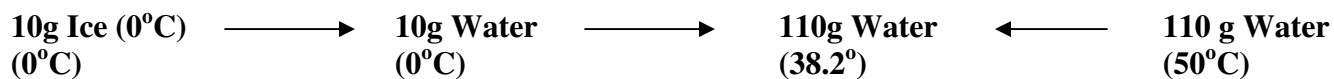


### Midterm Examination 3

1. If 10g of Ice at 0°C is mixed with 100g of Water at 50°C in a Dewar flask, 110g of Water at 38.2°C results. Determine  $\Delta S$  for this process.

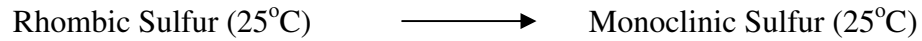
Thermochemical Data for Water

$$C_p = 4.2 \text{ J/gK}$$
$$\Delta H_{\text{fus}} = 6.0 \text{ kJ/mol}$$



$$\begin{aligned} \Delta S &= \frac{\Delta H}{T_m} + \int_{T_m}^{38.2} \frac{C_p}{T} dT + \int_{50.0}^{38.2} \frac{C_p}{T} dT \\ &= (10 \text{ g} / 18 \text{ g/mol}) (6000 \text{ J} / 273 \text{ K}) \\ &\quad + (10 \text{ g}) (4.2 \text{ J/gK}) \ln(311.2 \text{ K} / 273 \text{ K}) \\ &\quad + (100 \text{ g}) (4.2 \text{ J/gK}) \ln(311.2 \text{ K} / 323 \text{ K}) \\ &= 2.1 \text{ J/K} \end{aligned}$$

2. For the following transformation,  $\Delta G^\circ = 96 \text{ J/mole}$ .



Assuming the Entropy of each substance does not vary significantly with temperature, at what temperature will these two phases of Sulfur be in equilibrium?

$$S^\circ (\text{Rhom}) = 31.88 \text{ J/K mole}$$

$$S^\circ (\text{Mono}) = 32.55 \text{ J/K mole}$$

You must show your work!

$$\Delta G^\circ(\text{R} \rightarrow \text{M}, 298) = \Delta G^\circ(\text{R}, 298 \rightarrow \text{T}) + \Delta G^\circ(\text{R} \rightarrow \text{M}, \text{T}) + \Delta G^\circ(\text{M}, \text{T} \rightarrow 298)$$

$$= -S^\circ(\text{R}) \Delta T + \Delta G^\circ(\text{R} \rightarrow \text{M}, \text{T}) - S^\circ(\text{M}) \Delta T$$

$$\text{So, } 96 = - (31.88) (T - 298) + 0 - (32.55) (298 - T)$$

$$T = 441\text{K} = 168^\circ\text{C}$$

3. Consider stretching a rubber band with a tension ( $t$ ). Since  $\delta W = t dL$  for this process, we can write:

$$dG = - S dT + V dP - L dt$$

For a rubber band under limited tension,

$$L = \frac{t}{nbT^2}$$

where  $b$  is a positive constant. How does the Entropy ( $S$ ) of the rubber band vary with tension under constant pressure conditions? In other words, determine:

$$\left(\frac{\partial S}{\partial t}\right)_{T,P}$$

Hint: Think “Maxwell”!

$$\left(\frac{\partial G}{\partial T}\right)_{P,t} = - S$$

$$\left(\frac{\partial G}{\partial t}\right)_{P,T} = - L$$

$$\left(\frac{\partial^2 G}{\partial t \partial T}\right) = \left(\frac{\partial^2 G}{\partial T \partial t}\right)$$

$$-\left(\frac{\partial S}{\partial t}\right)_{P,T} = -\left(\frac{\partial L}{\partial T}\right)_{P,t}$$

So,

$$\left(\frac{\partial S}{\partial t}\right)_{P,T} = \left(\frac{\partial L}{\partial T}\right)_{P,t} = \frac{-2t}{nbT^3}$$

4. The densities of two Methanol-Water mixtures are:

$\rho$ [g/cm <sup>3</sup> ]	Composition
0.97942	13.636g Met + 100.000g Wat
0.97799	14.943g Met + 100.000g Wat

Estimate  $\bar{V}_{Met}$  at this concentration (~12.5% by weight) by direct application of the definition. ( $M_{Met} = 32.04$  g/mol)

$$\Delta V = (114.943\text{g} / 0.97799 \text{ g/cm}^3) - (113.636\text{g} / 0.97942 \text{ g/cm}^3) = 1.5 \text{ cm}^3$$

$$\Delta n_{Met} = (14.943\text{g} - 13.636\text{g}) / 32.04 \text{ g/mol} = 0.0408 \text{ mol}$$

$$\bar{V}_{Met} = \left( \frac{\partial V}{\partial n_{Met}} \right)_{n_{H_2O}} \sim \frac{\Delta V}{\Delta n_{Met}} = 1.5 \text{ cm}^3 / 0.0408 \text{ mol} = 37 \text{ cm}^3/\text{mol}$$

5. At 900°C, solid Zinc metal has a vapor pressure of 95.3 kPa. A sample of solid Brass is 20 mole percent Zinc;  $x_{\text{Zn}} = 0.20$ . The partial pressure of Zinc above this Brass sample at 900°C is found to be 5.73 kPa.

Determine the Activity Coefficient  $\gamma$  for Zinc in this Brass solution at 900°C. Take the Reference State to be the Ideal case.

$$\gamma_{\text{Zn}} = a_{\text{Zn}} / x_{\text{Zn}} = P_{\text{Zn}} / x_{\text{Zn}} P_{\text{Zn}}^* = 5.73 \text{ kPa} / (0.20) (95.3 \text{ kPa}) = 0.30$$

6. What does the Gibbs Function,  $G(T,P)$  measure? Why is this function important for chemists? How is this function useful? (Think in terms of the basic question of thermodynamics.)

**Measures**

**Available non-PV Work.**

**Importance**

**Embodies the laws of thermodynamics for systems at constant T & P; which are the conditions chemists tend to work under.**

**Usefulness**

**Equilibrium for constant T,P systems occurs when G is a minimum.**

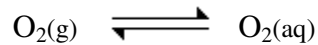
7. The solubility of O<sub>2</sub> in Water at various partial pressures at 25°C is:

<u>m [molality]</u>	<u>P<sub>O<sub>2</sub></sub> [atm]</u>
0.00123	1
0.00245	2
0.00485	4
0.00940	8
0.01340	12

- a) Provide a crude estimate of the Henry's Law constant K<sub>O<sub>2</sub></sub> for this system. (Hint: The usual form of Henry's Law holds when the concentration is expressed as molality; P<sub>j</sub> = K<sub>j</sub> m<sub>j</sub>.)

$$K_j = \lim_{m \rightarrow 0} \frac{P_j}{m} \sim (1 \text{ atm}) / (0.00123m) = 813 \text{ atm/m}$$

- b) Calculate ΔG°(T) for:



where:

$$\Delta G^\circ(T) = \mu^{***} - \mu^\circ$$

$$\mu^{***} - \mu^\circ = RT \ln (K/P^\circ) + RT \ln (m/m^\circ)$$

$$= (8.314 \text{ J/K mol}) (298 \text{ K}) \ln (813 \times 1 / 1) = + 16.6 \text{ kJ/mol}$$

Hints:

$$\text{Gases: } \mu = \mu^\circ + RT \ln(P/P^\circ)$$

$$\text{Soln's: } \mu = \mu^{***} + RT \ln(m/m^\circ)$$

## Useful Relations

### Relationships for an Ideal Gas

$$PV = nRT$$

$$\alpha = 1/T$$

$$\kappa = 1/P$$

### Some State Functions

$$dU = C_v dT + \Pi_T dV$$

$$dH = C_p dT - C_p \mu dP$$

$$dS = \frac{C_v}{T} dT + \frac{\alpha}{\kappa} dV$$

$$dS = \frac{C_p}{T} dT - V\alpha dP$$

### Some Definitions

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

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

$$\mu_{JT} = \left( \frac{\partial P}{\partial T} \right)_H$$