CHEM 1423
Chapter 16
Homework Questions

TEXTBOOK HOMEWORK

16.15 Express the rate of reaction in terms of the change in concentration of each of the reactants and products.

2 D(g) + 3 E(g) + F(g) → 2 G(g) + H(g)

When [D] is decreasing at 0.1 M/s, how fast is [H] increasing?

16.27 For the reaction: A(g) + B(g) + C(g) → D(g), the following data were obtained at constant temperature.

Expt	Initial Rate (mol/L·s)	Initial [A] (mol/L)	Initial [B] (mol/L)	Initial [C] (mol/L)
1	6.25×10^{-3}	0.0500	0.0500	0.0100
2	1.25×10^{-2}	0.1000	0.0500	0.0100
3	5.00×10^{-2}	0.1000	0.1000	0.0100
4	6.25×10^{-3}	0.0500	0.0500	0.0200

(a) What is the order with respect to each reactant?

(b) Calculate k (using the data from Expt. 1).

16.31 For the simple decomposition reaction AB(g) → A(g) + B(g)
rate = $k[AB]^2$ and k = 0.2 L/mol-s. How long will it take for [AB] to reach one-third of its initial concentration of 1.50 M?

16.32 For the reaction in Problem 16.31, what is [AB] after 10.0 s?

16.47 The rate constant of a reaction is $4.7\text{x}10^{-3}$ s^{-1} at 25 °C, and the activation energy is 33.6 kJ/mol. What is k at 75 °C?

16.48 The rate constant of a reaction is 4.50×10^{-5} L/mol-s at 195 °C and 3.20×10^{-3} L/mol-s at 258 °C. What is the activation energy of the reaction?
Added: What is the pre-exponential factor, A?

16.50 For the reaction $A_2 + B_2 \rightarrow 2\ AB$, E_a(fwd) = 125 kJ/mol and E_a(rev) = 85 kJ/mol. Assuming the reaction occurs in one step,

(a) draw a reaction energy diagram;

(b) calculate ΔH^o_{rxn}

16.52 Aqua regia, a mixture of HCl and HNO3, has been used since alchemical times to dissolve many metals, including gold. Its orange color is due to the presence of nitrosyl chloride. Consider this one-step reaction for the formation of this compound:

$$NO(g) + Cl_2(g) \rightarrow NOCl(g) + Cl(g) \qquad \Delta H^o = 83 \text{ kJ}$$

(a) Draw a reaction energy diagram, given E_a(fwd) is 86 kJ/mol.

(b) Calculate E_a(rev).

16.60 A proposed mechanism for the gas-phase reaction between chlorine and nitrogen dioxide is

(1) $Cl_2(g) + NO_2(g) \rightarrow Cl(g) + NO_2Cl(g)$ (slow)
(2) $Cl(g) + NO_2(g) \rightarrow NO_2Cl(g)$ (fast)

(a) What is the overall equation?
(b) Identify the reaction intermediate(s), if any.
(c) What are the molecularity and the rate law for each step?
(d) Is the mechanism consistent with the actual rate law: rate = $k[Cl_2][NO_2]$?

16.72 In acidic solution, the breakdown of sucrose into glucose and fructose has this rate law: rate = $k[H^+][\text{sucrose}]$. The initial rate of sucrose breakdown is measured in a solution that is 0.01 M H^+, 1.0 M sucrose, 0.1 M fructose, and 0.1 M glucose. How does the rate change if

(a) [Sucrose] is changed to 2.5 M?

(b) [Sucrose], [fructose], and [glucose] are all changed to 0.5 M?

(c) $[H^+]$ is changed to 0.0001 M?

(d) [Sucrose] and $[H^+]$ are both changed to 0.1 M?

16.75 A biochemist studying breakdown of the insecticide DDT finds that it decomposes by a first-order reaction with a half-life of 12 yr. How long does it take DDT in a soil sample to decompose from 275 ppbm to 10. ppbm (parts per billion by mass)?

SUPPLEMENTARY HOMEWORK

S1. In a reaction that is second-order with respect to reactant A and second-order with respect to reactant B, the rate of the reaction

a. doubles with a doubling of the concentration of either reactant

b. doubles with a doubling of the concentration of B

c. is quadrupled by a doubling of the concentration of B while the concentration of A is held constant

d. is quadrupled by doubling the concentrations of both A and B

e. is increased by a factor of 27 by tripling the concentrations of both A and B

S2. The rate of the chemical reaction involving two substances, A and B, is measured. It is found that if the initial concentration of A used is doubled, keeping the B concentration the same, the rate doubles. If the concentrations of both A and B are doubled, the rate is eight times that measured in the first experiment. The rate law for this reaction is rate =

a. k[A][B].

b. $k[A]^2[B]$.

c. $k[A][B]^2$.

d. 2k[A][B].

e. k[A][B]/2.

S3. A reaction displays zero-order kinetics for its single reactant. It therefore follows that a plot of _____ versus time is linear, and that the slope of this plot = _____.

a. [reactant]; -k

b. [reactant]; k

c. 1/[reactant]; -k

d. 1/[reactant]; k

e. ln[reactant]; -k

S4. The rate law for a given reaction is rate = $k[\text{reactant}]^2$, with $k = 2.64 \times 10^{-4}$ M^{-1} min^{-1}. If the initial concentration is 0.0250 M, what is the initial rate, with the correct units?

Use of the Integrated Rate Law

S5. Consider the second order decomposition of $N_2O(g)$ to $N_2(g) + O_2(g)$, with an initial concentration of 0.60 M:

$2\ N_2O(g) \rightarrow 2\ N_2(g) + O_2(g)$ Rate = $k[N_2O]^2$

a. When the initial concentration of N_2O is 0.60 M, the half-life is 1420 s. Calculate the rate constant, k, for this reaction (give Units).

b. Calculate the concentration of N_2O 2100 s after the start of the reaction?

c. Calculate the amount of time for the concentration of N_2O to decrease from its initial value (0.60 M) to 0.45 M.

S6. Consider the first order decomposition of $SO_2Cl_2(g)$ to $SO_2(g)$ and $Cl_2(g)$, with an initial concentration of 0.40 M:

$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$ Rate = $k[SO_2Cl_2]$

a. The half-life for this reaction is 520 min. Calculate the rate constant, k, for this reaction (give Units).

b. Calculate the concentration of SO_2Cl_2 300 min after the start of the reaction?

c. Calculate the amount of time for the concentration of SO_2Cl_2 to decrease from its initial value (0.40 M) to 0.15 M.

S7. The elimination of ethanol (C_2H_5OH) from the blood stream is accomplished by an enzyme (alcohol dehydrogenase) and is zeroth order with respect to the reactant (C_2H_5OH).

$$C_2H_5OH \xrightarrow[Enzyme]{k} C_2H_4O + H_2O \qquad R = k[C_2H_5OH]^0 = k$$

A blood alcohol content of 0.10 % corresponds to a concentration of approximately 20. μM.

a. When the initial ethanol concentration is 20. μM, the half-life for the reaction is 6.5 hr. Calculate the rate constant for this reaction (give Units).

b. Starting with an initial ethanol concentration of 20. μM, what is the concentration 3.0 hr after the start of the reaction?

c. Starting with an initial ethanol concentration of 20. μM how long will it take for the concentration to decrease to 5. μM?

Reaction Mechanisms

S8. For the reaction, $Hg_2^{2+}(aq) + Tl^{3+}(aq) \rightarrow 2\ Hg^{2+}(aq) + Tl^{+}(aq)$,. the accepted reaction mechanism is:

$$Hg_2^{2+} \underset{}{\overset{K}{\rightleftharpoons}} Hg + Hg^{2+} \qquad \text{Fast Pre-Equilibrium}$$

$$Tl^{3+} + Hg \xrightarrow{k_2} Tl^{+} + Hg^{2+} \qquad \text{Slow Rate Determining Step}$$

Develop a rate law for Rate = $\Delta[Tl^+]/\Delta t$, which is consistent with the above mechanism.

Application of the Beer-Lambert Law

S9. The amino acid, Tryptophan (Tryp, M = 204 g/mol) has an intense absorption in the UV spectrum at 290 nm.

(a) A sample of aqueous tryptophan is prepared by dissolving 8.6 mg of the compound in water and diluted to 300 mL. The percent transmission of this sample in a 0.75 cm cell is %T = 25.3%. Calculate the Molar Absorptivity (ε) of tryptophan at 290 nm (in M^{-1} cm^{-1}).

(b) The percent transmission of another tryptophan sample in a 1.5 cm cell is 42.8%. Calculate the concentration of tryptophan in this sample.

(c) Calculate the percent transmission of a 1.5×10^{-4} M aqueous tryptophan sample in a 0.5 cm cell?

S10. Consider a hypothetical Dye molecule which decomposes in basic aqueous solution via second order kinetics (with respect to [Dye]):

$Dye + OH^- \rightarrow \mathrm{Pr}oduct$,

$$Rate = -\frac{d[Dye]}{dt} = k[Dye]^2[OH^-] = k'[Dye]^2 \quad , \quad k' = k[OH^-]$$

The Dye has a visible absorption peak at 540 nm, with Molar Absorptivity: ε = 20,000 M^{-1} cm^{-1}.

When OH^- is added to an aqueous solution of the Dye in a 0.50 cm cell, the following percent transmission data was obtained.

t	**%T**
0 s	25.4%
150 s	54.8%

Use the above data to calculate the effective rate constant, k', for this reaction (in M^{-1} s^{-1}).

Enzyme Catalysis: $v_o = \frac{V_m[S]}{K_M + [S]}$

S11. When a substrate (S) binds strongly to an enzyme (E) to form the complex, ES:

a. V_m is small
b. V_m is large
c. K_M is small
d. K_M is large

S12. (a) What is the relation between v_o and V_m for [S] = ½[K_M]

(b) For what ratio, [S]/K_M, does one find that $v_o = 0.40V_m$

(c) Consider an enzyme catalyzed reaction with V_m = 150 μM, K_M = 35 μM, and [S] = 50 μM, what is the reaction velocity, v_o ?