Chem1B – General Chemistry II – Exam 1 Summer 2011

Name: ____KEY_____

GSI: _____

Write your name on all pages of the exam.

Read all questions carefully – make sure that you answer the question that is being asked.

Write neatly and clearly – if your answer cannot be understood, it cannot be graded.

Be sure to answer all questions to the best of your ability – it is always to your advantage
to at least try!

Explain your answers clearly and concisely – ALL of them!

You are not permitted to use any outside materials on this exam.

Relax and good luck!

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1. When the temperature increases, the rate of a reaction increases. In 2-3 sentences, explain the why the rate increases with increasing temperature.

   The rate increases with increasing temperature for two reasons: 1) the number of collisions that occur increases due to an increased molecular speed and 2) the fraction of particles with enough energy to surmount the activation barrier is greatly increased.

2. Reactions that occur in solution are very different from those that occur in the gas phase. Describe one factor that affects the rate of a reaction in solution and how the rate is affected (increased or decreased).

   We discussed four main factors in class:
   1) solvent hinders motion – decreases rate
   2) stabilization of transition state – increases rate
   3) increased collisions between species - increase rate
   4) bath can provide energy to reactive species - increase rate

3. Most biological reactions are catalyzed by enzymes.
   a. In 1-2 sentences, explain how an enzyme speeds up the rate of a reaction.

      Enzymes speed up reaction rates by providing an alternative pathway for the reaction which has a lower activation barrier.

   b. What is the general mechanism for enzyme catalysis?

      1) $E + S \leftrightarrows ES$ fast equilibrium
      2) $ES \rightarrow E + P$ slow (catalytic step)

   c. What does a large value of the Michaelis constant ($K_m$) indicate about an enzyme?

      The Michaelis constant is the equilibrium constant for the reverse of reaction 1 in the above mechanism. A large value of the $K_m$ indicates that the enzyme binds weakly to the substrate.

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4. The following data was collected for the reaction between nitrogen monoxide and hydrogen gases:

$$2\ SO_2\ (g) + O_2\ (g) \rightarrow 2\ SO_3\ (g)$$

| Experiment | $[SO_2]$ (M) | $[O_2]$ (M) | Rate (M/s) |
|---|---|---|---|
| 1 | 0.30 | 0.20 | $1.2 \times 10^{-2}$ |
| 2 | 0.30 | 0.10 | $6.0 \times 10^{-3}$ |
| 3 | 0.60 | 0.20 | $4.8 \times 10^{-2}$ |

a. Determine the rate law for this reaction. Show appropriate work.

rate = $k\,[SO_2]^2[O_2]$

(shown by comparing experiments – method of initial rates)

b. Calculate the rate constant for this reaction.

$k = 0.67\ M^{-2}s^{-1}$

c. Do you expect that this reaction occurs in a single elementary step? Explain your answer in 2-3 sentences.

It is possible that the reaction occurs in a single step since it meets all criteria: 1) experimentally determined rate law matches rate law that would be written directly from the reaction 2) overall reaction is the same as the reaction from the mechanism 3) mechanism matches experimental data (non given) and 4) plausible. The mechanism is, however, not probable since it requires a complicated termolecular step.

d. In the plot below, show how the concentrations of $O_2$ and $SO_2$ change as a function of time. Assume that 1.0 M concentrations of both species are present initially. Be sure to label your axes and identify which line corresponds to which species.

1 pt – y-axis
1 pt – x-axis
½ pt – reactants
½ pt – products
1 pt – $E_a$
1 pt – transition st.

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5. The decomposition of nitrogen dioxide occurs in a single step:

$$2\ NO_2\ (g) + \text{heat} \rightarrow 2\ NO\ (g) + O_2\ (g)$$

a. Derive an expression for the half-life of $NO_2$.

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \text{ and } [A]_{t_{1/2}} = \frac{1}{2}[A]_0$$

$$\frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} 0 = kt_{1/2}$$

$$2 - 1 = kt_{1/2}[A]_0$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

b. Sketch a picture of the transition state complex for this reaction.

Any reasonable structure which shows the two oxygen atoms with a partial bond and a partial breaking of the corresponding O-N bond. There should be a bracket around the transition state with the double dagger symbol.

c. Do you expect the orientation term (p) to have a relatively large or small value for this reaction? Explain your answer in 1-2 sentences.

The orientation term is large when a large fraction of collisions have the correct orientation. In this case, the particles can collide with a large number of possible arrangements and therefore the value of p should be large.

d. Sketch the potential energy diagram on the graph below. Label the axes, reactants, products, activated complex, and activation energy.

1 pt – units on axes
1 pt – axes labeled
1 pt – $O_2$ graph
1 pt – $SO_2$ graph

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6. Consider the reaction of nitrogen and hydrogen gases to produce ammonia gas:

   $N_2\,(g) + 3\,H_2\,(g) \rightarrow 2\,NH_3\,(g)$ $\quad \Delta H^o = -91.8$ kJ $\quad \Delta S^o = -198.1$ J/K

   a. In 1-2 sentences, physically explain the sign of the entropy change for this reaction.

      The entropy is a large negative number because there are four independent gas particles on the reactant side and only two gas particles on the right. The more independent gas particles present, the greater the entropy. **It is not enough to say that there is a change in the moles because the phase matters.

   b. Is this reaction spontaneous when 1 M quantities of nitrogen and hydrogen are combined at 20°C? Justify your answer with words and/or calculations.

      The reaction will spontaneously occur in the forward direction any time only reactants are present since the reaction must go forward (and cannot go backward) in order to reach equilibrium. **This question refers to the free energy change and not the standard free energy change.

   c. What is the value of $K_{eq}$ for this reaction: greater than 1, less than 1, or equal to 1? Explain your answer in 1-2 sentences.

      $K_{eq}$ will have a value that is dependent on the temperature. **You can use a temperature and then calculate using $DG^o$=-RTlnK or just calculate $DG^o$ and comment on the fact that a negative value indicates that the reaction must go forward (toward products) from standard conditions in order to reach equilibrium.

   d. Under what temperature conditions, if any, will this reaction be product favored? Explain your answer in 1-2 sentences.

      The reaction is enthalpically driven so the reaction will favor products at low temperatures where the entropy term is less important.

7. Trouton's rule states that the entropy of vaporization for most liquids is about the same (87 J/mol·K). Some substances, such as methanol, ethanol, and water,

do not adhere to Trouton's rule. These substances have a much higher entropy of vaporization. In 1-2 sentences, suggest why you think that this deviation exists.

Methanol, ethanol, and water all have hydrogen bonding which causes their solid phase structure to have a great deal of order. When vaporization occurs, the ordered liquid is disrupted more than a random liquid (one with weaker intermolecular forces).

8. In many redox reactions, hydrogen peroxide is a participant. For example:

$$H_2O_2(aq) + ClO_4^-(aq) \rightarrow O_2(g) + ClO_2^-(aq)$$

a. Balance the redox reaction that occurs in basic solution.

$2 \times (H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-)$

$ClO_4^- + 4H^+ + 4e^- \rightarrow ClO_2^- + 2H_2O$

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$2H_2O_2 + ClO_4^- + 4H^+ + 4e^- \rightarrow 2O_2 + 4H^+ + 4e^- + ClO_2^- + 2H_2O$

$2H_2O_2 + ClO_4^- \rightarrow 2O_2 + ClO_2^- + 2H_2O$

b. Which species is the oxidizing agent in the reaction?

The oxidizing agent is reduced (gains electrons): $ClO_4^-$

c. Sketch a diagram of the electrolytic cell that could be prepared based on the reaction above. In the diagram label the solutions, anode, cathode, direction of electron flow, direction of salt bridge anion/cation flow.

For labeling each correctly:
1 pt – solutions
1 pt – electron flow
1 pt – salt bridge ions
1 pt – anode/cathode

d. In order for the reaction to proceed in the direction written, which will have a larger (more positive) standard reduction potential $H_2O_2$ or $CO_4^-$? Explain your answer in 1-2 sentences.

In order for the reaction to proceed in the forward direction, it will need to have a positive overall cell potential. This will occur when the reduction potential of the perchlorate ion is greater than that of peroxide.

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e. This reaction could be used as a battery to supply a current. Under what conditions will the battery be "dead" (no longer supply a current)? Explain your answer in 1-2 sentences.

The battery will no longer supply a current once it reaches equilibrium since the motion of electrons will be equal in both directions.