NAME: Key

CHE371: Thermodyamics and Kinetics

EXAM #3

November 30, 2007

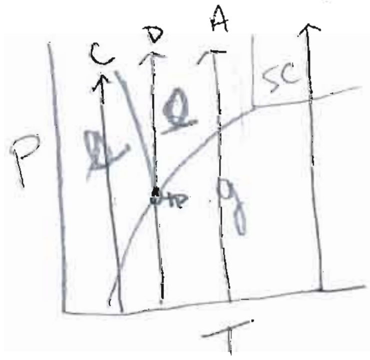
100 points

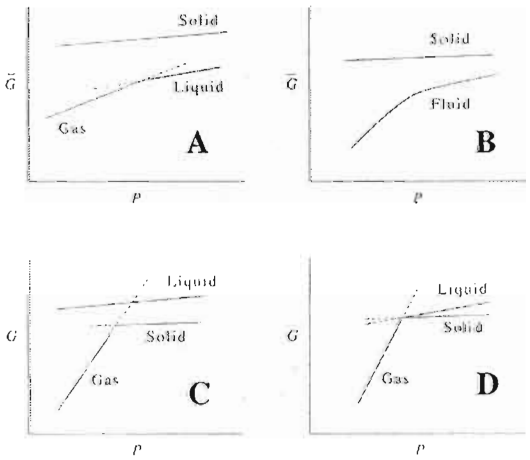
On my honor, I pledge that I have not given, received, or tolerated others' use of unauthorized aid in completing this work (including unauthorized aid from technological devices such as calculators and cell phones).

2 1. The symbol μ is stands for the chemical potential. Which of the following statements about chemical potential is **FALSE**?
   a. For a single pure substance, μ is the same as the molar Gibbs energy.
   b. For a liquid (l) and gas (g) of a pure substance in equilibrium, μ^g is always greater than μ^l.
   c. Matter flows from higher μ to lower μ.
   d. For a single pure substance, $\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P}$.
   e. μ is an intensive quantity.

8 2. The plots below, labeled A-D, are for benzene. Rank the plots in order of decreasing temperature.

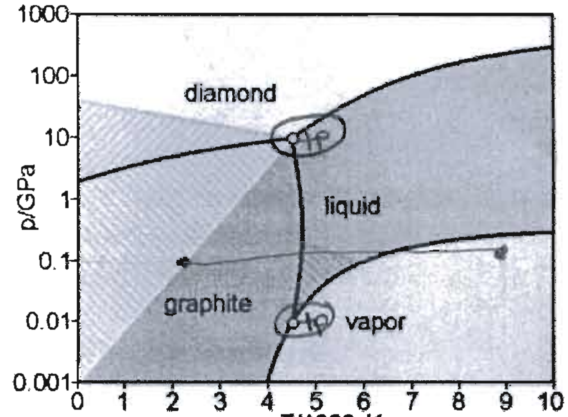
B > A > D > C





+10

3. The figure below is the P-T phase diagram for carbon. Use the figure to answer the questions below.



+2 a. Label the triple point(s) on the graph.

+3 b. How do the phases of carbon change along an isobaric line at 0.1 GPa from 2000K to 9000K?

At 0.1 GPa and 2000 K carbon is graphite. As the temp ~~pressure~~ increases, carbon ~~you~~ becomes a liquid and then a gas

+4.5 c. Which coexistence curve of fusion is more pressure dependent? Explain your choice.

There are two coexistence curves of fusion: one between graphite + the liquid + one between diamond and the liquid. The slope of the diamond/liquid curve is more pressure ~~is steeper~~ ... as you dependent b/c small changes in pressure can cause large changes in the melting temp.

~~+5~~ +8

4. Consider the reaction: H_2 (g) + CO_2 (g) $\rightleftarrows$ CO (g) + H_2O (g), $K_P = 1.6$. Initially, $P_{H2} = 0.5$ bar, $P_{CO2} = 0.2$ bar, $P_{CO} = 1.0$ bar, and $P_{H2O} = 0.1$ bar. Will ξ increase or decrease to achieve equilibrium? Show all work.

$$H_2 + CO_2 \rightleftarrows CO + H_2O$$

$$Q = \frac{P_{CO}\,P_{H_2O}}{P_{CO_2}\,P_{H_2}} = \frac{(1.0)(0.1)}{(0.5)(0.2)} = \frac{0.1}{0.1} = 1$$

$$Q < K_P$$

ξ will increase → reaction will proceed more to right (toward products)

+~~12~~ 15

5. Consider the reaction: $2K(g) \rightleftharpoons K_2(g)$. Initially, there are 2 mol K(g) present. Derive an expression for $K_P(T)$ in terms of ξ and P_{tot} with $P° = 1$ bar. What is $K_P(T)$ if $\xi = 0.5$ and $P_{tot} = 1.5$ bar at 298K? Show all work.

$$\begin{array}{lll} & 2K_{(g)} \rightleftharpoons & K_{2(g)} \quad (+2) \\ I & 2\text{ mol} & 0\text{ mol} \\ E & 2-2\xi & \xi \end{array}$$

total mol → $2-2\xi+\xi = 2-\xi$

$K_P = \dfrac{P_{K_2}}{P_K^2}$ (+1)

$P_{K_2} = X_{K_2} P_{tot} = \dfrac{\xi}{2-\xi} P_{tot}$ (+2)

$P_K = X_K P_{tot} = \dfrac{2-2\xi}{2-\xi} P_{tot}$ (+2)

$$K_P = \frac{\frac{\xi}{2-\xi}\cancel{P_{tot}}}{\left(\frac{2-2\xi}{2-\xi}\right)^2 P_{tot}^{\cancel{2}}} = \frac{\xi}{\cancel{2-\xi}} \cdot \frac{(2-\xi)^{\cancel{2}}}{(2-2\xi)^2 P_{tot}} \quad (+3)$$

$$K_P = \frac{0.5}{(2-2\cdot 0.5)^2} \cdot \frac{2-0.5}{1.5} = 0.5 \quad (+2)$$

+~~4~~ +6

6. The pressure of component 1 in a binary solution can be given by:

$$P_1 = 30x_1 e^{x_2^2/2+3x_2^3/2}$$

What is the Henry's law constant for component 1?

Henry's law $P_1 \to K_H x_1$ as $x_1 \to 0$, $x_2 \to 1$

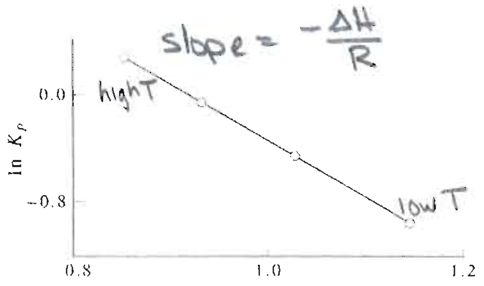
$P_1 \to 30e^{1/2+3/2} x_1$ as $x_1 \to 0$

$P_1 \to 221.67 x_1$ as $x_1 \to 0$

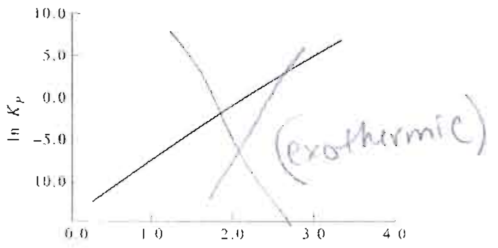
so $K_H = 221.67$

+~~3~~ 4

7. The following graphs, labeled A and B, show ln K_P vs. 1/T. Which graph describes an endothermic reaction?
$\Delta H > 0$



A



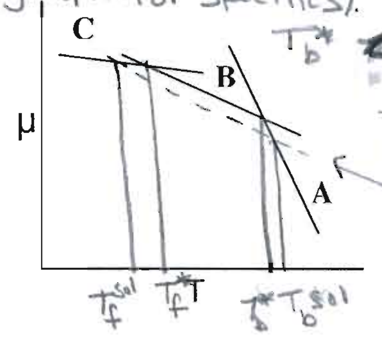
B

+10

8. The graph below plots chemical potential versus temperature.
   a. Which line represents SOLID __C__, LIQUID __B__, and GAS __A__?
   b. Draw a line on the graph representing an estimate of the chemical potential of a SOLUTION.
   c. Use the graph (and your answer to part b) to discuss and illustrate the colligative properties of freezing point depression and boiling point elevation.

The μ of a solvent is lowered when a solute is added (i.e., $\mu^* > \mu^{sol}$). Because of the shift in μ, the freezing pt + boiling pt of the solution also change (see marks on graph for specifics). $T_f^{sol} < T_f^*$ = freezing pt depression

$T_b^* < T_b^{sol}$ = boiling pt depression



$\boxed{\text{steepest slope = gas}}$

Solution

+12

9. Given the following table of data for ethanol/water at 25 °C determine whether the solution is ideal, shows positive deviations from Raoult's Law or shows negative deviations from Raoult's Law. **If the solution shows deviations, describe the forces responsible for the deviation.**

If followed Raoult's law $P_A = X_A P_A^*$

$X_{ethanol}$	$P_{ethanol}$ /torr		P_{water} / torr	
0.00	0.00	0.00	23.78	23.78
0.10	17.65	5.92	21.70	21.40
0.50	36.86	29.60	17.29	[illegible]
0.90	53.45	53.28	5.38	2.38
1.00	59.20	59.20	0.00	0.00

$P^*_{H_2O}$

$P^*_{ethanol}$

The real $P_{ethanol}$ + P_{water} are higher than that predicted from Raoult's law. Therefore, this solution shows positive deviations. Positive deviations from Raoult's law are due to the repulsive ~~molecules~~ forces of the molecules in solution. More molecules "leave" the solution than would be predicted for an ideal solution, causing positive deviations from Raoult's law.

+25

Put in Fas

10. Calculate the solubility of LiF (s) in water at 25 °C. Take $K_{sp} = 1.7 \times 10^{-3}$.

~~DAM~~

You may find the equations below useful (I_c + $\ln \gamma_\pm$).

Hint: (Stop when s is the same within 2 sig figs between cycles).

	$LiF_{(s)}$	$\longrightarrow$	$Li^+_{(aq)}$	+	$F^-_{(aq)}$
I	0.1 M		0		0
E	$0.1-\xi$		ξ		ξ

$$K_{sp} = \frac{a_{Li}\, a_{F^-}}{\cancel{a_{LiF}} \to 1} = C_{Li}\gamma_+ C_{F^-}\gamma_- = C_{Li^+}C_{F^-}\gamma_\pm^2 = 1.7\times10^{-3}$$

Cycle 1

① Let $C_{Li^+} = S = C_{F^-}$ + assume $\gamma_\pm^2 = 1$

$$S^2 \cdot 1 = 1.7\times10^{-3}$$

$$S = 0.0412\ M$$

②
$$I_c = \frac{1}{2}(z_+^2 \cdot c_+ + z_-^2 \cdot c_-)$$
$$= \frac{1}{2}(1\cdot 0.0412 + 1\cdot 0.0412)$$
$$= 0.0412\ M$$

③ $$\ln \gamma_\pm = \frac{-1.173|z_+z_-|\, I_c^{1/2}}{1 + I_c^{1/2}} = -0.198, \quad \gamma_\pm = 0.820, \quad \gamma_\pm^2 = 0.673$$

Cycle 2

④ ~~Let~~
$$S^2 \cdot 0.673 = 1.7\times10^{-3}$$
$$S = 0.0503\ M$$

⑤ $$I_c = \frac{1}{2}(z_+^2 c_+ + z_-^2 c_-)$$
$$= \frac{1}{2}(1\cdot 0.0503 + 1\cdot 0.0503)$$
$$= 0.0503\ M$$

⑥ $\ln \gamma_\pm = -0.215, \quad \gamma_\pm = 0.807, \quad \gamma_\pm^2 = 0.651$

Cycle 3

⑦ + ⑧ $S^2 \cdot 0.651 = 1.7\times10^{-3} \qquad S = 0.0511\ M = I_c$

⑨ $\ln \gamma_\pm = -0.216, \quad \gamma_\pm = 0.806, \quad \gamma_\pm^2 = 0.649$

⑩ $S^2 \cdot 0.649 = 1.7\times10^{-3}$

$$S = 0.0512\ M$$

$$S = 0.051\ M = C_{Li^+} = C_{F^-}$$