

# Chemistry 440 Final exam

## EXAM KEY

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

$$H = E + PV$$

$$A = E - TS$$

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

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

$$\kappa_T = - \left( \frac{\partial \ln V}{\partial P} \right)_T; \quad \alpha_P = \left( \frac{\partial \ln V}{\partial T} \right)_P$$

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

$$F = 2 + c - p$$

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

1. The laws

- (a) (6 pts) Prove that the energy  $E(N, S, V)$  of the system decreases for all spontaneous processes subject to the constraints on volume, entropy and number of particles.

$$Tds > dq \quad dE = dq - P_{\text{ext}} dV$$

but @ constant  $V$ ,  $dE = dq$

$$Tds > dE|_V \quad \text{and} \quad 0 \geq dE|_{S, V}$$

- (b) (6 pts) According to the Second Law, equilibrium is reached when  $A(N, T, V)$  reaches its minimum for all processes that occur at constant  $N, T, V$ . What variables are left after we fix  $N, T, V$ ?

order parameters associated with molecular alignment, molecular position + momentum

- (c) (6 pts) Two processes take place with  $T_1 \rightarrow T_2, P_1 \rightarrow P_2$ . Process A is reversible and process B is irreversible (i.e., spontaneous). Select the *two* true statements.

- $\Delta G(A) < \Delta G(B)$
  - $\Delta S(A) < \Delta S(B)$
  - $\Delta S_{\text{universe}}(A) > \Delta S_{\text{universe}}(B)$
  - $\Delta S_{\text{universe}}(A) < \Delta S_{\text{universe}}(B)$
  - $\Delta G(A) = \Delta G(B) = 0$
- ] true

- (d) (6 pts) For most of the Fall term we assumed that  $C_v$  was a constant. Show why this can not be true for a solid near absolute zero. State the law which would be violated were  $C_v$  to be a temperature-independent constant.

$$S(T) - S(0) = \int_0^T dT C_p / T$$

if  $C_p \sim \text{const}$ , then  $S(T) - S(0) = \text{const} \ln(T) \Big|_0^T$

By the 3rd law,  $S(T)$  goes smoothly to zero or to a constant as  $T \rightarrow 0$ .  
 diverges  $\rightarrow$

2. (12 pts) Express the following thermodynamic functions in SI units. Non-simplified answers will receive no credit.

(a)  $S(T, P)/R = \text{unitless (or moles)}$

(b)  $A(T, V)/V = \text{pressure} = \text{Pa}$

(c)  $\kappa_T = 1/\text{Pa}$

(d)  $T \frac{(C_p - C_v)}{V} = \text{Pa}$

3. Given the relation for the internal energy as a function of the number of particles,  $N$ , entropy and volume,

$$E(N, S, V) = aN^{5/3}V^{-2/3} \exp\left(\frac{2S}{3NR}\right) \quad (1)$$

(a) (12 pts) calculate the temperature  $T(N, E)$  and pressure  $P(E, V)$  for this material,

(b) (6 pts) and determine what type of material this is.

(a)  $dE = Tds - PdV$

$$T = \left(\frac{\partial E}{\partial S}\right)_V = \frac{2}{3NR} E, \quad \text{or} \quad E = \frac{3}{2} NRT$$

$$P = -\left(\frac{\partial E}{\partial V}\right)_S = \frac{2}{3} \frac{E}{V} = \frac{NRT}{V}$$

(b) Ideal gas

Table 1: Changes

	$T_2/T_1$	$P_2/P_1$	$w_{by}/(P_1V_1)$	$\Delta E/(P_1V_1)$
path a	1	1/8	$\ln(8)$	0
path b	$(1/8)^{2/5}$	$(1/8)^{7/5}$	$-\Delta E$	$\frac{5}{2} \left( \left( \frac{1}{8} \right)^{2/5} - 1 \right)$

4. (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  $C_v = \frac{5}{2}R$ .

(a) A reversible expansion at constant  $E(S, V)$ .

(b) A reversible expansion for which  $q_{rev} = 0$ .

$$a) \quad \frac{P_2}{P_1} = \frac{RT_1}{V_2} = \frac{V_1}{V_2} = \frac{1}{8}$$

$$\Delta E = 0 = dq_{by} - P_{ext}dV, \quad q_{by} = \int P dV = RT \ln(V_2/V_1) = RT \ln(8)$$

$$q_{by} = w_{by} = RT \ln 8$$

$$b) \quad \Delta E = q_{by} - \int P_{ext}dV$$

$$\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1}$$

$$\gamma = C_p/C_v = \frac{7/2}{5/2}$$

$$\gamma - 1 = \frac{7}{5} - 1 = 2/5$$

$$\frac{T_2}{T_1} = \left( \frac{1}{8} \right)^{2/5}$$

$$P_2 = P_1 \left( \frac{V_1}{V_2} \right)^{\gamma} = P_1 \left( \frac{1}{8} \right)^{7/5}, \quad \frac{P_2}{P_1} = \left( \frac{1}{8} \right)^{7/5}$$

$$\Delta E = C_v(T_2 - T_1) = \frac{5}{2}RT_1 \left( \frac{T_2}{T_1} - 1 \right)$$

$$\frac{\Delta E}{P_1V_1} = \frac{5}{2} \left( \left( \frac{1}{8} \right)^{2/5} - 1 \right) = -w_{by}$$

Table 2: Small changes

a, $\frac{\Delta E}{R}$	-90
b, $\frac{\Delta V}{V}$	$-6 \times 10^{-3}$
c, $\frac{\Delta G}{V}$	-0.10
d, $\Delta T(K)$	-2K

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

- (a) If the temperature decreases by 10 K, what is  $\Delta E/R$ ?
- (b) Calculate the fractional change in volume when the temperature is decreased by 10 K.
- (c) When the pressure is decreased by ten percent at constant temperature, what is the accompanying  $\frac{\Delta G}{V}$ ?
- (d) Determine the change in freezing point when 1 mole of solute are added to a kilogram of water.

$$(a) \Delta E = C_v \Delta T = 9R(-10) = -90R, \quad \frac{\Delta E}{R} = -90$$

$$(b) \alpha_P = +\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \Rightarrow \frac{\Delta V}{V} = \alpha_P \Delta T = (6 \times 10^{-4})(10) = 6 \times 10^{-3}$$

$$(c) dG = v dp, \quad \Delta G = v \Delta P, \quad \frac{\Delta G}{V} = -0.1$$

$$(d) \Delta T = K_f m = 2 \text{ K}$$

6. (30 pts) Prove or complete Eq(1) and Eq(2). Supply X and prove the resultant Eq(3).

$$dS(T, P) = \frac{C_p}{T} dT - V\alpha_p dP \quad (2)$$

$$dS = \underbrace{\left(\frac{\partial S}{\partial T}\right)_P}_{\uparrow \frac{C_p}{T}} dT + \underbrace{\left(\frac{\partial S}{\partial P}\right)_T}_{\downarrow} dP$$

$\rightarrow dG = -SdT + VdP \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

$$dS = \frac{C_p}{T} dT - \underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{\uparrow V\alpha_p} dP$$

$$\left(\frac{\partial T}{\partial V}\right)_A = \dots \quad (3)$$

$$dA = -SdT - PdV = 0$$

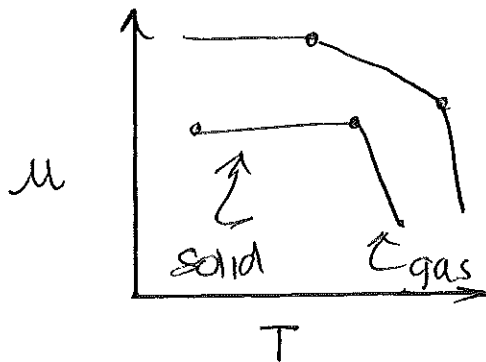
$$\left(\frac{\partial T}{\partial V}\right)_A = -\frac{P}{S}$$

$$\left(\frac{\partial(X/T)}{\partial T}\right)_V = -(E - C_v T) / T^2 \quad (4)$$

$$X = E,$$

$$\left(\frac{\partial(E/T)}{\partial T}\right)_V = -\frac{E}{T^2} + \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_V = -\frac{(E - C_v T)}{T^2}$$

7. (6 pts) Sketch the variation of chemical potential *vs.* temperature for a pure substance for a pressure where solid and gas phases can exist.



$$d\mu = -\bar{S}dT + \bar{V}dP$$

$$\bar{S}_{\text{solid}} < \bar{S}_{\text{Liq}} \ll \bar{S}_{\text{gas}}$$

8. (6 pts) The osmotic pressure  $\pi$  of a binary solution relative to that of pure solvent is defined by an equation involving the chemical potential of the solvent. Write this equation defining  $\pi$ . The equation is not  $\pi = \text{something}$ .

$$\underbrace{\mu_1(T, P + \pi, x_1)}_{\substack{\text{solute with} \\ \text{solute at} \\ \text{pressure } P + \pi}} = \underbrace{\mu_1(T, P)}_{\substack{\text{pure solvent}}}$$

9. (12 pts) A dense fluid of hard spheres (i.e., having no attractive forces) has the following virial coefficients:

$$B_n = (n^2 + n - 2)v_0^{n-1} \quad \forall n \geq 2 \quad (5)$$

where  $v_0$  is the volume of a particle.

- (a) Write the virial expansion in terms of the packing fraction for the pressure, retaining the second and third virial coefficients  
 (b) Using the equation of state, calculate the energy derivative  $\left(\frac{\partial E}{\partial V}\right)_T$  given that

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad (6)$$

and include *all* virial coefficients.

$$a) \quad P = \rho RT (1 + B_2 \rho + B_3 \rho^2)$$

$$B_2 = (4 + 2 - 2)v_0 = 4v_0$$

$$B_3 = (9 + 3 - 2)v_0^2 = 10v_0^2$$

$$\eta = v_0 \rho$$

$$P = \rho RT (1 + 4\eta + 10\eta^2)$$

b)

$$P = \rho RT Z(\rho)$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \rho R Z(\rho) \quad \text{and} \quad T \left(\frac{\partial P}{\partial T}\right)_V = P$$

$$\text{so that} \quad \left(\frac{\partial E}{\partial V}\right)_T = 0$$



10. (16 pts) In the theory of Regular Solutions, one augments the ideal entropy of mixing with an enthalpy of mixing. In so doing, we find that a critical point exists and that the free energy in the vicinity of this critical point obeys

$$G(T, P, x) = G_c + \frac{1}{2}a_1(T - T_c)(x - x_c)^2 + \frac{1}{4}a_2(x - x_c)^4 + \dots \quad (7)$$

where  $a_1, a_2$  are positive constants.

- (a) What phases are present for  $T < T_c$ ?

Two liquid phases

- (b) Calculate the two roots for the order parameter for  $T < T_c$ .

$$\left(\frac{\partial G}{\partial x}\right)_{T,P} = 0 = a_1(T - T_c)(x - x_c) + a_2(x - x_c)^3$$

$$\therefore (T - T_c)a_1 + a_2(x - x_c)^2 = 0$$

$$(x - x_c)^2 = \frac{a_1}{a_2}(T_c - T) \Rightarrow x - x_c = \pm \sqrt{\frac{a_1}{a_2}} \sqrt{T_c - T}$$

- (c) Derived from this theory is the pressure

$$P_1 = x_1 P_1^0 \exp(wx_2^2/(RT)) \quad (8)$$

Define  $P_1^0$  and show that Henry's law emerges from  $P_1$  in the proper limit.

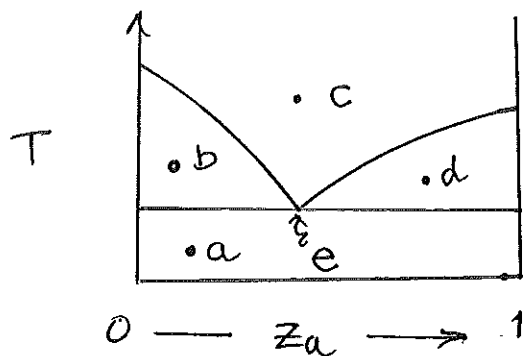
$P_1^0 =$  vapor pressure of pure liq A

$$RH = \lim_{x_2 \rightarrow 1} \frac{P_1^0 \exp(Wx_2^2/RT)}{P_1^0} = P_1^0 \exp(W/RT)$$

- (d) Define the conditions for a critical point in this circumstance, i.e., what two conditions are applied to the pressure?

$$\left(\frac{\partial G}{\partial x_1}\right)_{T,P} = \left(\frac{\partial^2 G}{\partial x_1^2}\right)_{T,P} = 0$$

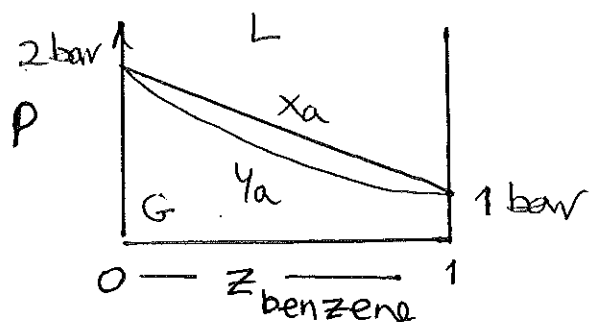
11. (10 pts) Shown below is a generic liquid(L)-solid(S) phase diagram. Label the points  $a \dots e$  according to the phases present, selecting labels from the list: A(S), B(S), A(L), B(S), AB(S), AB(L), B(L)



- a A(S), B(S)  
 b B(S), A(L), B(L)  
 c A(L), B(L)  
 d A(S), A(L), B(L)  
 e A(S), B(S), A(L), B(L)

12. (18 pts) A benzene-toluene solution is nearly ideal. The mole fraction of benzene in the liquid is 0.60 and the vapor pressures of pure benzene and pure toluene are 1 bar and 2 bar, respectively.

- (a) Draw the  $P$  vs.  $x_{benzene}$  and  $P$  vs.  $y_{benzene}$  phase diagram and label the dew point and bubble point curves. The curvature of the lines is important.



$x_a =$  bubble pt curve  
 $y_a =$  dew pt curve

- (b) Calculate the vapor pressure of the mixture.

$$x_{benzene} = 0.60$$

$$P = P_B^0 x_B + P_T^0 x_T = (0.60)(1 \text{ bar}) + (0.40)(2 \text{ bar}) = 1.4 \text{ bar}$$

- (c) Calculate the mole fraction of benzene in the vapor.

$$\frac{y_B}{1-y_B} = \frac{x_B P_B^0}{x_T P_T^0} = \frac{0.6}{0.4} = \frac{3}{2}, \quad y_B = \frac{3}{4}(1-y_B), \quad \frac{7}{4}y_B = \frac{3}{4}$$

$$y_B = \frac{3}{7}$$