Chemistry 440 Final exam

EXAM KEY

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\begin{aligned}
R &\simeq 8\ J/(K\cdot mol) \simeq 0.08\ L\cdot atm/(K\cdot mol)\\
1\ bar &= 10^5\ Pa\\
\Delta U &= q_{by} - P_{ext}\Delta V\\
dU(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 \qquad H = U + PV\\
dA(T,V,\{n_i\}) &= -SdT - PdV + \sum_i \mu_i dn_i \qquad A = U - TS\\
dG(T,P,\{n_i\}) &= -SdT + VdP + \sum_i \mu_i dn_i \qquad G = H - TS = \sum_i \mu_i n_i\\
C_v &= \left(\frac{\partial U}{\partial T}\right)_V; \qquad 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\\
P_1V_1^\gamma &= P_2V_2^\gamma; \qquad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}; \qquad \gamma = C_P/C_V;\ \text{adiabatic process}\\
\Delta G^o &= -RT\ln K(T)\\
H &= -T^2\left(\frac{\partial(G/T)}{\partial T}\right)_P; \qquad U = -T^2\left(\frac{\partial(A/T)}{\partial T}\right)_V\\
F &= 2 + C - P
\end{aligned}
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1. The laws

(a) (16 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. Define the terms in the equations.

1st law

$$\Delta U_{universe} = \Delta U_{sys} + \Delta U_{surroundings} = 0$$ (energy is conserved)

$$\Delta U_{sys} = dq_{by} + dW_{on}$$ ← work done on the system & heat absorbed by the system

2nd law

$$\Delta S_{univ} \geq 0$$ spontaneous processes create entropy, reversible process do not

$$\Delta S_{sys} \geq dq_{by}/T$$ for a fixed T, the entropy change exceeds dq/T, whereas for a reversible process, $dS = dQ/T$.

(b) (8 pts) Prove that the Gibbs energy of the system decreases for all spontaneous processes that occur when the temperature is constant and the system and external pressure are equal and constant.

$$dS \geq dq/T$$

If pressure is fixed,

$$dU = dq - P_{ext}dV,$$

$$dH = dq - PdV + VdP + PdV$$

and $P = P_{ext}$

$$dH = dq$$ so

$$dS \geq dH/T \Rightarrow dH - TdS \leq 0$$

and for fixed T $$d[H-TS]\Big|_{T,P} \leq 0$$

or $$dG\Big|_{T,P} \leq 0$$

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Table 1: Change is good.

	T_2/T_1	P_2/P_1	$\frac{w_{by}}{RT_1}$	$\frac{\Delta U}{RT_1}$
path a	5	1/2	9/2	12
path b	1	1/10	ln(10)	0

2. (32 pts) Complete Table 1 for the processes in which one mole of water vapor, initially at the state point P_1, V_1, T_1 is expanded to a final volume of $10V_1$ via the following paths. Assume water is an ideal gas with $C_v = 3R$. Express your answers in terms of the properties of the initial state.

   (a) Constant pressure expansion where $P_{ext} = \frac{1}{2}P_1 = P_2$

   (b) A reversible expansion at constant U.

a) $\frac{P_2V_2}{P_1V_1} = \frac{T_2}{T_1} = \frac{\frac{1}{2}P_1 \cdot 10V_1}{P_1V_1} = 5$

$W_{by} = P_{ext}\Delta V = \frac{1}{2}P_1(10-1)V_1 = 9/2$

$\Delta U = C_V \Delta T = 3R(5-1)T_1 = 12RT_1$

$P_2/P_1 = 1/2$

b) $\Delta U = 0, \ \Delta T = 0$

$\frac{P_2}{P_1} = \frac{V_1}{V_2} = \frac{V_1}{10V_1} = \frac{1}{10}$

$W_{by} = RT_1 \ln(V_2/V_1) = RT_1 \ln(10)$

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Table 2: The times are changing.

a, $\frac{\Delta V}{V}$	6×10^{-3}	4
b, ΔH	720 J	4
c, $\frac{\Delta A}{V}$	0.1 bar	4
d, ΔT	2K	4

3. (16 pts) Provide numerical values in Table 2 appropriate to one mole of liquid water at 300K and at a fixed pressure of one bar given that $C_P = 9R, \kappa_T = 5 \times 10^{-5}\ bar^{-1}$, $\alpha_P = 6 \times 10^{-4} K^{-1}$, $K_f = 2$ K/(mol/kg)).
   (a) Calculate the fractional change in volume when the temperature is increased by 10 K at a fixed pressure;
   (b) if the temperature changes by 10 K, what is the change in H?
   (c) when the volume is decreased by ten percent at constant T, what is $\frac{\Delta A}{V}$?
   (d) what is the change in freezing point when 2 moles of *dimerizing* solute are added to a kilogram of water.

a) $\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \frac{\Delta V}{V} = \alpha_P \Delta T = 6\times10^{-4} \cdot 10 = 6\times10^{-3}$

b) $\Delta H = C_P \Delta T = 9 \cdot R \cdot 10 = 90R = 720J$

c) $dA = -PdV, \quad \Delta A = -P\Delta V, \quad \frac{\Delta A}{V} = -P\frac{\Delta V}{V} = 0.1P$

$\frac{\Delta A}{V} = 0.1$ bar

d) $\Delta T = K_f m$ since it dimerizes, $m \rightarrow N/2$

$= 2K \cdot 2\text{moles} \times \frac{1}{2} = 2K$

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4. (30 pts) Prove the following. Hints: Eq(1), start from dG; Eq(2) start from Eq(1); Eq(3), you are on your own.

$$nd\mu = -SdT + VdP \tag{1}$$

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

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

Eq(1)

$dG = d(n\mu) = -SdT + VdP + \mu dn$

$dG = nd\mu + \mu dn =$ "

so $nd\mu = -SdT + VdP$

Eq(2)

$nd\mu = VdP$ @ fixed T

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

Eq(3)

$dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

$dU = TdS - PdV$

$\therefore (dU/dV)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$

but $dA = -SdT - PdV$

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

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

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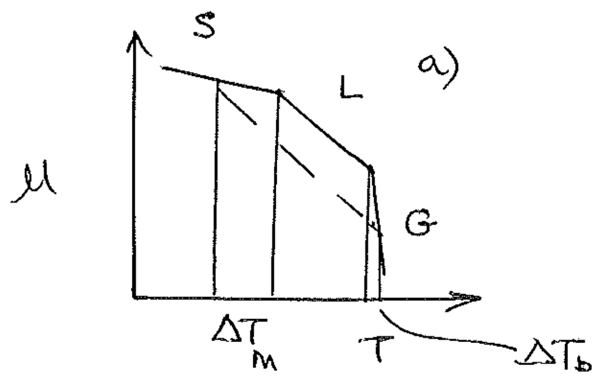
5. (12 pts) Binary mixtures.

(a) Sketch the chemical potential *vs.* temperature for a pure substance with liquid, solid and gas phases.

(b) What is the chemical potential of the solvent in a two component ideal liquid mixture? Write an equation.

(c) Show graphically why the increase in boiling point of the mixture is always much less than the decrease in freezing point.



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

b) $\mu(T,P,x) = \mu(T) + RT\ln x$

x: solvent mole fraction

c) As shown above ΔT_M (melting) > ΔT_b (boiling)

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6. (16 pts) Osmotic pressure.

(a) Define the osmotic pressure.

(b) Recall that for an ideal liquid solution the osmotic pressure of the solvent Π obeys

$$\Pi = \frac{n_2 RT}{V} = c_2 RT \tag{4}$$

where n_2 is the number of moles of dissolved substance and c_2 its molar concentration. Write a virial expansion for Π following the conventions and notations used for non-ideal gases.

(c) The osmotic pressure of polymer solutions shows a critical point. In direct analogy with gas-liquid behavior, what are the two conditions (equations) for a critical point of a polymer solution?

(d) On cooling of the polymer solution below its critical point, alluded to above, a phase transition occurs. Describe the two coexisting phases.

a) Osmotic pressure: the pressure exerted on a fluid mixture so as to equalize the chemical potential of pure solvent.

b) $\Pi = RT c_2 \{ 1 + B_2 c_2 + B_3 c_2^2 + \cdots \}$
osmotic virial coef's.

c) $\left(\partial \Pi / \partial c_2\right)_T = \left(\frac{\partial^2 \Pi}{\partial c_2^2}\right)_T = 0$

d) phase separation into two liquid phases, differing in the amount of dissolved polymer (i.e., one is polymer rich, the other, polymer poor)

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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, $k_{oxygen} = 4 \times 10^7$Pa, $k_{nitrogen} = 8 \times 10^7$ Pa. Recall Henry's and Dalton's law.

P_i = partial pressure $= y_i P = x_i k_i$

$x_i = \frac{y_i P}{k_i} = \frac{0.2 \cdot 1\,\text{bar}}{4\times10^{7}\,\text{Pa}} \times \frac{10^5\,\text{Pa}}{\text{bar}} = \frac{0.2}{4\times10^{2}} = 5\times10^{-4}$ for O_2

$x_i = \frac{0.8}{8\times10^{7}} 10^5 = 0.1\times10^{-2} = 1\times10^{-3}$ for N_2

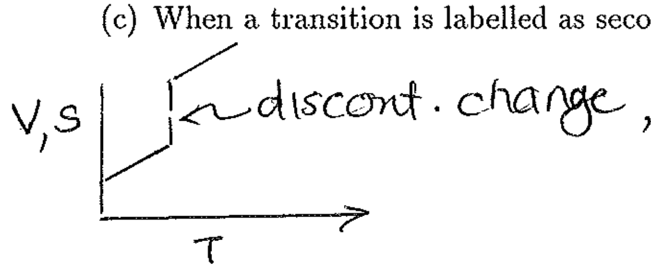
8. (12 pts) First and second order transitions.

(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?

(c) When a transition is labelled as second order, what criterium is satisfied?

a)



b) $\mu_L = \mu_G$

$P_L = P_G$

c) a singularity in the second derivative of G

$\left(\frac{\partial^2 G}{\partial P^2}\right)_T = \left(\frac{\partial V}{\partial P}\right)_T \to \infty$ or $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \to \infty$

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9. (33 pts) The phase diagram below represents gas, liquid and solid phases. The following points have special names attributed to them. Provide these terms:

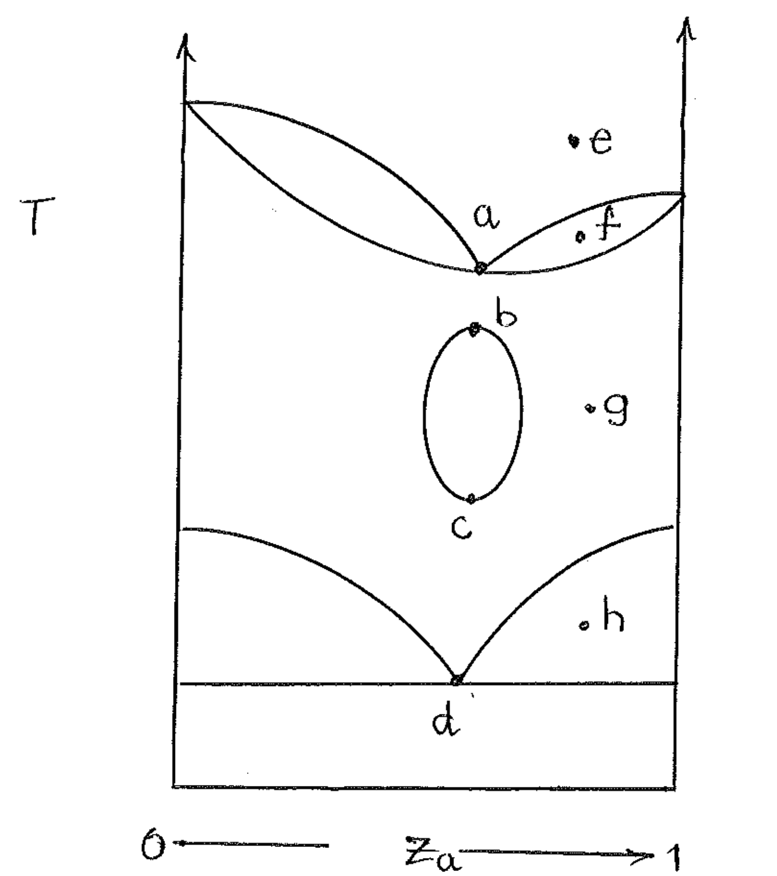
(a) azeotrope
(b) upper critical pt.
(c) low critical pt
(d) eutectic

Identify the phases present

(e) gas
(f) liquid and gas
(g) liquid
(h) ...liquid and solid

According to the phase rule, F variables are required to describe a point on the phase diagram. What are these variables for

(i) point b F=2, T + P
(j) point e F=3, T, P and y
(k) point f F=2, T+P or P and x



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10. (15 pts) Express the following thermodynamic functions in SI units

(a) α_P $= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right) \Rightarrow K^{-1}$

(b) dq $= J$

(c) P $=$ bar or Pa

(d) C_p $= J/K$

(e) dS $= J/K$

11. (2 pts) Facts: the universe is cooling and energy, even the dark variety, is thought to be constant.

Hence, the Helmholtz energy of the universe decreases with time. True or false.

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