Chemical Kinetics Problem Set 2

(All questions are no-calculator friendly.)

1) Understanding the high temperature formation and breakdown of the nitrogen oxides is essential for controlling the pollutants generated from power plants and cars. The first-order breakdown of dinitrogen monoxide to its elements has rate constants 0.80 at 727°C and 1.20 at 827°C. What is the activation energy of this reaction?
(Answer: about 40 kJ/mol)

2) The following rate constants were obtained for a first order reaction:

T(°C)	0	20	40	60
k(s^{-1})	2.46×10^{-5}	4.75×10^{-4}	5.76×10^{-3}	5.48×10^{-2}

   a) What would you graph to determine the E_a for this reaction? **(Answer: See your class notes)**
   b) The slope for your graph as plotted in part (a) is $= -1.2 \times 10^4$. What are the units associtated with this slope?
   c) Calculate E_a for this reaction. **(Answer: $E_a \cong 1.0 \times 10^2$ kJ/mol)**
   d) What is the half-life of this reaction at 0°C? **(Answer: about 3×10^4 seconds)**

3) Rate constants for the reaction

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

were determined at a series of temperatures. The data are given below,

T(°K)	298	308	318	328	338
k(s^{-1})	3.46×10^{-5}	13.5×10^{-5}	49.8×10^{-5}	150×10^{-5}	487×10^{-5}

Construction of an Arrhenius plot from the above data would give a line with a slope = -1.2×10^4. Determine the energy of activation for the above reaction.
(Answer: 1.0×10^2 kJ/mol)

4) Enzymes in the liver catalyze a large number of reactions that degrade ingested toxic chemicals. By what factor is the rate of a detoxification reaction changed if a liver enzyme lowers the activation energy of the reaction by 5 kJ/mol at 37°C?
(Answer: The catalyzed reaction is about 7 times faster.)

5) Write a rate equation, showing the dependence of rate on reactant concentrations, for each of the following elementary reactions:

a) $CS_2 \xrightarrow{k} CS + S$

b) $CH_3Br + OH^{-1} \xrightarrow{k} CH_3OH + Br^{-1}$

(Answers: (a) Rate = k[CS_2]; (b) Rate = k[CH_3Br][OH^{-1}])

6) The thermal decomposition of nitryl chloride, NO2Cl,

$2NO_2Cl(g) \longrightarrow 2NO_2(g) + Cl_2(g)$

is thought to occur by the following mechanism:

$NO_2Cl \xrightarrow{k_1} NO_2 + Cl$ (slow step)

$NO_2Cl + Cl \xrightarrow{k_2} NO_2 + Cl_2$ (fast step)

What rate law is predicted by this mechanism?

(Answer: Rate = k_1[NO_2Cl])

7) The oxidation of nitric oxide by oxygen

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

may have the following mechanism:

$NO + O_2 \overset{K}{\rightleftharpoons} NO_3$ (fast equilibrium)

$NO_3 + NO \xrightarrow{k} 2NO_2$ (slow step)

Derive the rate law from this mechanism. What will $k_{observed}$ be in terms of the equilibrium constant (K) and the rate constant k?

(Answer: Rate = kK[NO]^2[O_2] where k_{obs} = kK)

8) Nitramide, O_2NNH_2, decomposes slowly in aqueous solution according to the equation

$O_2NNH_2 \longrightarrow N_2O + H_2O$

The experimental rate law is

$$\frac{d[N_2O]}{dt} = k\frac{[O_2NNH_2]}{[H_3O^+]}$$

Which of the following proposed mechanisms is consistent with the experimental rate law?

a) $O_2NNH_2 \longrightarrow N_2O + H_2O$

b) $O_2NNH_2 + H_3O^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2NNH_3^+ + H_2O$ (fast)

$O_2NNH_3^+ \xrightarrow{k_3} N_2O + H_3O^+$ (slow)

c) $O_2NNH_2 + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2NNH^{-1} + H_3O^+$ (fast)

$O_2NNH^{-1} \xrightarrow{k_3} N_2O + OH^{-1}$ (slow)

$H_3O^+ + OH^{-1} \xrightarrow{k_4} 2H_2O$ (fast)

(Answer: Mechanism (c))

9) The catalytic destruction of ozone occurs via a two-step mechanism, where X can be any of several species:

$$X + O_3 \xrightarrow{k_1} XO + O_2 \qquad \text{(slow)}$$

$$XO + O \xrightarrow{k_2} X + O_2 \qquad \text{(fast)}$$

a) Write the overall reaction.
b) Write the rate law for each step.
c) What are the roles of X and XO in the mechanism above?
d) High-flying aircraft release NO into the atmosphere, which catalyzes this process. When the O_3 and NO concentrations are 5.0×10^{12} molecules/cm^3 and 1.0×10^9 molecules/cm^3 respectively, what is the rate of O_3 depletion? The rate constant (k) for the process is 6.0×10^{-15} cm^3/molecule-second.
e) Is the O_3 concentration in part (d) reasonable for this reaction, given that the concentration of stratospheric O_3 never exceeds 10 mg/L?

(Answers:

(a) $\mathbf{O_3 + O \longrightarrow 2O_2}$

(b) For step 1: rate = $\mathbf{k_1[X][O_3]}$

For step 2: rate = $\mathbf{k_2[XO][O]}$

(c) X is a catalyst and XO is an intermediate

(d) 3 x 10$^{\mathbf{7}}$ **molecules/cm**$^{\mathbf{3}}$**-sec**

(e) It is a reasonable value since 10 mg/L = 1.3 x 10$^{\mathbf{17}}$ **molecules/cm**$^{\mathbf{3}}$**)**

10) Acetone is one of the most important solvents in organic chemistry, used to dissolve everything from fats and waxes to airplane glue and nail polish. At high temperatures it decomposes in a first-order process to methane and ketene ($H_2C{=}C{=}O$). At 600°C, the rate constant is 8.7×10^{-3} s^{-1}.

a) What is the half-life of the reaction at 600°C?
b) How much time is required for 75% of a sample of acetone to decompose?
c) How much time is required for 90% of a sample of acetone to decompose?

(Answers:

(a) $\mathbf{t_{1/2} \cong 80}$ **seconds**

(b) about 1.6 x 10$^{\mathbf{2}}$ **seconds**

(c) about 2.5 x 10$^{\mathbf{2}}$ **seconds)**