This set of review questions will include the following four major topics: (1) **chemical kinetics** (Arrhenius equation, Activation Energy, 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***.

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
$$NO_2(g) \rightarrow NO(g) + O(g)$$
is given by the expression: $k = 2.6 \times 10^{12} \exp(-8900/T)$ L mol^{-1} s^{-1}
(a) Calculate the E_a for this reaction.
(b) Calculate the rate constant for the reaction at 298 K.
(c) Calculate the concentration of $NO_2(g)$ after 10 minutes, given that the initial concentration of $NO_2(g)$ was 3.5×10^{-2} mol L^{-1}.

2. A plot of **ln *k*** *versus* **1/T** for the reaction
$$S_2O_8^{2-}(aq) + 3\,I^-(aq) \rightarrow I_3^-(aq) + 2\,SO_4^{2-}(aq)$$
gave a straight line of slope −5758 K. Determine the activation energy for the reaction.

3. For the elementary reaction A + B → C
the activation energy is 30.0 kJ mol^{-1} and the enthalpy change, ΔH°, is −5.0 kJ mol^{-1}. The activation energy for the reverse reaction is:
(a) 25.0 kJ mol^{-1} (b) 35.0 kJ mol^{-1} (c) 30.0 kJ mol^{-1}
(d) 150.0 kJ mol^{-1} (e) 5.0 kJ mol^{-1}

4. A certain reaction has energy of activation 20 kJ and the enthalpy change for the reaction is +8 kJ. When the reaction proceeds with the catalyst, energy of activation is 12 kJ. Sketch the reaction profile with and without a catalyst and indicate energy of activations and enthalpy change for the reaction.

5. One mechanism for ozone destruction is:
$O_3(g) \rightleftharpoons O_2(g) + O(g)$ (rapid equilibrium)
$O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$ (slow)
$NO_2(g) + O(g) \rightarrow NO(g) + O_2(g)$ (fast)
Overall: $2\,O_3(g) \rightarrow 3\,O_2(g)$
Identify the intermediate(s) and the catalyst in this reaction.

6. Refer to the following mechanism consisting of two elementary steps:
(1) A + 2 B → C + D (slow)
(2) D + A → C + E (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: rate = $k\,[A]\,[B]^2$.
(e) If the concentration of B is tripled, the rate of reaction increases 6-fold.

7. The rate law for the reaction $2\,H_2(g) + 2\,NO(g) \rightarrow N_2(g) + 2\,H_2O(g)$ is:
rate = $k_{exp}\,[H_2][NO]^2$
Show which of the following mechanisms is consistent with the experimental rate law. Show your work clearly.
(a) $H_2 + NO \rightarrow H_2O + N$ (slow, k_1)
$N + NO \rightarrow N_2 + O$ (fast, k_2)
$O + H_2 \rightarrow H_2O$ (fast, k_3)

(b) $H_2 + 2\,NO \rightarrow N_2O + H_2O$ (slow, k_1)
$N_2O + H_2 \rightarrow N_2 + H_2O$ (fast, k_2)

8. For the general reaction: 2 A + B → D + E, the following mechanism has been proposed:
A + B → C (fast, k_1)
C → A + B (fast, k_{-1})
C + A → D + E (slow, k_2)
(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 = $k_{exp}\,[A]^2[B]$?

9. The rate law for the decomposition of phosgene $COCl_2(g) \rightarrow CO(g) + Cl_2(g)$ was found to be:

$$\text{rate} = k_{exp}[COCl_2][Cl_2]^{1/2}$$

(a) Show that the following mechanism is consistent with the rate law.
(Use Equilibrium Constant, K, to eliminate concentration of an intermediate.)

$Cl_2(g) \rightleftharpoons 2\,Cl(g)$ (rapid equilibrium, K)
$COCl_2(g) + Cl(g) \rightarrow COCl(g) + Cl_2(g)$ (slow, k_2)
$COCl(g) \rightarrow CO(g) + Cl(g)$ (fast, k_3)

(b) What is k_{exp} equal to when expressed in terms of K and k's?

10. The rate law for the reaction: $2\,H_2(g) + 2\,NO(g) \rightarrow N_2(g) + 2\,H_2O(g)$ is:

$$\text{rate} = k_{exp}[H_2][NO]^2$$

Is the following proposed mechanism consistent with the experimental rate law?
(Use Equilibrium Constant, K, to eliminate concentration of intermediate.)

$2\,NO \rightleftharpoons N_2O_2$ (fast equilibrium, K)
$N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow, k_2)
$N_2O + H_2 \rightarrow N_2 + H_2$ (fast, k_3)

11. For the overall reaction: $2\,O_3(g) \rightarrow 3\,O_2(g)$, the following mechanism has been proposed:

(i) $O_3 \rightarrow O + O_2$ (fast, k_1)
(ii) $O + O_2 \rightarrow O_3$ (fast, k_{-1})
(iii) $O + O_3 \rightarrow 2\,O_2$ (slow, k_2)

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 $K = k_1 / k_{-1}$.)
(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 = $k_{exp}\,[O_3]^2 / [O_2]$, 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:

$MgCl_2(s) + \frac{1}{2}O_2(g) \rightleftharpoons MgO(s) + Cl_2(g)$ $K_p = 2.95\ \text{atm}^{-1/2}$
$MgCl_2(s) + H_2O(g) \rightleftharpoons MgO(s) + 2\,HCl(g)$ $K_p = 8.40$ atm

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

$2\,Cl_2(g) + 2\,H_2O(g) \rightleftharpoons 4\,HCl(g) + O_2(g)$

2. Consider the chemical equilibrium:

$C(s) + 2\,H_2(g) \rightleftharpoons CH_4(g)$ $\Delta H_{rxn} = -75$ 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
(b) decrease in volume
(c) decrease in pressure of $H_2(g)$
(d) increase in pressure of $CH_4(g)$
(e) addition of C(s)
(f) addition of catalyst

What are the optimal conditions to get a high yield of $CH_4(g)$?

3. The decomposition of sulfur trioxide: $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$ is an endothermic reaction. The maximum formation of $SO_2(g)$ and $O_2(g)$ 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:

$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$

Exactly 0.80 mol $SO_2(g)$ and 0.60 mol $O_2(g)$ are mixed in an 1.0 L vessel, and when equilibrium is reached, 0.60 mol $SO_3(g)$ are found in the vessel. Calculate K_c for the reaction.

5. The equilibrium constant for the reaction $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$ is 3.0 at 400°C. If 1.0 mole $SO_2(g)$ and 1.0 mol $NO_2(g)$ are mixed in a 500 mL flask at 400°C, how many moles of $SO_3(g)$ and NO(g) will there be in the flask at equilibrium?

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

$NCl_5(g) \rightleftharpoons NCl_3(g) + Cl_2(g)$

At 298 K, equilibrium constant is 1.30×10^{-3} M. Calculate the concentration of $Cl_2(g)$ 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 $[CO_2] = [H_2] = 0.900$ M; and $[CO] = [H_2O] = 4.00$ 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 $N_2O_4(g)$ and 4.20 M $H_2O(g)$, an analysis at equilibrium gives 1.96 M of $O_2(g)$. Calculate equilibrium concentrations of all reactants and products.

10. 5.00 moles on $NH_3(g)$ 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:)
   - 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 = 1.86ºC 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 $BaCl_2{\cdot}2H_2O$ 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 −2.14ºC?

3. Calculate the concentration (mol L^{-1}) of NaCl solution in water at 37ºC 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) 5.1×10^{-3} mol L^{-1}
2. 48 kJ mol^{-1} 4. b
5. intermediates: O(g) and $NO_2(g)$; catalyst: NO(g) 6. e 7. Mechanism (b) is consistent.

PART B Gaseous Equilibria

1. $K_p = 8.11$ atm; $K_c = 9.88 \times 10^{-2}$ M 2. high pressure, low temperature
3. c 4. 30 M^{-1} 5. 0.63 moles
6. (a) 5.03×10^{-2} M (b) 1.08×10^{-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) −2.45ºC (b) −0.744ºC (c) −2.11ºC 2. 21.3 g
3. 0.15 mol L^{-1} 4. (a) 6.097×10^{-3} M (b) 244.4 ppm