KINETICS: RATES AND MECHANISMS OF CHEMICAL REACTIONS

Chapter 16 Outline

Text Problems: # 15, 27, 31, 32, 47, 48 (calc. A too), 50(a,b), 52(a,b), 60, 72, 75
+ Supplementary Questions (attached)

Text Sample Problems: The text has a number of excellent sample problems (solved in detail) in each section. I would recommend that you study these problems + the "follow up" problems, which have brief solutions at the end of the chapter.

Sect.	Title and Comments	Required?
1.	Focusing on Reaction Rate	YES
2.	Expressing the Reaction Rate	YES
3.	The Rate Law and its Components	YES
4.	Integrated Rate Laws: Concentration Changes over Time	YES
5.	Theories of Chemical Kinetics	YES
6.	Reaction Mechanisms: The Steps from Reactant to Product	YES
7.	Catalysis: Speeding up a Reaction	YES

Note: We will add a section on **"Spectroscopy in Chemistry"**, in which you'll learn how to apply the Beer-Lambert Law to determine concentrations and rate constants of reactions. This will help you perform the calculations in two laboratory experiments which you will be performing in CHEM 1440.

Note: We will also add an introduction to **"Enzyme Kinetics"**.

Chapter 16

Supplementary Homework Questions

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 N_2O concentration of 0.60 M:

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

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:

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g) \qquad \text{Rate} = k[SO_2Cl_2]$$

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:

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

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

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]):

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

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 ?

Answers to the Supplementary Homework Questions are posted on the course web site.
Questions about these Problems will be answered in Recitation