

Midterm Examination 3

1. Some thermochemical data for gaseous Benzene at 25°C is:

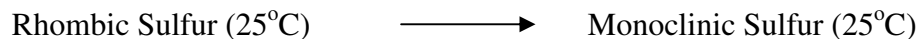
$$S^{\circ}(298.15) = 269.2 \text{ J/K mol}$$

$$\Delta H_f^{\circ}(298.15) = 82.927 \text{ kJ/mol}$$

$$C_p^{\circ}(298.15) = 85.3 \text{ J/K mol}$$

The equilibrium vapor pressure of Benzene at 25°C is 198 Torr. Calculate the Entropy of the vapor at this temperature and pressure. State any approximations made. Take $P^0 = 1 \text{ atm} = 760 \text{ Torr}$.

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?

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

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

3. The Helmholtz Free Energy of a droplet of surface area a and surface tension γ is given by:

$$dA = -S dT - P dV + \gamma da$$

Explicitly derive using an appropriate Second Mixed Partial Derivative the Maxwell Relation involving:

$$\left(\frac{\partial S}{\partial a}\right)_{T,V}$$

4. Recall, one form of the Gibbs-Helmholtz Equation is:

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = -\frac{H}{T^2}$$

The Gibbs Free Energy for a van der Waals Gas has the form:

$$G(T,P) = G^{\circ}(T) + RT \ln P + \left(b - \frac{a}{RT}\right) P$$

Derive an expression for $H(T,P) - H^{\circ}(T)$ for the van der Waals Gas.

5. Consider a gas whose Equation of State is represented by a Virial Equation truncated at 2nd order in P:

$$Z = 1 + \frac{B}{RT} P + \frac{C}{RT} P^2$$

Obtain expressions for $\mu(T,P)$ and $\bar{S}(T,P)$ for this gas. Recall that for a pure substance $\mu = G/n$.

6. Chemical Handbook data for Acetic Acid and Water at 20°C gives:

<u>Water</u>	<u>Acetic Acid</u>
M = 18.015 g/mol	M = 60.05 g/mol
$\rho = 0.9982 \text{ g/cm}^3$	$\rho = 1.049 \text{ g/cm}^3$

A solution prepared by mixing 10.10g (9.63 cm³) Acetic Acid into 1000.0g (1001.8 cm³) of Water has a Volume of 1010.5 cm³ and is rather dilute.

- a) Determine an approximate value for \bar{V}_2 at this concentration. (Hint: Apply the definition directly.)

- b) Determine \bar{V}_2^* .

7. Vapor Pressure data for the Water-Propanol system at 25°C is given below:

x_P	P_W [Torr]	P_P [Torr]
0.00	23.77	0
0.40	21.7	14.2
1.00	0	21.76

a) Determine the Activity Coefficients γ for both Water and Propanol at $x_P = 0.40$. Take the Reference State to be the Ideal case.

b) The Chemical Potentials for a Gas and for a Liquid Mixture can be represented by:

$$\mu_g(T,P) = \mu_g^o(T) + RT \ln\left(\frac{P}{P^o}\right)$$

$$\mu_{l,i}(T,P, x_i) = \mu_{l,i}^*(T,P) + RT \ln x_i$$

Determine $\mu_w^* - \mu_w^o$ for Water at 25°C. Take $P^o = 1 \text{ barr} = 750.1 \text{ Torr}$.

8. In a study of the solubility of gases in liquid solvents, the mole fraction of CH₃Br (Comp. 2) dissolved in 1-BromoOctane (Comp 1) at 25° was measured as a function of partial pressure.

x_2	P_2 [Torr]
0.077	100
0.151	200
0.222	300
0.289	400

- a) Provide a crude estimate of the Henry's Law constant K_2 for this system.
- b) Calculate the Activity Coefficient γ_2 for CH₃Br in the $x_2 = 0.222$ solution; reference state is Ideal-Dilute.

***** Not Covered Yet *****

9. What is the Freezing Point Depression for an aqueous solution whose Osmotic Pressure is 0.997 atm at 288K? $K_f = 1.86$ K kg/mol for Water. (Hint: For dilute aqueous solutions at Room Temperature $m \sim c$.)

***** Not Covered Yet *****

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

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

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

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