CHEM 1422 - Homework # 4

ANSWER KEY

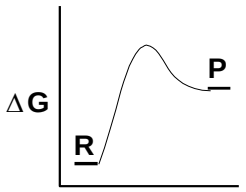
Equilibrium

Due Tuesday, March 3, 2009 (2 PM)

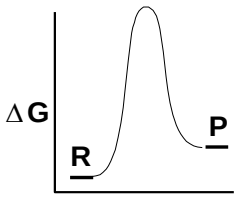
Check the box to the right if you want your graded homework to be placed out in the public rack outside Prof. Stanley's office. Otherwise you will have to pick up your homework from Prof. Stanley in person: ☐

1. (3 pts) A reaction has an equilibrium constant of 1×10^{-6} and reaches equilibrium very slowly. Circle the following potential energy diagram that best fits this data. Briefly and clearly discuss your reasoning.

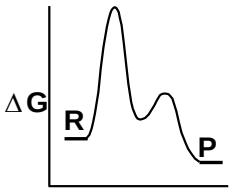
a)



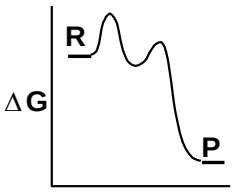
b)



c)



d)



The small K_{eq} value means that this reaction is non-spontaneous (ΔG = positive, reactants are lower in energy than products). Thus, you can rule out **c)** and **d)** since these are both *spontaneous* reactions that will have $K_{eq} > 1$. **a)** and **b)** are both non-spontaneous reactions. The height of the activation barrier has nothing to do with the thermodynamics or K_{eq}, but does control the speed or rate of reaction. The fact that the rxn reaches equilibrium ***slowly*** implies the larger activation barrier, which fits **b)**. But if your reasoning is OK you could also select **a)** and get full credit.

2. (3 pts) Consider the following equilibrium:

$$3C_2H_2(g) \rightleftharpoons C_6H_6(g) \qquad K_{eq} = 1 \times 10^{18}$$

If one starts with 6 *M* acetylene (C_2H_2) and lets the reaction reach equilibrium, what will be the equilibrium concentration of benzene (C_6H_6)? Circle the answer and clearly discuss your reasoning.

a) 0 *M* **b)** 0.6 *M* **c)** 1 *M* **d)** 2 *M* **e)** 6 *M*

Always think qualitatively about the problem and what the K_{eq} value is telling you. The huge K_{eq} value means that this reaction goes essentially to completion. So we will have all products and no reactants at equilibrium. The stoichiometry of the reaction, however, is that 3 molecules of acetylene combine to make one molecule of benzene. So if we start with 6 M acetylene, we will end up with 2 M benzene (3:1 reduction ratio).

3. (3 pts) The *initial* concentrations of reactants and products are all 2 *M*. What is the concentration of methanol (CH_3OH) at equilibrium for the following reaction? $K_{eq} = 25$ Circle the answer and clearly show your work!!

$$CH_3OH(g) + HI(g) \rightleftharpoons CH_3I(g) + H_2O(g)$$

a) 0 *M* **b)** 0.33 *M* **c)** 0.66 *M* **d)** 1.00 *M* **e)** 1.33 *M* **f)** 2.66 *M*

	$CH_3OH(g)$	+	$HI(g)$	$\rightleftharpoons$	$CH_3I(g)$	+	$H_2O(g)$
Initial:	2 *M*		2 *M*		2 *M*		2 *M*
@ eq:	2 – x		2 – x		2 + x		2 + x

If all the concentrations are initially equal and $K_{eq} = 25$, then the reaction has to make more products so the ratio of products over reactants is > 1. ($Q < K_{eq}$)

$$K_{eq} = \frac{[CH_3I][H_2O]}{[CH_3OH][HI]} = \frac{(2+x)^2}{(2-x)^2} = 25$$ now take the square root of both sides: $\frac{(2+x)}{(2-x)} = 5$

rearrange and solve for x: (2 + x) = (5)(2 – x); 2 + x = 10 – 5x; 6x = 8; x = 8/6 or x = 1.33 (but this isn't the answer!!)

The concentration of MeOH at equilibrium, therefore, is: **2 – x** or **0.67 *M***

4. (4 pts) Calculate the concentrations for all species at equilibrium for the following reaction. The initial concentrations are $[H_2] = [I_2] = 0\ M$, $[HI] = 4\ M$. Clearly show your work.

Initial:	**0 *M***	**0 *M***	**4 *M***	
	$H_2(g) + I_2(g)$	$\rightleftharpoons$	$2HI(g)$	$K_{eq} = 36$ (@ 1200 K)
@ eq:	**x**	**x**	**4 – 2x**	

plug the algebraic expressions into the equilibrium formula:

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = \frac{(4-2x)^2}{(x)^2} = 36$$ now take the square root of both sides: $\frac{(4-2x)}{x} = 6$

rearrange and solve for x: 4 – 2x = 6x; 4 = 8x; x = 0.5.

Now plug x into the @eq conditions to solve for the numerical values: **so, $[H_2] = [I_2] = 0.5$ M and $[HI] = 3$ M**

5. (6 pts) Consider the following reactions:

A) $Br_2(aq) + 2Cl^-(aq) \rightleftharpoons Cl_2(g) + 2Br^-(aq)$ $\Delta H_{rxn} = +68$ kJ/mol

B) $AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$ $\Delta H_{rxn} = -13$ kJ/mol

C) $2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g)$ $\Delta H_{rxn} = -30$ kJ/mol

D) $SiO_2(s) + 6HF(aq) \rightleftharpoons 2H_2O(l) + SiF_6^{2-}(aq) + 2H^+(aq)$

E) $Rh(H)(CO)(PPh_3)_2(aq) + CO(g) \rightleftharpoons Rh(H)(CO)_2(PPh_3)(aq) + PPh_3(aq)$

F) $\text{hemoglobin}(aq) + 4O_2(g) \rightleftharpoons \text{hemoglobin}(O_2)_4(aq)$

G) $2H_2O_2(aq) \rightleftharpoons 2H_2O(l) + O_2(g)$ exothermic

H) $S^{2-}(aq) + Fe^{2+}(aq) \rightleftharpoons FeS(s)$

I) $H_2(g) + D_2(g) \rightleftharpoons 2HD(g)$ $\Delta H_{rxn} = 0$ kJ/mol

Based on the information above, which of the equilibria will:

- produce more products when heated? **A**
- produce more products when the pressure is raised? **E, F**
- be unaffected by adding or substracting some product (so long as some remains)? **H**
- produce more reactants when heated? **B, C, G**
- produce more reactants when the pressure is raised? **A, C, G**
- be unaffected by temperature? **I**
- be unaffected by pressure? **B, D, H, I**

If you don't have any ΔH_{rxn} information (or know that it is exo- or endothermic, you can NOT state that a reaction is unaffected by temperature.

6. (4 pts) The ***initial*** concentrations for the following reaction are $[CH_3I] = [F^-] = 1\ M$, and $[CH_3F] = [I^-] = 9\ M$. What will be the concentrations of each species at equilibrium? Clearly show all your work.

Initial:	**1 *M***	**1 *M***		**9 *M***	**9 *M***
	$CH_3I(aq)$ +	$F^-(aq)$	$\rightleftharpoons$	$CH_3F(aq)$ +	$I^-(aq)$ $\quad K_{eq} = 16$
@Equilibrium:	**1 + x**	**1 + x**		**9 – x**	**9 – x**

*First you have to calculate **Q** (rxn quotient) to figure out which way the rxn will go to reach equilib.*

***Q** = 81, which is larger than K_{eq}, so the reaction has to go BACKWARDS to reach equilib.*

$K_{eq} = \dfrac{(9-x)^2}{(1+x)^2} = 16$, take the square root of each side to give: $\dfrac{(9-x)}{(1+x)} = 4$

multiply out to get: 9 – x = 4 + 4x, rearrange to get: 5x = 5, or **x = 1**. Plug **x = 1** back into the equilibrium conditions to get:

$[CH_3I] = [F^-] = 2\ M$, $[CH_3F] = [I^-] = 8\ M$

7. (4 pts) Which of the following salts is the ***least*** soluble (i.e., will give the lowest $Pb^{+2}(aq)$ concentration)? Circle your answer. Calculate the concentration of $[Pb^{+2}]$ for the answer and put it and the calculation details below.

a) $PbCO_3$ ($K_{sp} = 1 \times 10^{-13}$)

b) $Pb_3(AsO_4)_2$ ($K_{sp} = 1.1 \times 10^{-36}$)

c) $Pb(CrO_4)$ ($K_{sp} = 1 \times 10^{-14}$)

d) $Pb(OH)_2$ ($K_{sp} = 4 \times 10^{-16}$)

e) $Pb_3(PO_4)_2$ ($K_{sp} = 1.1 \times 10^{-44}$)

f) PbS ($K_{sp} = 1 \times 10^{-24}$)

a) $x^2 = 1 \times 10^{-13}$; $x = [Pb^{2+}] = 3.2 \times 10^{-7}\ M$

b) $108x^5 = 1.1 \times 10^{-36}$; $3x = [Pb^{2+}] = 7.5 \times 10^{-8}\ M$

c) $x^2 = 1 \times 10^{-14}$; $x = [Pb^{2+}] = 1 \times 10^{-7}\ M$

d) $4x^3 = 4 \times 10^{-16}$; $x = [Pb^{2+}] = 4.6 \times 10^{-6}\ M$

e) $108x^5 = 1.1 \times 10^{-44}$; $3x = [Pb^{2+}] = 1.9 \times 10^{-9}\ M$

f) $x^2 = 1 \times 10^{-24}$; $x = [Pb^{2+}] = 1 \times 10^{-12}$

8. (3 pts) What is the equilibrium concentration of $Ag^+(aq)$ in the presence of 1 *M* $CrO_4^{2-}(aq)$? Clearly show all your work.

Initial:	**excess**	**0**		**1 *M***
	$Ag_2CrO_4(s)$	$\rightleftharpoons$	$2Ag^+(aq)$ +	$CrO_4^{2-}(aq)$ $\quad K_{sp} = 4 \times 10^{-12}$
@Equilibrium:	**less excess**	**2x**		**1 + x**

$K_{sp} = [Ag^+]^2\,[CrO_4^{2-}] = (2x)^2\,(1 + x) = 4 \times 10^{-12}$: make the approximation that x << 1 M to simplify the algebra

$(2x)^2\,(1) = 4 \times 10^{-12}$

$4x^2 = 4 \times 10^{-12}$, now divide each side by 4 to give: $x^2 = 1 \times 10^{-12}$; take the square root of each side:

$x = 1 \times 10^{-6}$; but the concentration of Ag^+ is **2x**, not just x, so: **$[Ag^+] = 2x = 2 \times 10^{-6}\ M$**