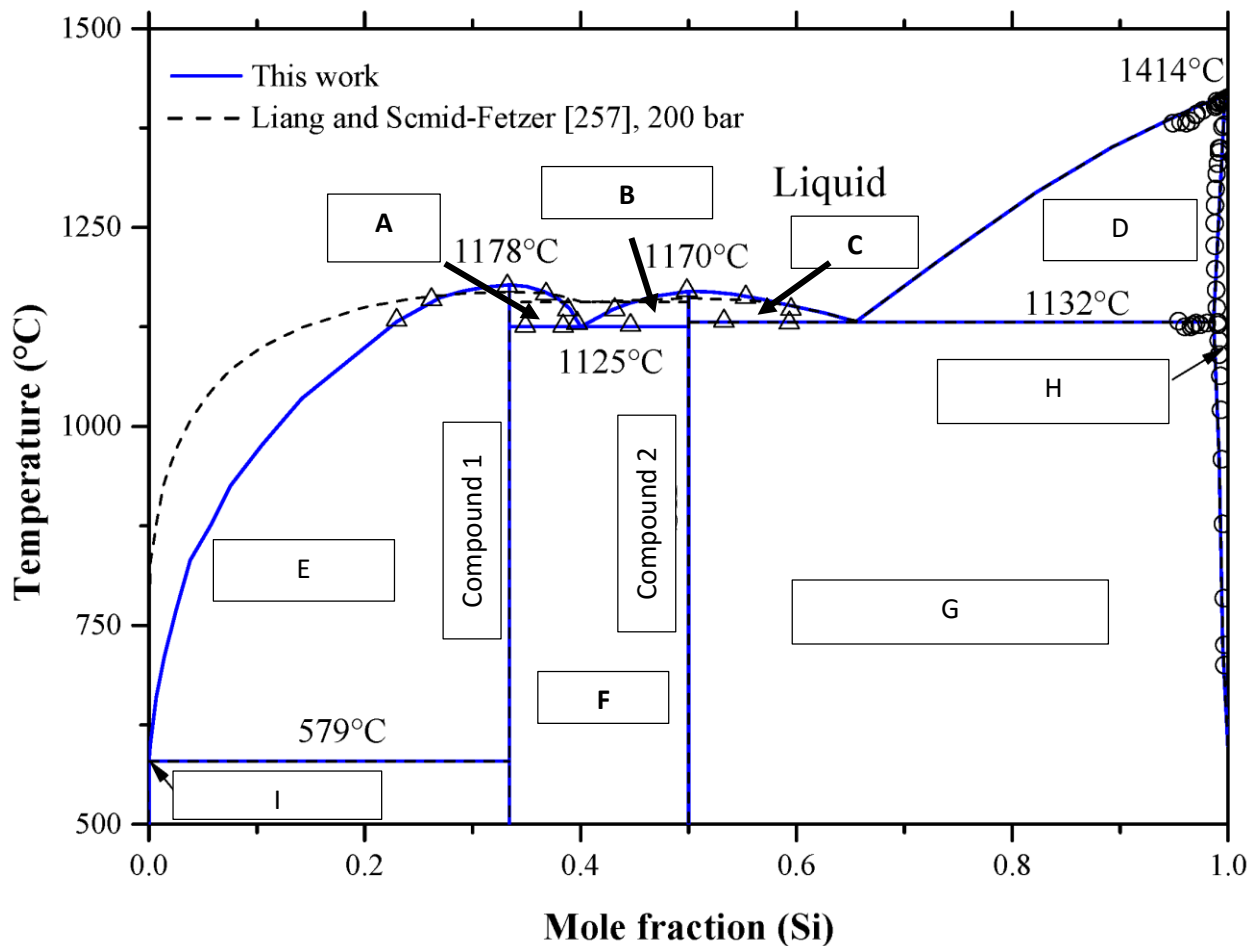
- The vapor in equilibrium with  $X=0.8$  is  $Y=0.7$ , and that will be the composition of the first vapor to come off when a solution of  $X=0.8$  is distilled.
- As the boiling continues, more of the EtAc will be removed. As the mole fraction of EtOH increases, the boiling point will also increase. Finally, the very last drop will be pure EtOH.
- The first vapor to come off will be the same as in part (a). However, when all the mixture is in the vapor state, the mole fraction of the vapor state will be 0.800 simply because that is the total mole fraction of EtOH in the mixture. Thus, to find the composition of last drop to evaporate, simply note the liquid ( $X_{\text{EtOH}}=0.9$ ) in equilibrium with the vapor that has 0.800 EtOH in it.

7. Explain the following observations about red blood cells in terms of chemical potential. When red blood cells are put into pure water, they burst. When they are put into a saline solution (a solution with a salt concentration similar to that of the liquid that surrounds the blood cells in your circulatory system)

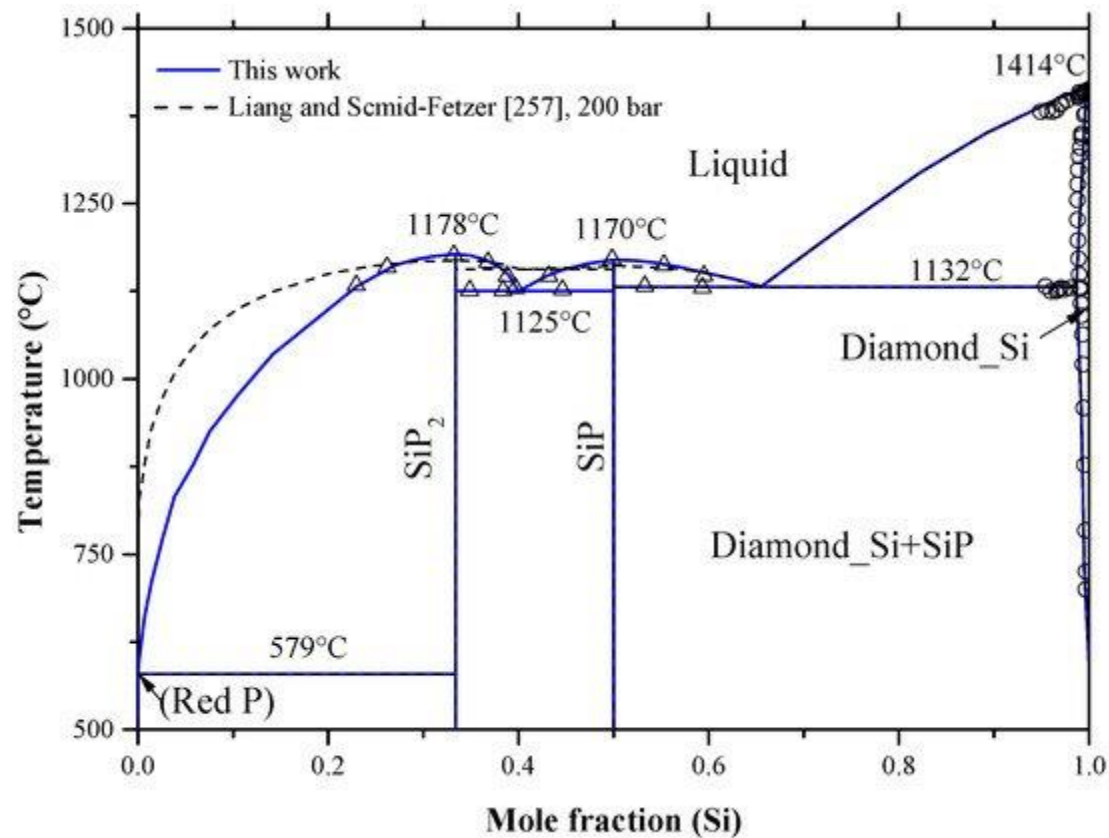
they retain their normal shape and size. When they are put into a saturated salt solution they shrivel up. Explain these observations. Include an expression for the chemical potentials inside and outside the cell. (You can think of a red blood cell as a cell surrounded by a structurally weak, semipermeable membrane that lets water go through but not much else. Note that inside a red blood cell there are a variety of salts, small organic molecules, proteins and other chemicals which are in an aqueous solution.)

Solution: Because there are a number of solutes inside a red blood cell, the chemical potential of water in the cell is significantly less than that of pure water,  $\mu_A(l) = \mu_A^*(l) + RT \ln(X_A)$ , where the mole fraction of the water is less than 1. Thus if you put red blood cells in pure water, water will migrate into them (since the chemical potential is lower there) until they burst due to the osmotic pressure. In saline solution, the chemical potential of water is the same on both sides of the cell membrane. In a high salt solution, the chemical potential is less on the outside of the cell and thus water travels out from the cell, causing it to shrivel.

8. The binary phase diagram of P-Si at 200 bar is shown below. (From *Materials* **2017**, 10(6), 676) For A-I, label the components and phases in each section. What are the formulas for compounds 1 & 2? Explain what happens at 1178 °C, 1170 °C, 1125 °C, and ,1414 °C.



## Solution



A – Solid SiP<sub>2</sub> and liquid (mixture of Si/P)

B – Solid SiP and liquid (mixture of Si/P)

C – Solid SiP and liquid (mixture of Si/P)

D – Liquid (mixture of Si/P) and Si

E – Liquid and solid SiP<sub>2</sub>

F -- solid SiP<sub>2</sub> and solid SiP

G – solid SiP and solid Si

H – solid Si

I - solid P and solid SiP<sub>2</sub>

Compound 1 – with X<sub>Si</sub>=0.33, the compound formula must be SiP<sub>2</sub>.

Compound 2 – with X<sub>Si</sub>=0.5, the compound formula must be SiP.

1178 °C – melting point of SiP<sub>2</sub>

1170 °C – melting point of SiP

1125 °C – eutectic between SiP<sub>2</sub> and Si.

1414 °C – melting point of Si

For extra practice on simpler problems, work on the following exercises: 4 A.1a; 4 A.2a; 4 A.3a; 4 A.4a; 4A.5a; 4B.5a; 4B.7a; 4B.9a; 4B.13a; 4B.14a;

1. A) If  $\text{KH}_2\text{PO}_4$  crystals are added to water, how many independent components are in the final solution? Explain. Note that  $\text{KH}_2\text{PO}_4$  ionizes to form  $\text{K}^+$  and  $\text{H}_2\text{PO}_4^-$ .  
B) If KOH solid (which ionizes to form  $\text{K}^+$  and  $\text{OH}^-$  ions) is then added to the solution in (A), converting half of the  $\text{H}_2\text{PO}_4^-$  to  $\text{HPO}_4^{2-}$  ( $\text{H}_2\text{PO}_4^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HPO}_4^{2-}$ ), how many independent components are there? Explain.  
C) Explain the number of degrees of freedom for each of the following systems at equilibrium.  
i) Ice and liquid water  
ii) Ice and water vapor  
iii)  $\text{CO}$ ,  $\text{O}_2$ , and  $\text{CO}_2$  in a single gas phase, with each substance added separately, but no catalyst present to allow the chemical reaction to come to equilibrium  
iv) The system in part (iii) but with a catalyst that allows the chemical reaction to equilibrate  
v) The system in part (iii) but with the system prepared by starting by adding  $\text{CO}_2$  only

(Ans. A. 2; B. 3 C. i) 1; ii) 1, iii) 4, iv) 3, v) 2)

*Solution: 1 A) Two, since the system can be defined by the amount of water and amount of  $\text{KH}_2\text{PO}_4$  added.*

*B) Three. Water is one. The remainder of the system can be described uniquely in terms of the amount of  $\text{KH}_2\text{PO}_4$  and the amount of KOH.*

*C) i)  $F = C - P + 2$ . There are two phases. Although there are two species (solid & liquid water), they cannot be varied independently because of the equilibrium constraint, so there is only one component. Therefore,  $F = 1 - 2 + 2 = 1$*

*ii) There are two phases (solid & vapor). There are two components, but they can't be varied independently since they are in equilibrium, so there is only one component. Therefore,  $F = 1 - 2 + 2 = 1$*

*iii) There is one gas phase. There are 3 separate substances that are independent since they are not in equilibrium with each other. Therefore,  $F = 3 - 1 + 2 = 4$*

*iv) There is still the one gas phase. However, since the reaction  $2\text{CO} + \text{O}_2 \rightleftharpoons 2\text{CO}_2$  governs the equilibrium, the concentration of only 2 species can be varied independently, and the third will be determined by the equilibrium expression. Therefore, there are only two components. So,  $F = 2 - 1 + 2 = 3$ .*

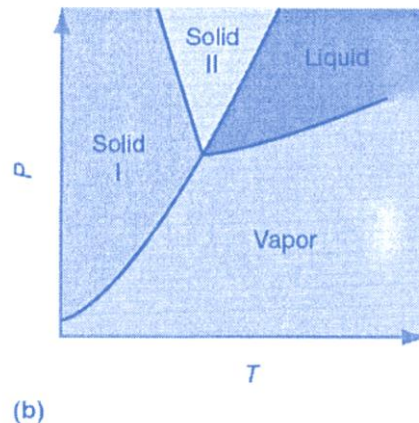
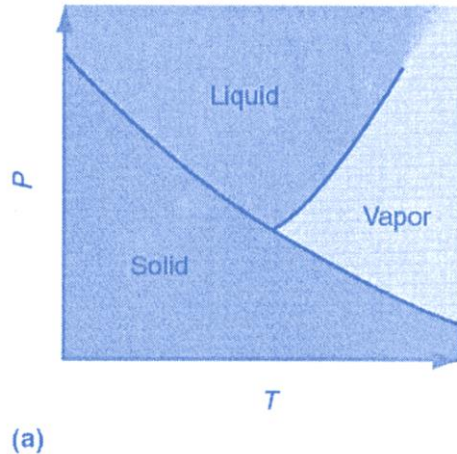
*v) There is still the one gas phase. Since only  $\text{CO}_2$  was added to the container, the other two species cannot be varied independently because of mass balance (all material must originate from the  $\text{CO}_2$  added in the first place) and the equilibrium constraint. Therefore, there is only one component. So,  $F = 1 - 1 + 2 = 2$*

2. Prove that a substance for which the solid-liquid coexistence curve has a negative slope contracts upon melting.

*Solution: Rearranging the Clapyeron equation  $\frac{dP}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V}$  to solve for the change in volume and substituting for the specific phase change (solid-liquid) gives  $\Delta_{fus}V = \frac{\Delta_{fus}S}{\frac{dP}{dT}}$ .*

*Since the entropy change upon melting is always positive,  $\Delta_{fus}S > 0$ . If the slope  $\frac{dP}{dT}$  is negative, then  $\Delta_{fus}V$  must be negative, meaning that  $V_\ell < V_s$ .*

3. Both phase diagrams for pure substances shown below are physically impossible. Point out the feature(s) of each diagram that cannot be observed in reality.



*Solution:*

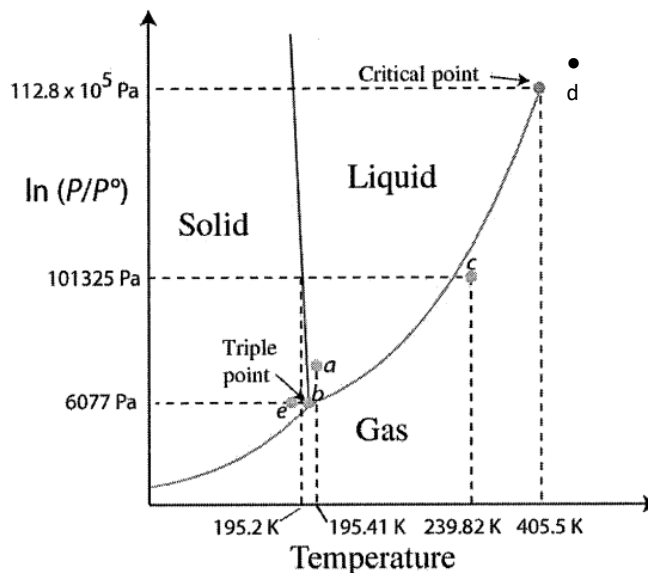
- a) *From the Clapyeron equation,  $\frac{dP}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V}$ , the solid-vapor line must have a positive slope since both terms on the right hand side of the equation are positive: volume increases upon sublimation and the entropy also increases. The slope of the liquid-solid coexistence line can be positive or negative, but will be much larger in magnitude than the slope of the vapor-solid coexistence line.*
- b) *Four phases of a pure substance cannot co-exist according to Gibbs' Phase Rule.*

4. The phase diagram of  $\text{NH}_3$  can be characterized by the following information. The normal melting and boiling points are 195.2 and 239.82 K, respectively; the triple point pressure and temperature are 6077 Pa and 195.41 K, respectively. The critical point is found at  $112.8 \times 10^5$  Pa and 405.5 K. Make a sketch of the P-T phase diagram (not necessarily to scale). Place a point in the phase diagram for the following conditions. State which and how many phases are present.
- 195.41 K, 9506 Pa
  - 195.41 K, 6077 Pa
  - 245.5 K, 101325 Pa
  - 415 K, 115000 Pa
  - 185.5 K, 6077 Pa

(Ans. single phase liquid; triple point (gas, liquid, solid); single phase gas; single phase super critical fluid; single phase solid)

**Solution**





- 195.41 K, 9506 Pa single phase liquid
- 195.41 K, 6077 Pa triple point (gas, liquid, solid)
- 245.5 K, 101325 Pa single phase gas
- 415 K, 115000 Pa single phase super critical fluid
- 185.5 K, 6077 Pa single phase solid

5. It has been suggested that the surface melting of ice plays a role in enabling speed skaters to achieve peak performance. Carry out the following calculation to test this hypothesis. At 1 atm pressure, ice melts at 273.15 K,  $\Delta_{\text{fus}}H = 6010 \text{ J mol}^{-1}$ , the density of ice is  $920 \text{ kg m}^{-3}$ , and the density of liquid water is  $997 \text{ kg m}^{-3}$ .
- What pressure is required to lower the melting temperature by  $4.0^\circ\text{C}$ ?
  - Assume that the width of the skate in contact with the ice is  $19 \times 10^{-3} \text{ cm}$ , and the length of the contact area is 18 cm. If the skater of mass 78 kg is balanced on one skate, what is the pressure exerted by the skater on the ice?
  - What is the melting point of the ice under this pressure?
  - If the temperature of the ice is  $-4.0^\circ\text{C}$ , do you expect melting of the ice at the ice-skate interface to occur? Explain.
- (Ans. 582 bar; 224 bar;  $-1.5^\circ\text{C}$ ; no)

Solution:

- Use the Clapyeron equation. Find the volumes of the solid and liquid using molar mass and densities. Find entropy using entropy and the phase transition temperature.

$$\frac{dP}{dT} = \frac{\Delta_{\text{fus}}H}{T_{\text{fus}} \left( \frac{M}{\rho_{\ell}} - \frac{M}{\rho_s} \right)} = \frac{6010 \frac{\text{J}}{\text{mol}}}{273.15 \text{ K} \left( \frac{0.01802 \frac{\text{kg}}{\text{mol}}}{997 \frac{\text{kg}}{\text{m}^3}} - \frac{0.01802 \frac{\text{kg}}{\text{mol}}}{920 \frac{\text{kg}}{\text{m}^3}} \right)} = -1.45 \times 10^7 \frac{\text{Pa}}{\text{K}} = -145 \frac{\text{bar}}{\text{K}}$$

Therefore, to lower the temperature by 4 degrees, the pressure would need to be increased by  $-145 \frac{\text{bar}}{\text{K}} \cdot 4\text{K} = 582 \text{ bar}$

$$\text{b. } P = \frac{F}{A} = \frac{ma}{A} = \frac{78 \text{ kg} \cdot 9.8 \frac{\text{m}}{\text{s}^2}}{19 \times 10^{-3} \text{ cm} \times 18 \text{ cm} \frac{1 \text{ m}^2}{10000 \text{ cm}^2}} = 2.24 \times 10^7 \text{ Pa} = 224 \text{ bar}$$

- c.  $\Delta T = \frac{dT}{dP} \Delta P = -\frac{1}{145 \text{ bar}} (224 \text{ bar}) = -1.5 \text{ K}$ .  $T_m = 271.61 \text{ K} = -1.5 \text{ }^\circ\text{C}$
- d. No. The lowering of the melting temperature is less than the temperature of the ice.
6. Consider the transition between two forms of solid tin  $\text{Sn}(s, \text{gray}) \rightarrow \text{Sn}(s, \text{white})$ . The two phases are in equilibrium at 1 bar and 18 °C. The densities for gray and white tin are 5750 and 7280 kgm<sup>-3</sup>, respectively, and the molar entropies for gray and white tin are 44.14 and 51.18 J K<sup>-1</sup> mole<sup>-1</sup>, respectively. Calculate the temperature at which the two phases are in equilibrium at 350 bar. (Ans. -3.5 °C)

Solution:

At equilibrium the chemical potentials of the two phases must be equal.  $\mu_\alpha(P, T) = \mu_\beta(P, T)$  Remember that for pure substances, the chemical potentials are purely molar Gibbs Free Energies, and  $d\mu_{m\alpha} = -S_{m\alpha}dT + V_{m\alpha}dP = -S_{m\beta}dT + V_{m\beta}dP = d\mu_{m\beta}$  (from  $dG = VdP - SdT$ ).

Gathering like terms,  $(S_{m\beta} - S_{m\alpha})dT = (V_{m\beta} - V_{m\alpha})dP$

Assuming that the entropies and volume are constant, we can integrate the left hand side with respect to temperature and the right hand side with respect to pressure, where  $T_1 = 18 \text{ }^\circ\text{C}$ ,  $T_2$  is what we are solving for,  $P_1 = 1 \text{ bar}$ , and  $P_2 = 350 \text{ bar}$ .

$(S_{m\beta} - S_{m\alpha})(T_2 - T_1) = (V_{m\beta} - V_{m\alpha})(P_2 - P_1)$ . Substituting in all the values gives

$(S_{m\beta} - S_{m\alpha})(T_2 - T_1) = (V_{m\beta} - V_{m\alpha})(P_2 - P_1)$ .

$$(51.18 - 44.14) \frac{\text{J}}{\text{K mol}} (T_2 - 291.15 \text{ K}) = \left( \frac{0.11871 \frac{\text{kg}}{\text{mol}}}{7280 \frac{\text{kg}}{\text{m}^3}} - \frac{0.11871 \frac{\text{kg}}{\text{mol}}}{5750 \frac{\text{kg}}{\text{m}^3}} \right) (350 - 1) 10^5 \text{ Pa}$$

$$T_2 = 269.64 \text{ K} = -3.5 \text{ }^\circ\text{C}$$

7. The vapor pressure of an unknown solid is given by  $\ln(P/\text{torr}) = 22.413 - \frac{2211}{T}$  and the vapor pressure of the liquid phase is given by  $\ln(P/\text{torr}) = 18.352 - \frac{1736}{T}$ .
- a. Calculate  $\Delta_{\text{vap}}H$ ,  $\Delta_{\text{sub}}H$ , and  $\Delta_{\text{fus}}H$ .
- b. Calculate the triple point temperature and pressure.  
(Ans. 14.4 kJ/mol; 18.4 kJ/mol, 4.0 kJ/mol; 117 K and 33.5 Torr)

- a. From the Clausius-Clayperon equation,  $\frac{d \ln P}{d(1/T)} = \frac{-\Delta_{\text{vap}}H}{R}$ ,  $d \ln P = \frac{-\Delta_{\text{vap}}H}{R} d(1/T)$ . Integrating indefinitely gives  $\ln P = \frac{-\Delta_{\text{vap}}H}{R} (1/T) + \text{constant}$ .

Comparing the liquid vapor pressure equation  $\ln(P/\text{torr}) = 18.352 - \frac{1736}{T}$  to the general one above reveals that  $\frac{-\Delta_{\text{vap}}H}{R} = -1736$ , or  $\Delta_{\text{vap}}H = 14433 \frac{\text{J}}{\text{mole}} = 14.4 \text{ kJ/mol}$

Doing the same comparison for the sublimation pressure reveals  $\frac{-\Delta_{\text{sub}}H}{R} = -2211$  or  $\Delta_{\text{sub}}H = 18382 \frac{\text{J}}{\text{mole}}$  or 18.4 kJ/mole.

By Hess's Law,  $\Delta_{\text{fus}}H = \Delta_{\text{sub}}H - \Delta_{\text{vap}}H = 18.4 - 14.4 = 4.0 \text{ kJ/mol}$

- b. At the triple point, the vapor pressure and sublimation pressures are equal and these lines intersect. To solve, set them equal to each other.

$$22.413 - \frac{2211}{T} = 18.352 - \frac{1736}{T} \quad T = 117 \text{ K.}$$

Now, put this temperature back into either equation to solve for P:

$$\ln(P/\text{torr}) = 22.413 - \frac{2211}{T} = 22.413 - \frac{2211}{117} = 3.51$$

$$(P/\text{torr}) = 33.45 \text{ torr}$$

8. Autoclaves that are used to sterilize surgical tools require a temperature of 120 °C to kill some bacteria. If water is used for this purpose, at what pressure must the autoclave operate? Be sure to cite the source of data that you use. (Ans. 1.95 atm)

Solution: Use the integrated form of the Clausius-Clayperon equation and the enthalpy of vaporization of water (40.656 kJ/mol, Table 2C.1) and the normal boiling point of water at 1 atm, 373.15 K.

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{P_2}{1 \text{ atm}}\right) = -\frac{40.656 \times 10^3 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{Kmol}}} \left(\frac{1}{393.15\text{K}} - \frac{1}{373.15\text{K}}\right) = 0.6666$$

$$P_2 = 1.95 \text{ atm}$$

# Physical Chemistry II - Homework 7

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March 26<sup>th</sup> 2019

**1. Using the Boltzmann distribution calculate the ratios of populations at 25°C of energy levels separated by (a) 100 cm<sup>-1</sup> and (b) 10 kJ/mole**

$$\text{Ratio of populations: } \frac{N_i}{N_j} = e^{-\frac{\epsilon_i - \epsilon_j}{k_B T}}.$$

a.

$$\Delta\epsilon = 100 \text{ cm}^{-1} = 100 \text{ cm}^{-1} \times \frac{100 \text{ m}^{-1}}{1 \text{ cm}^{-1}} \times 6.626 \times 10^{-34} \text{ J.s} \times 2.998 \times 10^8 \text{ m.s}^{-1} = 1.986 \times 10^{-21} \text{ J}$$

$$\frac{N_i}{N_j} = e^{-\frac{1.986 \times 10^{-21}}{1.386 \times 10^{-23} \text{ J.K}^{-1} \times (25 + 273.15) \text{ K}}} = \boxed{0.617}$$

$$\text{b. } \frac{N_i}{N_j} = e^{-\frac{10\,000 \text{ J.mol}^{-1} / 6.02214 \times 10^{23} \text{ molecules.mol}^{-1}}{1.386 \times 10^{-23} \text{ J.K}^{-1} \times (25 + 273.15) \text{ K}}} = \boxed{0.0177}$$

**2. Derive the expression for the translational partition function for a molecule that is moving along a line, rather than in 3D space.**

Consider a molecule in a 1-D box (a line): the energy of the molecule is calculated to be:

$$E_n = \frac{n^2 h^2}{8mL^2}$$

where n = 1, 2, 3, ..., m is mass of the molecule, and L is the length of the line.

The translational partition function for that molecule is:

$$q^T = \sum_{n=1}^{\infty} e^{-\frac{h^2}{8mkT} \times \frac{n^2}{L^2}}$$

$$\approx \int_0^{\infty} e^{-\frac{h^2}{8mkT} \times \frac{n^2}{L^2}} dn$$

$$\text{Applying } \int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \times \left(\frac{\pi}{a}\right)^{1/2}$$

$$= \frac{1}{2} \times \frac{2\sqrt{2}L(mkT\pi)^{1/2}}{h}$$

$$q^T = \boxed{\frac{(2mkT\pi)^{1/2}L}{h}}$$

**3. Evaluate the rotational partition function for ONCl at T=298 K.  $\widetilde{B}_A$  (ONCl)=2.84 cm<sup>-1</sup>,  $\widetilde{B}_B$  (ONCl)=0.191 cm<sup>-1</sup>,  $\widetilde{B}_C$  (ONCl)=0.179 cm<sup>-1</sup>.**

$$T = 298K, \sigma = 1, c = 2.998 \times 10^8 ms^{-1}, h = 6.626 \times 10^{-34} Js, k = 1.3806 \times 10^{-23} JK^{-1}$$

$$\Theta^r = \frac{hc\tilde{B}}{k}$$

$$\widetilde{B}_A = 2.84cm^{-1} = 284m^{-1} \rightarrow \Theta_A = 4.086K$$

$$\widetilde{B}_B = 0.191cm^{-1} = 19.1m^{-1} \rightarrow \Theta_B = 0.275K$$

$$\widetilde{B}_c = 0.179cm^{-1} = 17.9m^{-1} \rightarrow \Theta_C = 0.258K$$

$$q^R = \frac{\pi^{1/2}}{\sigma} \times \left( \frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} = \boxed{16934}$$

**4. In a rotational spectrum of HBr ( $\tilde{B} = 8.46cm^{-1}$ ), the maximum intensity is observed for the J=4 to 5 transition. At what temperature was the spectrum obtained?**

$$\frac{N_J}{N_0} = (2J+1)e^{-\frac{\Theta J(J+1)}{T}}$$

The maximum of the function above is determined by its derivative at  $J_{max}$ .

$$\frac{d(\frac{N_J}{N_0})}{dJ} = 0$$

$$\rightarrow [2 - (2J+1)^2 \frac{\Theta}{T}] \left( \frac{\Theta}{T} \right) e^{-\frac{\Theta J(J+1)}{T}} = 0$$

$$\rightarrow [2 - (2J+1)^2 \frac{\Theta}{T}] = 0$$

$$\rightarrow T = \frac{\Theta(2J_{max}+1)^2}{2}$$

$$\text{With } \Theta = \frac{hc\tilde{B}}{k} \text{ and } J_{max} = 4$$

$$\rightarrow T = \frac{6.626 \times 10^{-34} Js \times 2.998 \times 10^{10} cms^{-1} \times 8.46cm^{-1} \times (2 \times 4 + 1)^2}{2 \times 1.3806 \times 10^{-23} JK^{-1}} = \boxed{493K}$$

**5. The normal mode vibrational frequencies of  $H_2O$  are 3657, 1595, and 3756  $cm^{-1}$ . What is the value of the vibrational partition function at 2000 K? What is the value of the vibrational energy at 2000 K? How does this energy compare to the value predicted by the equipartition theorem?**

$$\text{Vibrational partition function: } q^v = \frac{1}{1 - e^{-\frac{\Theta^v}{T}}} \text{ where } \Theta^v = \frac{hc\tilde{\nu}}{k} = 1.4388\tilde{\nu}.$$

The characteristic vibrational temperatures of water are:

$$\Theta_{1595} = 2294.9K, \Theta_{3657} = 5261.7K, \Theta_{3756} = 5404.2K$$

For water (a polyatomic molecule) at  $T = 2000K$ , the total partition function is the product of vibrational functions for each frequency.

$$p^v = \prod_{i=1}^n \frac{1}{1 - e^{-\frac{\Theta^{v,i}}{T}}} = \frac{1}{1 - e^{-\frac{2294.9}{2000}}} \times \frac{1}{1 - e^{-\frac{5261.7}{2000}}} \times \frac{1}{1 - e^{-\frac{5404.2}{2000}}} = \boxed{1.692}$$

For a polyatomic molecule, the vibrational energy is the sum of the contributions from each normal mode:

Equipartition theorem:

$$E^v = 3RT = 3 \times 8.314 JK^{-1} mol^{-1} \times 2000K = \boxed{49.89 kJ mol^{-1}}$$

Vibrational energy of one normal mode is given as:

$$e_v = \frac{hc\tilde{\nu}}{e^{\frac{\Theta}{T}} - 1}$$

Total vibrational energy is the sum of all normal mode energies:

$$E_v = hc \times \left[ \frac{1595}{(e^{\frac{\Theta_{1595}}{T}} - 1)} + \frac{3657}{(e^{\frac{\Theta_{3657}}{T}} - 1)} + \frac{3756}{(e^{\frac{\Theta_{3756}}{T}} - 1)} \right]$$

With  $T = 2000K$ , and  $\Theta$ ,  $\tilde{\nu}$  values above:

$$E_v = \boxed{15.5 kJ mol^{-1}}$$

Energy is over predicted by the equipartition theorem because the theorem assumes all of the vibrations water are fully excited, in fact, they are not.

**6. What fraction of HCl molecules are in the state  $v=2$ ,  $J=7$  at  $500^\circ C$ ? (Use your resource table 11C.1 to find the characteristic rotational and vibrational temperatures).**

Values for HCl adapted from Atkin's Physical Chemistry 10th edition:

$$\Theta^v = 4304K, \quad \Theta^r = 15.2K$$

$$p = \frac{N_i}{N} = \frac{e^{-\frac{\epsilon_i}{kT}}}{q}$$

For rotational level  $J=7$ :

$$q_r = \frac{T}{\sigma \Theta^r}, \quad \epsilon_r = J(J+1)\Theta^r k, \quad 2J+1 \text{ is the degeneracy}$$

$$p_r = (2J+1) \frac{e^{-\frac{J(J+1)\Theta^r}{T}}}{\frac{T}{\sigma \Theta^r}}$$

With  $J = 7$ ,  $\sigma = 1$ ,  $T = 773K$ ,  $\Theta^r = 15.2K$

$$p_r = 0.098$$

For vibrational level  $v= 2$ :

$$q_v = \frac{1}{1 - e^{-\frac{\Theta^v}{T}}}, \quad \epsilon_v = v\Theta^v k$$

$$p_v = \frac{e^{-\frac{v\Theta^v}{T}}}{\frac{1}{1 - e^{-\frac{\Theta^v}{T}}}}$$

With  $\Theta^v = 4304K$ ,  $v = 2$ ,  $T = 773K$

$$p_v = 1.452 \times 10^{-5}$$

$$p = p_r \times p_v = 0.098 \times 1.452 \times 10^{-5} = \boxed{1.42 \times 10^{-6}}$$

7. The lowest nine energy levels for gaseous vanadium (V) have the following energies and degeneracies. What is the value for the electronic partition function for V at 298 K? What terms are important, and which may be neglected?

Level (n)	Energy (cm <sup>-1</sup> )	Degeneracy	Energy (J)		
			$\epsilon = hc\tilde{\nu}$	$q_i = g \cdot e^{-\beta\epsilon}$	
0	0	4	0	4	Important terms
1	137.38	6	2.72905E-21	3.090883424	
2	323.46	8	6.42552E-21	1.678166112	
3	552.96	10	1.09845E-20	0.69264747	
4	2112.28	2	4.19604E-20	0.0000744464	May be neglected
5	2153.21	4	4.27734E-20	0.0001221937	
6	2220.11	6	4.41024E-20	0.0001326964	
7	2311.36	8	4.59151E-20	0.0001138828	
8	2424.78	10	4.81681E-20	0.0000823267	
h	6.62607E-34		$q = \sum q_i$	9.462222553	
c (cm/s)	29980000000				
k	1.38065E-23				
T	298				
beta	2.43053E+20				

8. Using methods of statistical mechanics, calculate the molar entropy of neon at 25°C, 1 bar.

Molar entropy for monoatomic gas (Ne):

$$S = \frac{5}{2}R + R \ln \left[ \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \times \frac{Vg}{N_A} \right]$$

With  $T = 298K$ ,  $P = 1bar$ ,  $R = 0.08314 L bar mol^{-1} K^{-1}$

$$V = \frac{RT}{P} = \frac{0.08314 L bar mol^{-1} K^{-1} \times 298K}{1bar} = 24.776 L mol^{-1}$$

$$m = 20.2amu \times \frac{1.66 \times 10^{-27} kg}{1amu} = 3.3532 \times 10^{-26} kg$$

$$N_A = 6.022 \times 10^{23}, k_B = 1.3806 \times 10^{-23} JK^{-1}, h = 6.626 \times 10^{-34} Js, g = 1, R = 8.314 JK^{-1} mol^{-1}$$

$$S = \boxed{146.33 J mol^{-1} K^{-1}}$$

**9. Tabulate the translation, vibrational, and rotational contributions to  $C_V^\theta$  for H,  $H_2$ ,  $H_2O$ , and  $NH_3$  that are expected classically. Compare them to the statistically mechanically predicted contributions at 298.15 K. The vibrational temperatures for hydrogen, water, and ammonia are 6338.2; 2294.27, 5261.71, 5403.78; and 1367, 2341 (2), 4800, 4955 (2) K, respectively.**

For classical	Type	Number of atoms	translational	rotational	vibrational	total
H	monoatomic	1	1.50	0	0	1.50
H <sub>2</sub>	linear diatomic	2	1.50	1	1	3.50
H <sub>2</sub> O	nonlinear polyatomic	3	1.50	1.50	3	6
NH <sub>3</sub>	nonlinear polyatomic	4	1.50	1.50	6	9

For statistical	$\theta^v(k)$	translational	Rotational	Vibrational	Total
H		1.50	0.00	0	1.50
H <sub>2</sub>	6338.2	1.50	1.00	2.646E-07	2.50
H <sub>2</sub> O	2294.27			0.02697	
	5261.71	1.50	1.50	0.000006745	3.02698
	5403.78			0.000004417	
NH <sub>3</sub>	1367			0.2189	
	2341			0.02401	
	2341			0.02401	
	4800	1.50	1.50	0.00002641	3.2669
	4955			0.00001673	
	4955			0.00001673	

**10. For  $I_2$ ,  $v = 6.395 \times 10^{12} s^{-1}$  and the intermolecular distance is  $2.67 \text{ \AA}$ . For  $I_2$  (g), use statistical mechanical methods to calculate  $U_m^\ominus(500) - U_m^\ominus(0)$ ,  $H_m^\ominus(500) - U_m^\ominus(0)$ ,  $S_m^\ominus(500)$ . First calculate the vibrational and rotational temperatures.**



$$\Theta_T^v = \frac{\sigma hc}{k} = \frac{vh}{k} = \frac{6.395 \times 10^{12} s^{-1} \times 6.626 \times 10^{-34}}{1.38 \times 10^{-23}} = \boxed{306.9K}$$

$$\Theta_T^r = \frac{\sigma \tilde{B} hc}{k} = \frac{\sigma h^2}{8k\pi^2 I}$$

$$I = mr^2 = \frac{0.1269 kg/mol (2.67 \times 10^{-10} m)^2}{6.022 \times 10^{23}} = 1.5022 \times 10^{-44} kgm^2$$

$$with \quad h = 6.626 \times 10^{-34} Js, \quad k = 1.38 \times 10^{-23} J/K, \quad \sigma = 2$$

$$\Theta_T^r = \boxed{0.05362K}$$

$$< \epsilon^T > = 3/2 kT = 3/2 \times 1.38 \times 10^{-23} JK^{-1} mol^{-1} \times 500K = 1.0355 \times 10^{-20} J/mol$$

$$< \epsilon^v > = \frac{hc\tilde{\nu}}{e^{\frac{\Theta_T^v}{T}} - 1} = \frac{k\Theta_T^v}{e^{\frac{\Theta_T^v}{T}} - 1} = \frac{306.9K \times 1.38 \times 10^{-23} JK^{-1} mol^{-1}}{e^{\frac{306.9K}{500K}} - 1} = 4.999 \times 10^{-21} J/mol$$

$$< \epsilon^r > = kT = 1.38 \times 10^{-23} JK^{-1} mol^{-1} = 6.903 \times 10^{-21} J/mol$$

$$< \epsilon^{total} > = < \epsilon^T > + < \epsilon^v > + < \epsilon^r > = 2.2237 \times 10^{-20} J/mol$$

$$U_m^\Theta(500) - U_m^\Theta(0) = < \epsilon^{total} > \times N_A = 2.2237 \times 10^{-20} \times 6.022 \times 10^{23} = \boxed{13.39 kJ/mol}$$

$$\begin{aligned} H_m^\Theta(500) - U_m^\Theta(0) &= U_m^\Theta(500) + PV - U_m^\Theta(0) = U_m^\Theta(500) + nRT - U_m^\Theta(0) \\ &= 13390 J/mol + 1 mol \times 8.314 JK^{-1} mol^{-1} \times 500K = \boxed{17.547 kJ/mol} \end{aligned}$$

$$V_m = RT/P = \frac{8.31447 \times 500}{10^5} = 0.04157 m^3$$

$$\Lambda = \frac{h}{\sqrt{2\pi mkT}} = \frac{6.626 \times 10^{-34}}{\sqrt{2 \times \pi \times \frac{0.1269 kg}{6.022 \times 10^{23}} \times 1.38 \times 10^{-23} J/K 500K}} = 6.9308 \times 10^{-12} m$$

$$S_m^\Theta(500) = R \times [1 + \ln\left(\frac{T}{\Theta^r}\right) + \frac{\frac{\Theta^v}{T}}{e^{\frac{\Theta^v}{T}} - 1} - \ln(1 - e^{-\frac{\Theta^v}{T}}) + \ln \frac{V_m e^{5/2}}{N_A \times \Lambda^3}]$$

$$With \quad R = 8.314462 JK^{-1} mol^{-1}, \quad T = 500K, \quad \Theta^r = 0.5362K, \quad \Theta^T = 306.9K, \quad V_m = 0.04157 m^3, \quad and \quad \Lambda = 6.9308 \times 10^{-12} m.$$

$$S_m^\Theta = \boxed{276.82 JK^{-1} mol^{-1}}$$

11. Calculate the value of the equilibrium constant at 900 K for  $CO_2(g) + H_2(g) \rightleftharpoons H_2O(g) + CO(g)$  The value of  $\Delta E_0 = 40.33 \text{ kJ/mol}$

Molecule	$\theta_v/K$	$\theta_{rA}/K$	$\theta_{rB}/K$	$\theta_{rC}/K$	T = 900 K
$CO_2$	1997		0.56155		
	960				
	960				
	3380				
$H_2$	6323.8		87.5		
$H_2O$	5254	40.16	20.9	13.38	
	2295				
	5404				
$CO$	3122		2.78		
$q^T = \frac{V}{\left(\frac{h}{\sqrt{2\pi mKT}}\right)^3} = \frac{m_{H_2O}^{3/2} m_{CO}^{3/2}}{m_{CO_2}^{3/2} m_{H_2}^{3/2}} = 13.65$					
<p>For linear: <math>q^R = \frac{T}{\sigma \theta^R}</math>      For non – linear: <math>q^R = \frac{T^{3/2} \pi^{1/2}}{\sigma (\theta_A^R \theta_B^R \theta_C^R)^{1/2}}</math></p> $q^{Rtotal} = \frac{\frac{T}{2\theta_R^{CO}} \cdot \frac{T^{3/2} \pi^{1/2}}{2(\theta_A^{H_2O} \theta_B^{H_2O} \theta_C^{H_2O})^{1/2}}}{\frac{T}{2\theta_R^{CO_2}} \cdot \frac{T}{2\theta_R^{H_2}}} = 17.74$					
$q^v = \frac{1}{1 - e^{-\frac{\theta_v}{T}}} = \frac{\left(\frac{1}{1 - e^{-\frac{\theta_{v1}^{H_2O}}{T}}}\right) \cdot \left(\frac{1}{1 - e^{-\frac{\theta_{v2}^{H_2O}}{T}}}\right) \cdot \left(\frac{1}{1 - e^{-\frac{\theta_{v3}^{H_2O}}{T}}}\right) \cdot \left(\frac{1}{1 - e^{-\frac{\theta_v^{CO}}{T}}}\right)}{\left(\frac{1}{1 - e^{-\frac{\theta_{v1}^{CO_2}}{T}}}\right) \cdot \left(\frac{1}{1 - e^{-\frac{\theta_{v2}^{CO_2}}{T}}}\right) \cdot \left(\frac{1}{1 - e^{-\frac{\theta_{v3}^{CO_2}}{T}}}\right) \cdot \left(\frac{1}{1 - e^{-\frac{\theta_{v4}^{CO_2}}{T}}}\right) \cdot \left(\frac{1}{1 - e^{-\frac{\theta_v^{H_2}}{T}}}\right)} = 0.42$					
$q^E = e^{-\Delta E_0/RT} = 4.56 \times 10^{-3}$					
$K = q^T q^V q^R q^E = 0.464$					

For extra practice on simpler problems, work on the following exercises: 13: A 3a, 5a, 6a; B 1a, 4a, 5a, 7a, 8a, 10a, 12a; C 1a, 3a, 5a, 7a; 13 D 1a; E 4a, 5a, 7a, 9a; F 1a, 3a, 5a, 7a, 9a; 17: A 2a, 5a, 8a, 9a; B 1a, 3a, 4a, 5a, 6a; C 1a, 2a

1. Consider the following sets of populations for 4 equally spaced energy levels. Demonstrate that all of these have the same energy. Calculate the number of configurations for each distribution. Which is more probable? Do any of these represent a Boltzmann distribution? ( $1.21 \times 10^{27}$ ,  $1.31 \times 10^{27}$ , and  $1.56 \times 10^{27}$ , C, C)

E/k <sub>b</sub>	Set A	Set B	Set C
300	5	3	4
200	7	9	8
100	15	17	16
0	33	31	32

Solutions: Calculate the energy at each level and then sum the contribution for each population set.

E <sub>300</sub>	1500	900	1200
E <sub>200</sub>	1400	1800	1600
E <sub>100</sub>	1500	1700	1600
E <sub>0</sub>	0	0	0
E <sub>sum</sub> :	4400	4400	4400

The number of configurations of a system with N particles is given by  $W = \frac{N!}{N_1!N_2!N_3!N_4!}$ . In the case of set A,  $W = \frac{60!}{5!7!15!33!} = 1.21 \times 10^{27}$ . For set B, that corresponds to  $1.31 \times 10^{27}$  and for set C  $1.56 \times 10^{27}$ .

For a Boltzmann distribution, the ratio of populations is given by  $\frac{n_2}{n_1} = \exp\left(-\frac{\Delta E}{kT}\right)$ . For equally spaced levels, this means that  $\frac{n_2}{n_1} = \frac{n_3}{n_2}$ . This is only true for C, so set C is a Boltzmann distribution, which makes sense since it has the most configurations and is therefore more probable than A or B's.

n <sub>2</sub> /n <sub>1</sub> A	n <sub>2</sub> /n <sub>1</sub> B	n <sub>2</sub> /n <sub>1</sub> C
0.454545455	0.548387	0.5
n <sub>3</sub> /n <sub>2</sub> A	n <sub>3</sub> /n <sub>2</sub> B	n <sub>3</sub> /n <sub>2</sub> C
0.466666667	0.529412	0.5

2. For a set of energy levels with  $\theta=0, 100$ , and  $200$  K (all  $g=1$ ), calculate the Boltzmann populations and partition function at  $T=20, 200$ , and  $2000$  K. What is the high temperature limit for  $p_i$  and  $q$ ?

(Ans.  $T=20$ :  $q=1.0068, 0.9932, 0.0067, 4.51 \times 10^{-5}$ ;  $T=200$ :  $q=1.974, 0.5065, 0.3072, 0.1863$ ;  $T=2000$ :  $q=2.8561, 0.3501, 0.3331, 0.3168, 0.3333, 3$ )

Solution: Calculate the exponential term for each energy level at each temperature; calculate  $q$  by summing the exponential terms for each temperature.  $q = \sum_i \exp(-E_i/kT)$ . Divide each exponential term to get  $p_i$  for each state.  $p_i = \frac{\exp(-E_i/kT)}{q}$

T	20	200	2000		20	200	2000
E/k	exp(-Ei/kT)				pi=exp()/q		
0	1	1	1		0.993262	0.50648	0.350132
100	0.006737947	0.606531	0.951229		0.006693	0.307196	0.333056
200	4.53999E-05	0.367879	0.904837		4.51E-05	0.186324	0.316812
q	1.006783347	1.97441	2.856067				

At the high temperature limit, all levels should be equally occupied, so pi=0.33. Also, at the high temperature limit, q=3.

3. Show that a two-level system has  $C_v = \frac{R\theta^2 e^{\theta/T}}{T^2(1+e^{\theta/T})^2}$ .

$$U = -kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_V \quad q = \left( \exp \left( -\frac{0}{T} \right) + \exp \left( -\frac{\theta}{T} \right) \right)^N = \left( 1 + \exp \left( -\frac{\theta}{T} \right) \right)^N$$

$$U = -NkT^2 \left( \frac{\partial \ln \left( 1 + \exp \left( -\frac{\theta}{T} \right) \right)}{\partial T} \right)_V = N\theta k \frac{\exp \left( -\frac{\theta}{T} \right)}{1 + \exp \left( -\frac{\theta}{T} \right)}$$

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

$$C_V = N\theta k \left( \frac{\partial}{\partial T} \left( \frac{\exp \left( -\frac{\theta}{T} \right)}{1 + \exp \left( -\frac{\theta}{T} \right)} \right) \right)_V = N\theta k \left( \frac{\partial}{\partial T} \left[ \exp \left( -\frac{\theta}{T} \right) \left( 1 + \exp \left( -\frac{\theta}{T} \right) \right)^{-1} \right] \right)_V$$

$$\text{Use the product rule to get: } N\theta k \left[ \exp \left( -\frac{\theta}{T} \right) \left( - \left( 1 + \exp \left( -\frac{\theta}{T} \right) \right)^{-2} \right) \frac{\theta}{T^2} \exp \left( -\frac{\theta}{T} \right) + \frac{\theta}{T^2} \exp \left( -\frac{\theta}{T} \right) \left( 1 + \exp \left( -\frac{\theta}{T} \right) \right)^{-1} \right]$$

$$\text{Simplifying gives } C_V = N\theta k \left[ \frac{\theta}{T^2} \frac{\exp \left( -\frac{\theta}{T} \right)}{\left( 1 + \exp \left( -\frac{\theta}{T} \right) \right)^2} \right] = \left[ \frac{R\theta^2}{T^2} \frac{\exp \left( \frac{\theta}{T} \right)}{\left( 1 + \exp \left( \frac{\theta}{T} \right) \right)^2} \right] \text{ since } Nk=R.$$

4. Calculate the standard entropy of atomic O at 298.15 K and 1000 K. (**143.43 J/Kmol, 168.59 J/Kmole**)

$$S_m = R \left( -1.151693 + \frac{3}{2} \ln A_r - \ln \frac{P}{P^\theta} + \frac{5}{2} \ln \frac{T}{K} \right) = 8.314 \left( -1.151693 + \frac{3}{2} \ln(15.994) - \ln \frac{1}{1} + \frac{5}{2} \ln 298.15 \right) = 143.4304 \frac{\text{J}}{\text{Kmol}}$$

$$\text{With } T=1000, S_m = 8.314 \left( -1.151693 + \frac{3}{2} \ln(15.994) - \ln \frac{1}{1} + \frac{5}{2} \ln 1000 \right) = 168.585 \frac{\text{J}}{\text{Kmol}}$$

5. For the molecule Cl<sub>2</sub>, calculate the vibrational partition function and the population of the first three vibrational levels at T=300 and 1000 K. Use data from table included in notes. (**Ans.**

**1.0727, 3.765596; At 300 K, 0.932187, 0.063214, 0.004287; At 1000 K: 0.553939, 0.247091, 0.110217)**

The constant for vibration can be found from Table 16.2 in notes:  $\theta_v=807.3$  K.

Since the vibrational partition function is given as  $q^v = \frac{1}{1 - e^{-\frac{\theta_v}{T}}}$ , at 300 K,  $q^v = \frac{1}{1 - e^{-\frac{807.3}{300}}} =$

1.0727. At 1000 K,  $q^v = 1.8053$

Boltzmann's law gives the fraction of molecules in each state  $n=0, 1, 2$ .

$$p_n = \frac{\exp(-n\theta_v/T)}{1 - \exp(-\theta_v/T)}$$

$\theta_v=807.3$	300	1000
n=0	1	1
1	0.067813	0.446061
2	0.004599	0.19897

q=	1.072746	1.805252
$p_n=$		
0	0.932187	0.553939
1	0.063214	0.247091
2	0.004287	0.110217

6. Calculate the percent population of the first 10 rotational levels of HI at 300 K. It will be easiest if you write the rotational energy levels in terms of  $\Theta_r$  instead of I or  $\tilde{B}$ . (**Ans. 0.03123, 0.088017, 0.129468, 0.150284, 0.150506, 0.134609, 0.109363, 0.081496, 0.056038, 0.035699**)

The rotational constant can be found in Table 16.2 from the notes  $\Theta_r=9.369$  K with a symmetry number of 1.  $q_r = \frac{T}{\sigma\Theta_r}$  gives the rotational partition function.

Substitution in the values gives  $q_r = \frac{300}{1 \cdot 9.369} = 32.0205$

The energy of the rotational levels is given by  $\epsilon_r = \frac{J(J+1)\hbar^2}{8\pi^2 I} = J(J+1)k\Theta_r$ . (Where the latter manipulation was made with  $\theta^r = \frac{hc\tilde{B}}{k}$  and  $\tilde{B} = \hbar/4\pi cI$ .) The degeneracy of each level is  $(2J+1)$ . So, the population of each level is given by

$$p_J = \frac{(2J+1)\exp(-J(J+1)\Theta_r/T)}{q_r}, \text{ with } J=0, 1, 2, \dots, 9$$

Using the values of  $q_r=32.0205$ ,  $\Theta_r=9.369$ ,  $T=300$  K, and  $J=0-9$  gives

J	$p_J$
0	0.03123
1	0.088017
2	0.129468
3	0.150284
4	0.150506
5	0.134609

6	0.109363
7	0.081496
8	0.056038
9	0.035699

7. Calculate the standard entropy of O<sub>2</sub> at 298.15 K and 2500 K. Compare the first value to that on Table 2C.7. (Ans. **198.908 J/Kmol; 263.372 J/Kmol**)

Need to calculate the entropy contribution from translation, rotation, and vibration. You can use the table in the notes to determine the contributions, given that the molecule is symmetric and linear with only one vibration.

$$S_m^\theta = R \left( (1.5 \ln A_r + 2.5 \ln T - 1.1567) + \left( 1 + \ln \frac{T}{\sigma \theta_r} \right) + \frac{\frac{\theta_v}{T}}{\exp\left(\frac{\theta_v}{T}\right) - 1} - \ln \left( 1 - \exp\left(-\frac{\theta_v}{T}\right) \right) \right)$$

From Table 16.2  $\Theta_r=2.079$ ;  $\Theta_v=2273.64$ ;  $M=31.9988$  g/mol;  $\sigma=2$

$$S_m^\theta = 8.31451 \left( 1.5 \ln 31.9988 + 2.5 \ln 298.15 - 1.1567 + 1 + \ln \frac{298.15}{2 \cdot 2.079} + \frac{\frac{2273.64}{298.15}}{\exp\left(\frac{2273.64}{298.15}\right) - 1} - \ln \left( 1 - \exp\left(-\frac{2273.64}{298.15}\right) \right) \right) = 195.908 \frac{J}{K \text{ mole}}$$

$$S_m^\theta = 8.31451 \left( 1.5 \ln 31.9988 + 2.5 \ln 2500 - 1.1567 + 1 + \ln \frac{2500}{2 \cdot 2.079} + \frac{\frac{2273.64}{2500}}{\exp\left(\frac{2273.64}{2500}\right) - 1} - \ln \left( 1 - \exp\left(-\frac{2273.64}{2500}\right) \right) \right) = 263.37 \frac{J}{K \text{ mole}}$$

Table 2.C7 gives a standard molar entropy of 205.138 J/K at 298.15 K, which has a difference of about 4% from the calculated value.

8. Tabulate the translation, vibrational, and rotational contributions to  $\bar{C}_V^\theta/R$  for H, H<sub>2</sub>, H<sub>2</sub>O, and NH<sub>3</sub> that are expected classically. Compare them to the statistically mechanically predicted contributions at 298.15 K. (total classical 1.5, 3.5, 6, 9; total by stat mech 1.5, 2.5, 3.03, 3.27) Use the spectral constants from the table in the notes.

		N	translation	rotation	vibration	total

H	monatomic	1	1.50	0	0	1.50
H <sub>2</sub>	diatomic	2	1.5	1	1	3.50
H <sub>2</sub> O	nonlinear polyatomic	3	1.5	1.5	3	6.00
NH <sub>3</sub>	nonlinear polyatomic	4	1.5	1.5	6	9.00

The stat mech contributions are

		translation	rotation	vibration		total
H	monatomic	1.50	0	0		1.50
H <sub>2</sub>	diatomic	1.5	1	$\frac{u^2 e^u}{(e^u - 1)^2}$	2.64633E-07	2.50
H <sub>2</sub> O	nonlinear polyatomic	1.5	1.5	$\frac{u^2 e^u}{(e^u - 1)^2}$	0.026982992	3.03
NH <sub>3</sub>	nonlinear polyatomic	1.5	1.5	$\frac{u^2 e^u}{(e^u - 1)^2}$	0.267028105	3.27

Where  $u = \theta_V/T$ ; sum overall vibration. Find the vibrational constants in Table 16.2 in the notes.

H	monatomic							
H <sub>2</sub>	diatomic	6338.2						
	nonlinear							
H <sub>2</sub> O	polyatomic	2294.27	5261.71	5403.78				
	nonlinear							
NH <sub>3</sub>	polyatomic	1367	2341	2341	4800	4955	4955	

Using the vibrational constants above and  $\frac{u^2 e^u}{(e^u - 1)^2}$ , the vibrational terms for each vibration are found in the table below and summed at the right.

H <sub>2</sub>	2.64633E-07							2.64633E-07
H <sub>2</sub> O	0.026971828	6.75E-06	4.42E-06					0.026982992
NH <sub>3</sub>	0.218958587	0.024005	0.024005	2.64E-05	1.67E-05	1.67E-05		0.267028105

So, classical calculates predict higher C<sub>v</sub> than statistical mechanics in every case but monatomic gases.