Chemistry 132   Exam #2: Kinetics and Electrochemistry   3-18-04

1. Short answers (30 points total, 5 points each)

(a) Give an example of experimental results that would prove to you that the reaction $H_2 + I_2 \rightarrow 2HI$ is not elementary (2 sentences).

(b) Briefly explain the Greenhouse effect at a level suitable for a non-technical friend. Your explanation should include what the effect is, how it works, what it has to do with greenhouses and why it is important. (1 paragraph)

(a) The Nernst equation is written $\xi = \xi^0 - (0.0592/n)\log_{10}Q$. Explain each what the variables ξ, ξ^0, n and Q stand for and give the units of each (1 sent).

(d) Give an example of when you would use the Nernst equation in part (c).

(e) In lecture 20, I spent some time discussing the electrolysis of water which involves the half reactions

$2\ H^+ + 2\ e^- \rightarrow H_2(g)$ $\xi^0 = 0.00$ V   and
$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$ $\xi^0 = 1.23$ V.

I showed that the acid concentration ($[H^+]$) does not affect the voltage required for electrolysis, calculating that it is 1.23 V under standard conditions (298 K, 1 M $[H^+]$) as well as for ordinary water of pH = 7 (298 K, 10^{-7} M [H+]). Nevertheless, in practical electrolysis of water we add acid rather than use pure water even though it adds expense and reduces safety. Explain why.

(f) What will happen if I dip a silver wire into a 1 M solution of $Cu(SO_4)$? Explain how you know (1 sent).

2. Kinetics (20 points, 5 each)

Ethyl chloride decomposes via the reaction $C_2H_5Cl\ (g) \rightarrow C_2H_4\ (g) + HCl\ (g)$. The reaction is found to be first order and the rate constant is measured to be $4.2 \times 10^{-5}\ sec^{-1}$ at 700 K and is found to double at 712 K.

(a) Find the activation energy for the reaction in KJ/mol.

(b) If the reaction is run at 700 K for 10 minutes, what fraction of the original amount of C_2H_5Cl (g) remains?

(c) If I double the initial concentration of C_2H_5Cl (g), will I get a different result for (b)? Explain your answer.

(d) If I add a catalyst, will I get a different result for (b)? Explain your answer.

3. Reaction Mechanisms and Rate Laws (20 points, 5 each)

Consider the following hypothetical mechanism for the overall reaction

$$N_2O_4\,(g) \rightarrow 2\,NO_2(g):$$

Step 1: $N_2O_4\,(g) \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} N_2O_4^*\,(g)$

Step 2: $N_2O_4^*\,(g) \overset{k_2}{\rightarrow} 2\,NO_2\,(g)$

(a) Assume that the forward reaction in the equilibrium of step 1 is endothermic and that the overall reaction is exothermic. Sketch a well labeled diagram of energy versus reaction coordinate including reactants, products and intermediates on the diagram.

(b) Suppose that the rates in step 1 are fast and step 2 is slow. Write the rate law for the reaction in terms of k_1, k_{-1} and k_2.

(c) Suppose that step 2 is fast and the rates in step 1 are much slower. Write the rate law for the reaction in terms of k_1, k_{-1} and k_2.

(d) If we did not know which step was fast, we learned that we can use the steady state approximation to determine a rate law from a mechanism. Briefly explain the premise behind this approximation and explain without mathematics how you would go about deriving a rate law (3 sents).

4. Electrochemistry and Batteries (30 points)

You are interested in making a tiny battery for a hearing aid based on the half reactions $Cu^{2+} + 2e^- \rightarrow Cu(s)$ and $Ni^{2+} + 2e^- \rightarrow Ni(s)$. Initially, you have 0.1 mL of 1 M $Cu(SO_4)$ with a Cu electrode as your cathode and 0.5 mL of 1 M $Ni(SO_4)$ with a Ni electrode as your anode.

(a) Calculate the cell voltage at 25°C when the battery is fresh. (5 points)

(b) When the battery is dead (i.e. reaches equilibrium), what will the voltage be? (5 points)

(c) At equilibrium, what will the Ni^{2+} and Cu^{2+} concentrations be? (10 points)

(d) Assuming that the voltage remains adequate until equilibrium is almost reached, will you be able to run a hearing aid that requires 10 milliampere currents for the length of a 2 hour movie? Document your conclusion quantitatively. (10 points)