

Chemistry 440 Final exam

EXAM KEY

Department of Chemistry, Oregon State University

12 December 2013

$$dE(S, V, \{n_i\}) = TdS - PdV + \sum_i \mu_i dn_i$$

$$dH(S, P, \{n_i\}) = TdS + VdP + \sum_i \mu_i dn_i$$

$$dA(T, V, \{n_i\}) = -SdT - PdV + \sum_i \mu_i dn_i$$

$$dG(T, P, \{n_i\}) = -SdT + VdP + \sum_i \mu_i dn_i$$

$$nd\mu(T, V) = -SdT + VdP$$

$$H = E + PV$$

$$A = E - TS$$

$$G = H - TS = \sum_i \mu_i n_i$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V ; \quad C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

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

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

$$\Delta G^0 = -RT \ln K(T)$$

$$H = -T^2 \left(\frac{\partial(G/T)}{\partial T} \right)_P ; \quad E = -T^2 \left(\frac{\partial(A/T)}{\partial T} \right)_V$$

$$F = 2 + c - p$$

$$P_1 V_1^\gamma = P_2 V_2^\gamma ; \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1} = \left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} ; \quad \gamma = C_P/C_V ; \text{ adiabatic process}$$

1. The laws

- (a) (12 pts) State the First and Second Laws of Thermodynamics in terms of properties of the universe and next, in terms of properties of the system.

1st law: The energy of the universe is conserved.

2nd law: The entropy of the universe increases for all spontaneous processes.

1st law: $\Delta E = q_{by} + W_{on} \equiv$ energy of the system increases if heat is absorbed or if work is done on the system

2nd law $\Delta S \geq dq_{by}/T$ the change in entropy is bounded by the ratio of heat absorbed + sys temp.

- (b) (8 pts) Prove that the Helmholtz energy, A , of the system decreases for all spontaneous processes that occur when the temperature and volume are fixed.

$$TdS \geq dq \quad \text{but} \quad dE = dq - P_{ext}dV \Rightarrow dq_V = dE$$

$$TdS \geq dE|_V \Rightarrow 0 \geq d(E - TS)|_{T,V} \text{ so}$$

$$dA|_{T,V} \leq 0$$

- (c) (4 pts) On the basis of the above, if A is a function of an order parameter Q , then the mathematical condition for equilibrium involving $A(Q)$ is ...

$$\left(\frac{\partial A}{\partial Q}\right)_{T,V} = 0$$

- (d) (4 pts) Two processes take place between the same endpoints. Process 1 is reversible and process 2 is irreversible (i.e., spontaneous). Select the two true statements.

• $\Delta S(1) > \Delta S(2)$

• $\Delta S(1) = 0$

• $\Delta S(1) = \Delta S(2)$

• $\Delta S_{universe}(1) > \Delta S_{universe}(2)$

• $\Delta S_{universe}(1) < \Delta S_{universe}(2)$

true

- (e) (6 pts) Debye derived C_v for solids near zero Kelvin and found $C_v = aT^3$ where a is a constant for each material. Show that this C_v is consistent with the Third Law of Thermodynamics.

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T} = aT^2 \Rightarrow ds = aT^2 dT$$
$$\text{and } S(T) - S(0) = \frac{1}{3}aT^3$$

which means that $S(T)$
approaches $T \rightarrow 0$ limit continuously

2. (12 pts) Express the following thermodynamic functions in SI units. Simplify when possible.

- (a) $\alpha_P = 1/K$
(b) $G/V = J/m^3$
(c) $PV = J$
(d) $\left(\frac{\partial S}{\partial T}\right)_V = J/K^2$

Table 1: Change is good.

	T_2/T_1	P_2/P_1	$w_{by}/(P_1V_1)$	$\Delta E/(P_1V_1)$	
path a	$1/2$	$1/16$	$3/2$	$-3/2$	10
path b	1	$1/8$	$\ln(8)$	0	16

3. (32 pts) Complete Table I for the two processes in which one mole of an ideal gas, initially at the state point P_1, V_1, T_1 is expanded to a final volume of $8V_1$ via the following paths. Assume $C_v = 3R$. Note: the final volume was chosen to make the arithmetic nice for part a.

(a) A reversible expansion at constant S .

(b) A reversible expansion at constant H .

$$a) \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{V_1}{V_2}\right)^{1/3} = \left(\frac{1}{8}\right)^{1/3} = \frac{1}{2} \quad \therefore \frac{T_2}{T_1} = \frac{1}{2}$$

$$\gamma = C_p/C_v = 4/3$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma} = \left(\frac{1}{8}\right)^{4/3} = \frac{1}{8} \cdot \frac{1}{2} = \frac{1}{16}, \quad \Delta E = C_v \Delta T = 3R \left(\frac{1}{2}T_1 - T_1\right)$$

$$\Delta E = -\frac{3}{2}RT_1$$

$$\Delta E = q_{by} - w_{by} = -w_{by} \quad \frac{\Delta E}{P_1V_1} = -\frac{3}{2}$$

$$b) \quad \Delta E = 0 = q_{by} - \int P dV \Rightarrow q_{by} = w_{by} = \int \frac{RT}{V} dV = RT \ln(V_2/V_1)$$

$$\frac{w_{by}}{P_1V_1} = \ln(8), \quad P_1V_1 = P_2V_2 \Rightarrow \frac{P_2}{P_1} = \frac{V_1}{V_2} = \frac{1}{8}$$

Table 2: Small change

a, $\frac{\Delta V}{V}$	6×10^{-3}
b, $\frac{\Delta H}{R}(K)$	90
c, $\frac{\Delta A}{V}(\text{bar})$	-1/10
d, $\Delta T(K)$	-1

4. (16 pts) Provide numerical values in Table II appropriate to one mole of liquid water at 300K and at a fixed pressure of 1 bar. Use $C_p = 9R$, $\kappa_T = 5 \times 10^{-5} \text{ bar}$, $\alpha_P = 6 \times 10^{-4} \text{ K}^{-1}$, $K_f = 2 \text{ K}/(\text{mol}/\text{kg})$.

- Calculate the fractional change in volume when the temperature is increased by 10 K. (An incidental thought: consequently, the sea level will rise.)
- If the temperature increases by 10 K, what is $\Delta H/R$?
- When the volume is decreased by ten percent at constant temperature, what is the accompanying $\frac{\Delta A}{V}$?
- Determine the change in freezing point when 1 mole of *dimerizing* solute are added to a kilogram of water.

$$\text{a) } \alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \approx \left(\frac{\Delta V}{V} \right) \frac{1}{\Delta T} \quad \therefore \frac{\Delta V}{V} = \alpha_P \Delta T = \left(6 \times 10^{-4} \frac{1}{\text{K}} \right) 10 \text{ K} = 6 \times 10^{-3}$$

$$\text{b) } \Delta H = C_p \Delta T = 9R \cdot 10 \text{ K}, \quad \frac{\Delta H}{R} = 90 \text{ K}$$

$$\text{c) } dA = -P dV \Rightarrow \frac{\Delta A}{V} = -P \frac{\Delta V}{V} = -\left(\frac{1}{10} \right) \text{ bar}$$

$$\text{d) } \Delta T = K_f m = \left(\frac{1}{2} \right) K_f = \left(\frac{1}{2} \right) 2 \text{ K} = 1 \text{ K}$$

5. (27 pts) Prove the following. Hints: Eq(1), start from dG ; Eq(2), start from Eq(1); Eq(3), you are on your own.

$$nd\mu = -SdT + VdP \quad (1)$$

$$\rho \left(\frac{\partial \mu}{\partial \rho} \right)_T = \left(\frac{\partial P}{\partial \rho} \right)_T \quad (2)$$

$$\left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad (3)$$

(1) $dG = (d\mu)n + \mu dn = -sdt + vdp + \mu dn$
 $\therefore nd\mu = -sdt + vdp$

(2) @ const T , $nd\mu = vdp$

$$\frac{n}{V} d\mu = dp \Rightarrow \rho \left(\frac{\partial \mu}{\partial \rho} \right)_T = \left(\frac{\partial P}{\partial \rho} \right)_T$$

(3) $dE = Tds - pdv$

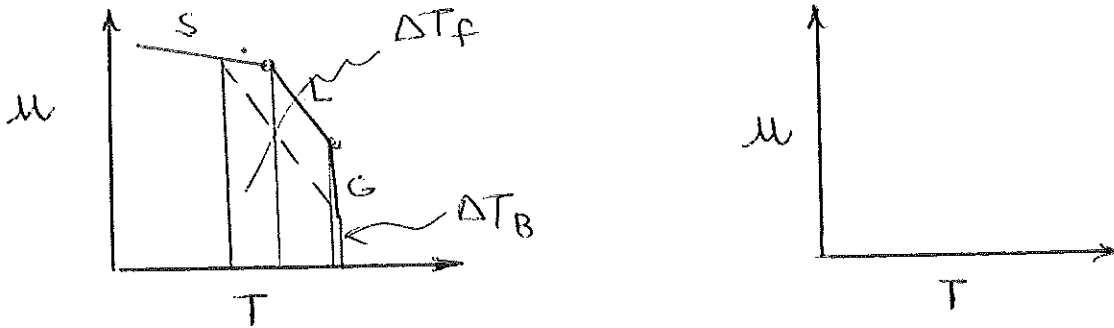
$$\left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - P$$

From A,
 $\left(\frac{\partial S}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V$

and $\left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$

6. (12 pts) Binary mixtures.

- (a) Sketch the chemical potential vs. temperature for a pure substance with liquid, solid and gas phases.
 (b) Show graphically why the increase in boiling point is always much less than the decrease in freezing point when a small amount of solute is added to a pure liquid phase.



$$d\mu = -s dT \Big|_P \quad \text{clearly } \Delta T_B < \Delta T_F$$

7. (8 pts) The mole fractions of oxygen and nitrogen in air at sea level (pressure of 1 bar) are roughly 0.20 and 0.80, respectively. Calculate the mole fractions of these species when dissolved in water. The Henry's law constants for oxygen and nitrogen are, $k_{\text{oxygen}} = 400 \text{ bar}$, $k_{\text{nitrogen}} = 800 \text{ bar}$.

$$P_O = 0.20 \times 1 \text{ bar} = 0.2 \text{ bar} = k_{O_2} X_{O_2} = 400 \text{ bar} X_{O_2}$$

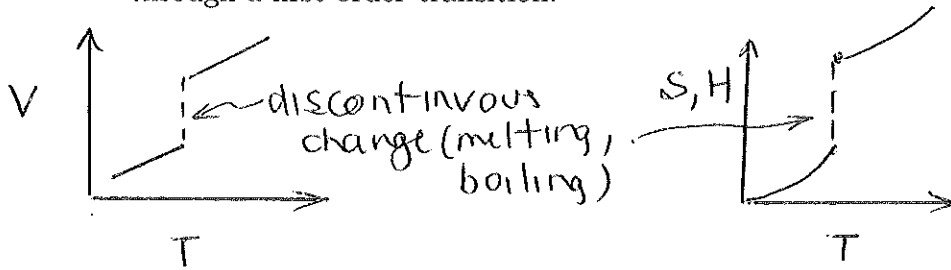
$$P_N = 0.8 \text{ bar} = k_{N_2} X_{N_2} = 800 \text{ bar} X_{N_2}$$

$$\text{So, } X_{O_2} = \frac{0.2}{400} = 5 \times 10^{-4}$$

$$X_{N_2} = \frac{0.8}{800} = 1 \times 10^{-3}$$

8. (18 pts) First and second order transitions.

(a) Plot the temperature dependence of a quantity (label the quantity) as it passes through a first order transition.



(b) If a liquid and a gas phase of a pure substance coexist in equilibrium, what are two conditions that must be satisfied?

$$P(\rho_G, T) = P(\rho_L, T)$$

$$\mu(\rho_G, T) = \mu(\rho_L, T)$$

(c) Consider the power series expression in density for the pressure along the critical isotherm ($T = T_c$),

$$P = P_c + \left(\frac{\partial P}{\partial \rho}\right)_T (\rho - \rho_c) + \frac{1}{2} \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T (\rho - \rho_c)^2 + \frac{1}{3!} \left(\frac{\partial^3 P}{\partial \rho^3}\right)_T (\rho - \rho_c)^3 + \dots \quad (4)$$

What is the critical exponent for the equation of state, i.e., what is δ in the equation

$$|P - P_c| = |\rho - \rho_c|^\delta \quad (5)$$

and how did you arrive at this conclusion?

Since $\left(\frac{\partial P}{\partial \rho}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T_c} = 0$ @ the critical point,

then $\Delta P \sim \frac{1}{3!} \left(\frac{\partial^3 P}{\partial \rho^3}\right)_c (\Delta \rho)^3$ and $\delta = 3$

for all eqns of state.

9. (12 pts) Equilibrium.

(a) Prove that

$$d(G/T) = -(H/T^2)dT + (V/T)dP \quad (6)$$

(b) Given the above, determine the differential equation for the pressure dependence of the equilibrium constant.

$$\begin{aligned} (a) \quad d(G/T) &= (1/T)dG - (G/T^2)dT = \frac{-SdT + VdP}{T} - \frac{G}{T^2}dT \\ &= -\frac{(ST+G)dT}{T^2} + \frac{V}{T}dP = -\frac{H}{T^2}dT + \frac{V}{T}dP \end{aligned}$$

$$(b) \quad \Delta G^\circ = -RT \ln K_{eq} \Rightarrow$$

$$-R d \ln K_{eq} = (\Delta V^\circ / T) dP \quad \text{or} \quad d \ln K_{eq} = -\frac{\Delta V^\circ}{RT} dP$$

10. (12 pts) In Hildebrand's theory of Regular solutions, the Gibbs energy of mixing ΔG_{mix} and the vapor pressure of component 1, P_1 are

$$\Delta G_{mix} = n(wx_1x_2 + RT(x_1 \ln x_1 + x_2 \ln x_2)) \quad (7)$$

$$P_1 = x_1 P_1^0 e^{wx_2^2/RT} \quad (8)$$

Derive ΔS_{mix} and the Henry's law constant, k_H , for component 1.

$$dG = -SdT + VdP$$

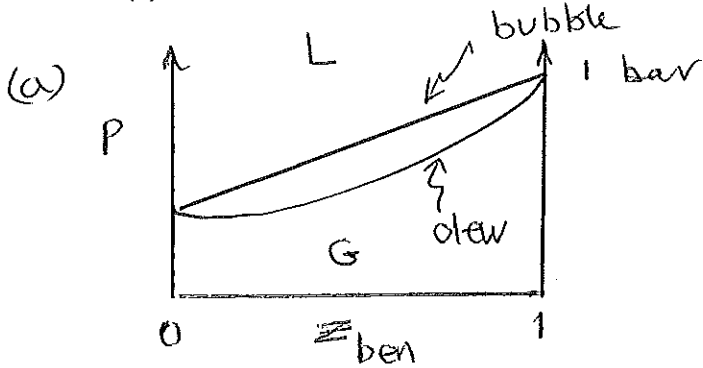
$$\Delta S_{mix} = -\left. \frac{\partial \Delta G_{mix}}{\partial T} \right|_P = -nR(x_1 \ln x_1 + x_2 \ln x_2)$$

$$P_1 = x_1 P_1^0 \exp(wx_2^2/RT) \rightarrow x_1 k_H \quad \text{when } x_1 \rightarrow 0$$

$$\text{so } k_H = P_1^0 \exp(w/RT)$$

11. (18 pts) A benzene-toluene solution is nearly ideal. Suppose that the mole fraction of benzene in the prepared mixture is 0.40 and that the vapor pressures of pure benzene and toluene are 1 bar and 0.5 bar, respectively.

- Draw the P vs. x_{benzene} and P vs. y_{benzene} phase diagram and label the dew point and bubble point curves.
- Calculate the vapor pressure of the mixture.
- Calculate the mole fraction of toluene in the vapor.



(b)

$$P = x_b P_b^0 + x_t P_t^0$$

$$= (0.4)(1 \text{ bar}) + (0.6)(0.5 \text{ bar})$$

$$= 0.7 \text{ bar}$$

(c) $P_t = x_t P_t^0 = y_t P$

$$y_t = x_t P_t^0 / P = \frac{0.6 \times 0.5}{0.7} = \frac{3}{7}$$