CHM 109 Exam III Study Guide F 09

Show logic and calculations for all problems. Remember to include units and be careful with sig. fig. Please put your name on the back of the last page and your initials on the back of the other pages

1. *The following mechanism has been proposed:*

$$\text{Step 1 } O_3 \xrightarrow{k_1} O_2 + O$$

$$\text{Step 2 } O + O_3 \xrightarrow{k_2} 2\,O_2$$

a) *Write a balanced equation for the overall reaction.*

b) *Write the predicted rate law for the overall reaction if k2 is much larger than k1.*

c) *Identify any reaction intermediates.*

a) $2\,O_3 \rightarrow 3\,O_2$

b) rate = $k_1[O_3]^1$

c) The only intermediate (produced in an early step, used in a later step) is the oxygen atom: O.

2. *Given these data for the reaction of Fe^{3+} with I^-:*

$$2\,Fe^{3+}(aq) + 2\,I^-(aq) \rightarrow 2\,Fe^{2+}(aq) + I_2(aq)$$

Exp#	$[Fe^{3+}]$ (M)	$[I^-]$ (M)	Initial rate (M/s)
1	0.0400	0.0300	8.10×10^{-4}
2	0.0800	0.0300	1.62×10^{-3}
3	0.0400	0.0600	3.24×10^{-3}

Be sure to ***explain*** *the logic for your answers.*

a) *Write a general rate law for the reaction.*

b) *Use the initial rate data to write the specific rate law consistent with the data. Make sure you solve to obtain a numerical value for k.*

c) *Write a chemical rxn. for the reactant side of the rate limiting step in the rxn. mechanism.*

d) *What is the initial rate of the rxn. with 0.090 M Fe^{3+} and 0.50 M I^-?*

e) *If I told you that the value of k that you obtained is relatively large, what height hill would you draw for this reaction on a reaction progress diagram (vertical axis = G°).*

a) rate = $k[Fe^{3+}]^x[I^-]^y$

b) $\frac{rate2}{rate1} = \frac{1.62 \times 10^{-3}}{8.10 \times 10^{-4}} = \frac{k[0.0800]^x[0.0300]^y}{k[0.0400]^x[0.0300]^y}$ Note: $\frac{k}{k}$ and $\frac{[0.0300]^y}{[0.0300]^y}$ cancel.

$\frac{1.62 \times 10^{-3}}{8.10 \times 10^{-4}} = 2^x$ $2 = 2^x$ $x = 1$

$\frac{rate\,3}{rate\,1} = \frac{3.24 \times 10^{-3}}{8.10 \times 10^{-4}} = \frac{k(.0400)^x(.0600)^y}{k(.0400)^x(.0300)^y}$ $4 = 2^y$ $y = 2$

$1.62 \times 10^{-3} = k(0.0800)(.0300)^2$

$k = \frac{1.62 \times 10^{-3}}{(.0800)(.0300)^2} = 22.5$

Rate $= 22.5[Fe^{3+}][I^-]^2$

c) $Fe^{3+} + 2\,I^- \longrightarrow$

d) Rate $= 22.5(0.090)(0.50)^2 = 0.51\ \frac{M}{s}$

e) If k is relatively large, that means the rate is relatively fast which means the hill would be relatively small.

3. How does decreasing the temperature usually alter the rate of a chemical reaction? Explain your answer with reference to rate laws and collision theory.

It usually (almost always) decreases the rate of the chemical reaction. Logic: Decreasing the temperature of a population of molecules decreases the average speed of the molecules and markedly decreases the fraction of molecules moving at the very high speeds needed to reach the transition state in a collision (re. E_{act}). Because a smaller fraction of molecules is moving at a high enough speed to have their collisions reach the transition state, a smaller fraction of collisions will be productive, and the rate of the reaction will decrease accordingly.

4. Write equilibrium constant expressions for the following reactions:

a) $2\,H_2(g) + 2\,NO(g) \rightarrow 2\,H_2O(g) + N_2(g)$

b) $Fe(s) + CO_2(g) \rightarrow FeO(s) + CO(g)$

a) $K_{eq} = \dfrac{[H_2O]^2[N_2]}{[H_2]^2[NO]^2}$

b) $K_{eq} = \dfrac{[CO]}{[CO_2]}$

6. Shown below is a balanced equation for the decomposition of H_2S to form H_2 and S_2.

$2\,H_2S(g) \rightarrow 2\,H_2(g) + S_2(g)$

a) Write an equilibrium constant expression for the reaction.

b) Given the equilibrium concentrations: $[H_2S] = 0.1007$ M, $[H_2] = 0.0219$ M, and $[S_2] = 3.30 \times 10^{-3}$ M, calculate the numerical value of Keq.

c) Assume the equilibrium is perturbed. When equilibrium is reestablished, the following concentrations are observed: $[H_2] = 0.00287$ M and $[S_2] = 0.171$ M. Calculate $[H_2S]$ under these new conditions.

d) What can you say about the forward and reverse reaction rates when the system is at equilibrium?

e) What can you say about the forward and reverse rate constants, whether the system is at equilibrium or not?

a) $K_{eq} = \dfrac{[S_2][H_2]^2}{[H_2S]^2}$

b) $K_{eq} = \dfrac{(3.30\times10^{-3})(0.0219)^2}{(0.1007)^2} = 1.56\times10^{-4}$

c) $([H_2S]^2)(K_{eq}) = [S_2][H_2]^2$

$[H_2S]^2 = \dfrac{[S_2][H_2]^2}{K_{eq}}$

$[H_2S] = \sqrt{\dfrac{[S_2][H_2]^2}{K_{eq}}}$

$= \sqrt{\dfrac{(.171)(.00287)^2}{1.56\times10^{-4}}}$

$= 0.0950$ M

d) At equilibrium: the rate forward reaction = rate reverse reaction

e) $\dfrac{k_f}{k_r} = K_{eq}$

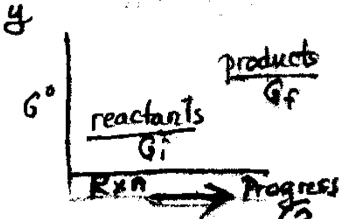
7. Qualitatively, for the reaction shown #6, would the ΔG° value be positive or negative? Explain your logic. Calculate the ΔG° value if the experiment in problem #6 was carried out at 150.5° C.

$150.5 + 273.15 = 423.65$ K

ΔG would be positive. When Keq is less than 1, the relative amount of products is less than reactants. Whatever there is more of must be more stable, so it is lower on the energy diagram. Gf − Gi is positive.

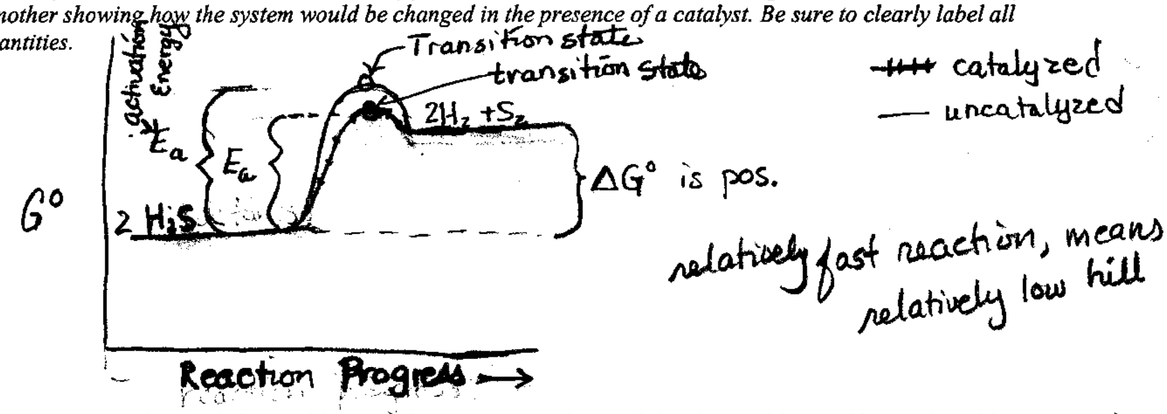
$\Delta G° = -RT\ln K_{eq} = -(8.3145\ \frac{J}{K\cdot mol})(423.65\ K)\ln(1.56\times10^{-4})$

$= +30,876\ J/mol \rightarrow +30,880\ J/mol$



(2)

8. Assuming I told you the reaction in #6, was relatively fast. Draw a reaction coordinate diagram that describes that system. Then draw another showing how the system would be changed in the presence of a catalyst. Be sure to clearly label all important quantities.



9. Why is it necessary to understand chemical kinetics if you want to understand the chemical basis of human health?

All living things must increase the rates of specific chemical reactions to stay healthy & alive. The presence of genetic diseases that occur in humans who do not produce sufficient amounts of enzyme activities is strong support for this assertion. One example of this that we have considered is PKU.

10. What is the definition of a Brønsted-Lowry acid?

An acid is a substance that can donate an H^+.

11. Identify the acid and base on the reactant side of the equation shown below. Predict the products of the reaction and indicate the conjugate of each reactant.

$NH_3 + HBr \rightarrow$

$NH_3 + HBr \longrightarrow NH_4^+ + Br^-$

base   acid   cj acid   cj base

12.(a) Write a balanced chemical reaction for the dissociation of acetic acid (CH_3COOH) in water, and then (b) write the K_a expression for that rxn. Acetic acid is a relatively weak acid. (c) What could you say about the strength of its conjugate base? Formic acid is a slightly stronger acid than acetic acid. (d) Would formic acid dissociate to a greater or lesser extent in water compared to acetic acid? (e) Which acid would have the larger pK_a?

a) $CH_3COOH + H_2O \longrightarrow CH_3COO^- + H_3O^+$

b) $K_{eq} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$

c) relatively strong cj base

d) formic acid would dissociate to a greater extent

e) acetic acid would have the larger pKa

13.(a) Calculate the [H_3O^+], [OH^-], and pH of a 7.00 x 10^{-3} M solution of HNO_3. (b) Is this solution acidic, basic or neutral? (c) Would the pH be the same for a 7.00 x 10^{-3} M solution of acetic acid? Explain.

a) HNO_3 is a strong acid - completely dissociates

so $[H_3O^+] = 7.00 \times 10^{-3} M$

$pH = -\log 7.00 \times 10^{-3} = 2.155$

$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1 \times 10^{-14}}{7.00 \times 10^{-3}} = 1.43 \times 10^{-12}$

b) acidic

c) no the pH would be higher (less acidic) because acetic acid is a weak acid and would not dissociate as much.

14. How does a buffer function to keep the pH of a solution relatively constant when strong acid or base is added? Make sure your answer includes equations for chemical reactions.

A buffer is composed of a weak acid (HA) and it cj base (A^-).

The weak acid neutralizes added strong base.

$HA + OH^- \longrightarrow A^- + H_2O$

The conjugate base neutralizes added strong acid (H_3O^+).

$A^- + H_3O^+ \longrightarrow HA + H_2O$

15. What weak acid could be used to make a buffer that was effective around pH 4.25? You must explain your answer thoroughly to receive full credit.

An effective buffer must have reasonable quantities of both weak acid and conjugate base components

ideally $[HA] = [A^-]$

From the Henderson-Hasselbalch expression, when $[HA] = [A^-]$ then $pH = pK_a$

Because the indicated pH = 4.25, we need a weak acid with a pK_a of ~ 4.25.

16. Three coal miners are trapped in a closed space within the mine after a cave-in. Although they have oxygen tanks with enough O_2 to provide for their respiratory needs, they are still likely to incur health risks associated with gas exchange. Describe one risk that is likely to occur. Be sure to include chemical rxns. as necessary to support your answer.

There is a risk of respiratory acidosis.

The reason for this is that CO_2, released by the miner's normal respiratory processes, will build up in the mine. (ie - the concentration of CO_2 will increase)

As external [CO_2] increases, the rate of efflux of CO_2 from the miners will decrease. This would cause the miner's internal [CO_2] to go up, causing more CO_2 to dissolve in the blood. These equations would shift to the right (towards products).

$H_2O + CO_2 \rightleftharpoons H_2CO_3$

$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$

This acid will lower the blood pH causing acidosis.

18. Write a balanced chemical reaction for the dissociation of water, and then write the Kw expression for that rxn.

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$ $K_w = [H_3O^+][OH^-]$