Chemical Kinetics (no calculator)

(All questions may be completed without the use of a calculator. All answers given were generated without a calculator.)

1) The rate equation for the reaction:

   $2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$

   is second order in NO(g) and first order in H_2(g).

   a) Write an equation for the rate of appearance of N_2(g).
   b) If concentrations are expressed in mol/Liter, what units would the rate constant,k, have?
   c) Write an equation for the rate of disappearance of NO(g). Would k in this equation have the same numerical value as k in the equation of part (a)?

2) For a reaction in which A and B form C, the following data were obtained:

Rate of formation of C (M/s)	[A] (M)	[B] (M)
4.5×10^{-4}	0.30	0.15
18.0×10^{-4}	0.60	0.30
9.0×10^{-4}	0.30	0.30

   a) What is the rate equation for the reaction? **(Answer: Rate = k[A][B])**
   b) What is the numerical value of the rate constant, k? **(Answer: 1×10^{-2} L-mol^{-1}s^{-1})**

3) For a reaction in which A and B form C, the following data were obtained:

Rate of formation of C (M/s)	[A] (M)	[B] (M)
1.8×10^{-5}	0.03	0.03
7.2×10^{-5}	0.06	0.06
16.2×10^{-5}	0.06	0.09

   a) What is the rate equation for the reaction? **(Answer: Rate = k$[B]^2$)**
   b) What is the numerical value of the rate constant, k? **(Answer: 2×10^{-2} L-mol^{-1}s^{-1})**

4) In acidic solution, the breakdown of sucrose into glucose and fructose has the rate law rate = k[H^+][sucrose]. The initial rate of sucrose breakdown is measured in a solution that is 0.010 M H^+, 1.0 M sucrose, 0.10 M fructose, and 0.10 M glucose. How does the rate change if:

a) The concentration of sucrose is changed to 2.5 M?
b) The concentrations of sucrose, fructose, and glucose are all changed to 0.50 M?
c) The concentration of H^+ is changed to 0.00010 M?
d) The concentrations of sucrose and H^+ are both changed to 0.10 M?

(Answers: (a) Rate would be 2.5 times faster.
(b) Rate would be half as fast.
(c) Rate would be 100 times slower.
(d) Rate would be the same.)

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:

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

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

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:

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

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

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 = $k_{obs}[NO]^2[O_2]$ 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 x 10^{12} molecules/cm^3 and 1.0 x 10^9 molecules/cm^3 respectively, what is the rate of O_3 depletion? The rate constant (k) for the process is 6.0 x 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) $O_3 + O \longrightarrow 2O_2$

(b) For step 1: rate = $k_1[X][O_3]$

For step 2: rate = $k_2[XO][O]$

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

(d) 3 x 10^7 molecules/cm^3-sec

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

10) The single-step reaction $NO_2Cl(g) + NO(g) \longrightarrow NO_2(g) + ONCl(g)$ is reversible; $E_{a,forward}$ = 28.9 kJ/mol and $E_{a,reverse}$ = 41.8 kJ/mol. Draw a potential energy diagram for the reaction. Indicate $E_{a,forward}$, $E_{a,reverse}$ and ΔH on the diagram.

(Answer: See your class notes or your textbook for a potential energy diagram.)

11) The reaction: $C_2H_5Cl(g) \longrightarrow C_2H_4(g) + HCl(g)$ is first order in C_2H_5Cl. The rate constant is 1.6 x 10^{-7} sec^{-1} at 600 K and 1.6 x 10^{-6} sec^{-1} at 650 K. Calculate the energy of activation for this reaction.

(Answer: 1.5 x 10^2 kJ/mol)

12) For the reaction: $NO_2Cl(g) + NO(g) \longrightarrow NO_2(g) + ONCl(g)$, the pre-exponential factor A is 1 x 10^{10} and the energy of activation is 40 kJ/mol. The rate equation is first order in NO_2Cl and first order in NO. What is the rate constant, k, at 500 K?

(Answer: 7 x 10^5 M^{-1}s^{-1})

13) What is the energy of activation of a reaction that increases tenfold in rate when the temperature is increased from 300 K to 310 K?
(Answer: 1.8 x 10^2 kJ/mol)

14) 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)

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

T(°C)	0	20	40	60
k(s^{-1})	2.46 x 10^{-5}	4.75 x 10^{-4}	5.76 x 10^{-3}	5.48 x 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 x 10^4. What are the units associated with this slope?
c) Calculate E_a for this reaction. **(Answer: E_a ≅ 1.0 x 10^2 kJ/mol)**
d) What is the half-life of this reaction at 0°C? **(Answer: about 3 x 10^4 seconds)**

16) Rate constants for the reaction

$N_2O_5(g) \longrightarrow 2NO_2(g) + ½O_2(g)$

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

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

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

17) 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.)

18) In the study of a first order kinetics reaction for the decomposition of A to form products the following data were obtained:

[A] (M)	1.00	0.80	0.60	0.35	0.15
Time (s)	0	110	255	525	950

a) What must you graph in order to show that this reaction follows first order kinetics? **(Answer: See your class notes)**
b) If a suitable plot is made using the above data and a straight line with slope = -2.0×10^{-3} is obtained, what is k for this reaction and its units? **(Answer: See your class notes)**
c) What is the half-life of this reaction at the same temperature? **(Answer: $t_{1/2} = 3.5 \times 10^{2}$ s)**

19) In the study of a second order kinetics reaction for the decomposition of A to form products the following data were obtained:

[A] (M)	0.50	0.40	0.30	0.20	0.10
Time (min)	0	50	130	300	800

a) What must you graph in order to show that this reaction follows second-order kinetics? **(Answer: See your class notes)**
b) If a suitable plot using the above data was made, and a straight line with slope = 1.0×10^{-2} obtained, what is k for this reaction and its units? **(Answer: See your class notes)**
c) How long does it take for [A] to reach half of its original concentration of 0.50 M? **(Answer: $t_{1/2} = 2.0 \times 10^{2}$ minutes)**
d) Would it take the same amount of time for [A] to subsequently decrease by another half? EXPLAIN. **(Answer: No, the half-life would be different since it is a second order reaction. The half-life for it to decrease [A] to 0.25 M would be twice the value calculated in part (c).)**

20) For the simple decomposition reaction

$$AB(g) \longrightarrow A(g) + B(g)$$

the rate law is rate = $k[AB]^2$, and k = 0.2 L/mol-s. How long will it take for [AB] to reach 1/3 of its initial concentration of 1.50 M?
(Answer: 20/3 seconds ≅ 7 seconds)

18) 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 $8.7 \times 10^{-3}\ s^{-1}$.

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) $t_{1/2} \cong$ 80 seconds
(b) about 1.6×10^2 seconds
(c) about 2.5×10^2 seconds)