This set of review questions will include the following four major topics: (1) chemical kinetics (Arrhenius equation, Activation Energy, Reaction Profile, Catalysis and Reaction Mechanisms); (2) gaseous equilibria (Equilibrium Constant and its calculation, Non-equilibrium System and its calculation, Le Chatelier’s Principle and kinetics versus equilibrium); (3) photochemical smog and general level ozone; and (4) water (colligative properties, freezing point depression, osmotic pressure and water hardness). These questions are intended to provide you with practice at solving quantitative problems. It is in your best interests to work through all these questions independently before the exam.

A very good source of the review materials for the final exam is midterm exams and midterm review questions. The "Problem Lab" is available to all CHEM*130 students. You can come in the lab at any designated time slot for the assistance in the week of "Problem Lab". It is advantageous for you to ask questions if you are experiencing difficulties with the review questions. Remember the lab demonstrator is there to help you!

Complete answers to these review questions are placed in a binder which is available at the Reserve Desk in the MacLaughlin Library. Remember that photocopying the answers to the questions in no way substitutes for working through the questions on your own!

PART A Chemical Kinetics (II)

1. The rate constant for the reaction
   \[ \text{NO}_2(g) \rightarrow \text{NO}(g) + \text{O}(g) \]
   is given by the expression: \[ k = 2.6 \times 10^7 \exp(-8900/T) \text{ L mol}^{-1} \text{ s}^{-1} \]
   (a) Calculate the \( k \) for this reaction.
   (b) Calculate the rate constant for the reaction at 298 K.
   (c) Calculate the concentration of \( \text{NO}_2(g) \) after 10 minutes, given that the initial concentration of \( \text{NO}_2(g) \) was \( 3.5 \times 10^{-2} \text{ mol L}^{-1} \).

2. A plot of \( \log k \ vs \ 1/T \) for the reaction
   \[ \text{S}_2\text{O}_5^2^-(aq) + 3 \text{I}^-(aq) \rightarrow \text{I}_2(aq) + 2 \text{SO}_4^{2-}(aq) \]
   gave a straight line of slope \(-2500 \text{ K} \). Determine the activation energy for the reaction.

3. The rate of reaction of hydrogen with iodine: \( \text{H}_2(g) + \text{I}_2(g) \rightarrow 2 \text{HI}(g) \)
   has rate constant of \( 1.41 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \) at 393°C and \( 1.40 \times 10^4 \text{ M}^{-1} \text{ s}^{-1} \) at 443°C. Calculate the activation energy, in kJ mol\(^{-1}\), for this reaction.

4. For the elementary reaction \( \text{A} + \text{B} \rightarrow \text{C} \)
   the activation energy is \( 30.0 \text{ kJ mol}^{-1} \) and the heat energy change is \(-5.0 \text{ kJ mol}^{-1} \). The activation energy for the reverse reaction is:
   (a) \( 25.0 \text{ kJ mol}^{-1} \)
   (b) \( 35.0 \text{ kJ mol}^{-1} \)
   (c) \( 30.0 \text{ kJ mol}^{-1} \)
   (d) \( 150.0 \text{ kJ mol}^{-1} \)
   (e) \( 5.0 \text{ kJ mol}^{-1} \)

5. A certain reaction has energy of activation \( 20 \text{ kJ} \) and the enthalpy change for the reaction is \( +8 \text{ kJ} \). When the reaction proceeds with the catalyst, energy of activation is \( 12 \text{ kJ} \). Sketch the reaction profile with and without a catalyst and indicate energy of activations and enthalpy change for the reaction.

6. One mechanism for ozone destruction is:
   \[ \text{O}_3(g) \rightarrow \text{O}_2(g) + \text{O}(g) \] (rapid equilibrium)
   \[ \text{O}_2(g) + \text{NO}(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g) \] (slow)
   \[ \text{NO}_2(g) + \text{O}(g) \rightarrow \text{NO}(g) + \text{O}_3(g) \] (fast)
   Overall: \( 2 \text{O}_2(g) \rightarrow 3 \text{O}_3(g) \)
   Identify the intermediate(s) and the catalyst in this reaction.

7. Refer to the following mechanism consisting of two elementary steps:
   \[ (1) \quad \text{A} + 2 \text{B} \rightarrow \text{C} + \text{D} \quad \text{(slow)} \]
   \[ (2) \quad \text{D} + \text{A} \rightarrow \text{C} + \text{E} \quad \text{(fast)} \]
   Which of the following statements is incorrect?
   (a) The species D is an intermediate.
   (b) The first step is the rate-determining step.
   (c) The second step is a bimolecular elementary step.
   (d) The rate law for the first step is: \( \text{rate} = k [\text{A}][\text{B}]^2 \).
   (e) If the concentration of B is tripled, the rate of reaction increases 6-fold.

8. The rate law for the reaction \( 2 \text{H}_2(g) + 2 \text{NO}(g) \rightarrow \text{N}_2(g) + 2 \text{H}_2\text{O}(g) \) is:
   \[ \text{rate} = k_{exp} [\text{H}_2][\text{NO}]^2 \]
   Show which of the following mechanisms is consistent with the experimental rate law. Show your work clearly.
   (a) \( \text{H}_2 + \text{NO} \rightarrow \text{H}_2\text{O} + \text{N} \) (slow, \( k_1 \))
   \( \text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O} \) (fast, \( k_3 \))
   \( \text{O} + \text{H}_2 \rightarrow \text{H}_2\text{O} \) (fast, \( k_3 \))
   (b) \( \text{H}_2 + 2 \text{NO} \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \) (slow, \( k_3 \))
   \( \text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O} \) (fast, \( k_3 \))
9. For the general reaction: \(2 A + B \rightarrow D + E\), the following mechanism has been proposed:

\[
\begin{align*}
A + B & \rightarrow C \quad \text{(fast, \(k_1\))} \\
C & \rightarrow A + B \quad \text{(slow, \(k_2\))} \\
C + A & \rightarrow D + E \quad \text{(slow, \(k_3\))}
\end{align*}
\]

(a) Use steady-state approach to deduce the rate law for the reaction.
(b) Under what conditions would the rate law be simplified to \(rate = k_{exp}[A][B]\)?

10. The rate law for the decomposition of phosgene \(\text{COCl}_2(g) \rightarrow \text{CO}(g) + \text{Cl}_2(g)\) was found to be:

\[
rate = k_{exp} [\text{COCl}_2][\text{Cl}_2]^3
\]

(a) Show that the following mechanism is consistent with the rate law.

(Use Equilibrium Constant, \(K\), to eliminate concentration of an intermediate.)

\[
\begin{align*}
\text{Cl}_2(g) & \rightarrow 2 \text{Cl}(g) \quad \text{(rapid equilibrium, \(K\))} \\
\text{COCl}_2(g) + \text{Cl}(g) & \rightarrow \text{COCl}(g) + \text{Cl}_2(g) \quad \text{(slow, \(k_1\))} \\
\text{COCl}(g) & \rightarrow \text{CO}(g) + \text{Cl}(g) \quad \text{(fast, \(k_2\))}
\end{align*}
\]

(b) What is \(k_{exp}\) equal to when expressed in terms of \(K\) and \(k_i\)?

11. The rate law for the reaction: \(2 \text{H}_2(g) + 2 \text{NO}(g) \rightarrow \text{N}_2(g) + 2 \text{H}_2\text{O}(g)\) is:

\[
rate = k_{exp}[\text{H}_2][\text{NO}]^2
\]

Is the following proposed mechanism consistent with the experimental rate law?

(Use Equilibrium Constant, \(K\), to eliminate concentration of intermediate.)

\[
\begin{align*}
2 \text{NO} & \rightarrow \text{N}_2\text{O}_2 \quad \text{(fast equilibrium, \(K\))} \\
\text{N}_2\text{O}_2 + \text{H}_2 & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \quad \text{(slow, \(k_1\))} \\
\text{N}_2\text{O} + \text{H}_2 & \rightarrow \text{N}_2 + \text{H}_2 \quad \text{(fast, \(k_2\)}
\end{align*}
\]

12. For the overall reaction: \(2 \text{O}_2(g) \rightarrow 3 \text{O}_3(g)\), the following mechanism has been proposed:

\[
\begin{align*}
\text{O}_3 & \rightarrow \text{O} + \text{O}_2 \quad \text{(fast, \(k_1\))} \\
\text{O} + \text{O}_2 & \rightarrow \text{O}_3 \quad \text{(fast, \(k_2\))} \\
\text{O} + \text{O}_3 & \rightarrow 2 \text{O}_2 \quad \text{(slow, \(k_3\)}
\end{align*}
\]

From the proposed mechanism, deduce the rate law using:
(a) Steady-state approach to eliminate an intermediate.
(b) Equilibrium Constant, \(K\), to eliminate an intermediate. (Note that \(K = k_1/k_2\)).
(c) Under what conditions would the rate laws derived by the methods (a) and (b) be the same?
(d) if the experimentally found rate law is: \(rate = k_{exp}[\text{O}_3]^2/[\text{O}_3]\), under what conditions would the proposed mechanism be consistent with the experimental data?

**PART B  Gaseous Equilibria**

1. Given the equilibrium constants at 1000 K for the following reactions:

\[
\begin{align*}
\text{MgCl}_2(s) + \frac{1}{2} \text{O}_2(g) & \rightleftharpoons \text{MgO}(s) + \text{Cl}_2(g) \quad K_p = 2.95 \text{ atm}^{\frac{1}{2}} \\
\text{MgCl}_2(s) + \text{H}_2\text{O}(g) & \rightleftharpoons \text{MgO}(s) + 2 \text{HCl}(g) \quad K_p = 8.40 \text{ atm}
\end{align*}
\]

determine the equilibrium constants \(K_p\) and \(K_c\) at 1000 K for the reaction:

\[
2 \text{Cl}_2(g) + 2 \text{H}_2\text{O}(g) \rightleftharpoons 4 \text{HCl}(g) + \text{O}_3(g)
\]

2. Consider the chemical equilibrium:

\[
\text{C}_\text{s}(s) + 2 \text{H}_2(g) \rightleftharpoons \text{CH}_4(g) \quad \Delta H_{\text{rxn}} = -75 \text{kJ}
\]

Predict the way the above equilibrium will shift in response to each of the following changes in conditions. (Note the equilibrium may also be unaffected by the change.)

(a) decrease in temperature (d) increase in pressure of \(\text{CH}_4(g)\)
(b) decrease in volume (e) addition of \(\text{C}_\text{s}(s)\)
(c) decrease in pressure of \(\text{H}_2(g)\) (f) addition of catalyst

What are the optimal conditions to get a high yield of \(\text{CH}_4(g)\)?

3. The decomposition of sulfur trioxide: \(\text{SO}_3(g) \rightleftharpoons \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g)\) is an endothermic reaction. The maximum formation of \(\text{SO}_2(g)\) and \(\text{O}_2(g)\) is favoured by:

(a) low \(T\) + low \(P\) (b) low \(T\) + high \(P\) (c) high \(T\) + low \(P\)
(d) high \(T\) + high \(P\) (e) high \(T\), but the pressure does not matter

4. Sulfur dioxide and oxygen react reversibly to give sulfur trioxide:

\[
2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)
\]

Exactly 0.80 mol \(\text{SO}_2(g)\) and 0.60 mol \(\text{O}_2(g)\) are mixed in an 1.0 L vessel, and when equilibrium is reached, 0.60 mol \(\text{SO}_3(g)\) are found in the vessel. Calculate \(K_c\) for the reaction.

5. The equilibrium constant for the reaction \(\text{SO}_3(g) + \text{NO}(g) \rightleftharpoons \text{SO}_2(g) + \text{NO}_2(g)\) is 3.0 at 400°C. If 1.0 mole \(\text{SO}_3(g)\) and 1.0 mole \(\text{NO}(g)\) are mixed in a 500 mL flask at 400°C, how many moles of \(\text{SO}_3(g)\) and \(\text{NO}(g)\) will there be in the flask at equilibrium?

6. A decomposition of nitrogen pentachloride proceeds according to the following reaction when:

\[
\text{NCl}_3(g) \rightleftharpoons \text{NCl}_2(g) + \text{Cl}_2(g)
\]

At 298 K, equilibrium constant is 1.30 \(\times 10^{-3}\) M. Calculate the concentration of \(\text{Cl}_2(g)\) when:
(a) 2.00 moles of NCl\(_5\)\(_g\) were introduced to 1.00 L container
(b) 0.100 moles of NCl\(_5\)\(_g\) were introduced to 1.00 L container

7. Phosphorus trichloride and chlorine react according to the following equation:

\[
PCL_3(g) + Cl_2(g) \rightleftharpoons PCL_5(g)
\]

At 544 K, \(K_c\) is 1.60. Calculate the concentration of chlorine when 6.00 moles of PCl\(_3\)\(_g\) and 3.00 moles of Cl\(_2\)\(_g\) are added to a 3.00 L container and allow to reach equilibrium. (This question requires you to solve the quadratic equation.)

8. At a certain temperature, the reaction:

\[
CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)
\]

is at equilibrium when \([CO] = [H_2] = 0.900\, M\); and \([CO_2] = [H_2O] = 4.00\, M\).

(a) Calculate \(K_c\).
(b) An additional 1.00 M of CO\(_g\) and H\(_2O\)\(_g\) are added to the container. Calculate the reaction quotient, \(Q_c\).
(c) In which direction will reaction go?

9. Consider the reaction:

\[
2\, N_2O_4(g) + 6\, H_2O(g) \rightleftharpoons 4\, NH_3(g) + 7\, O_2(g)
\]

Starting with 2.20 M N\(_2\)O\(_4\)\(_g\) and 4.20 M H\(_2\)O\(_g\), an analysis at equilibrium gives 1.96 M of O\(_2\)\(_g\). Calculate equilibrium concentrations of all reactants and products.

10. 5.00 moles of NH\(_3\)\(_g\) were introduced into 2.00 L container at 500 K. At equilibrium, 30% of NH\(_3\)\(_g\) has dissociated according to the equation:

\[
2\, NH_3(g) \rightleftharpoons N_2(g) + 3\, H_2(g)
\]

(a) Calculate the equilibrium concentrations of NH\(_3\)\(_g\), N\(_2\)\(_g\) and H\(_2\)\(_g\).
(b) Calculate \(K_c\) of the reaction at 500 K.

PART C

Photochemical Smog and Ground Level Ozone

1. Hydroxyl radical (OH\(_\cdot\))
   - its importance in the atmosphere; its lifetime, its concentration
   - two characteristic reactions of OH
   - a mechanism of its formation

2. Photochemical smog
   - conditions required for formation of photochemical smog; justify
   - characteristics of chemical smog; explain
   - list main toxic/irritating components of photochemical smog; explain their formation
   - reduction of photochemical smog: emission controls
   - formation of ozone and PAN

PART D

Water (Chapter 10)

1. Given \(k_f\) of water = 1.86°C kg mol\(^{-1}\), calculate the freezing point of the following aqueous solutions:
   (a) 45.0 g sucrose C\(_{12}\)H\(_{22}\)O\(_{11}\) in 100 g water
   (b) 0.100 mol FeCl\(_3\) in 1 kg water
   (c) 0.0200 mol BaCl\(_2\)·2H\(_2\)O dissolved in 52.2 g water

2. How many grams of CaCl\(_2\) should you dissolve in 500 g of water to make a solution that has a freezing point -2.14°C?

3. Calculate the concentration (mol L\(^{-1}\)) of NaCl solution in water at 37°C needed to produce an aqueous solution which is isotonic with that of blood when the osmotic pressure \(\pi = 7.6\) atm.

4. A 50.00 mL sample of water is titrated against 0.01346 mol L\(^{-1}\) EDTA solution to the Eriochrome Black indicator endpoint. It takes 22.65 mL of the EDTA to reach the endpoint. Calculate the hardness of water as expressed in:
   (a) mol L\(^{-1}\) of Ca\(^{2+}\)
   (b) ppm of Ca\(^{2+}\)

ANSWERS

PART A

Chemical Kinetics (II)

1. (a) 74 kJ
   (b) 0.28 L mol\(^{-1}\) s\(^{-1}\)
   (c) \(5.1 \times 10^{-3}\) mol L\(^{-1}\)

2. 48 kJ mol\(^{-1}\)

3. 182 kJ mol\(^{-1}\)

6. intermediates: O(g) and NO\(_2\)\(_g\); catalyst: NO\(_g\)

7. e

8. Mechanism (b) is consistent.

PART B

Gaseous Equilibria

1. \(K_p = 8.11\) atm; \(K_c = 9.88 \times 10^{-3}\) M

2. high pressure, low temperature

3. e

4. b

5. 0.63 moles

6. (a) 5.03 \times 10^{-3} M
   (b) 1.08 \times 10^{-2} M

7. 0.32 M

8. (a) 0.0506
   (b) 0.0324
   (c) Left to Right

9. \([N_2O_4] = 1.64\, M;\ [H_2O] = 2.52\, M;\ [NH_3] = 1.12\, M;\ [O_2] = 1.96\, M)

10. (a) \([NH_3] = 1.75\, M;\ [N_2] = 0.375\, M;\ [H_2] = 1.125\, M\)

   (b) 0.174 M\(^2\)

PART D

Water Hardness

1. (a) \(-2.45°C\)
   (b) \(-0.744°C\)
   (c) \(-2.11°C\)

2. 21.3 g

3. 0.15 mol L\(^{-1}\)

4. (a) 6.097 \times 10^{-3} M
   (b) 244.4 ppm