

CHAPTER 12-Chemical Kinetics

12.1 Reaction Rates- defined as the change in concentration of a reactant or product per unit time

$$\text{rate} = \frac{\Delta[\text{product or reactant}]}{\Delta T}$$

Instantaneous rate- rate at a particular point in time(slope of the tangent line of a graph where rate is plotted [] vs. time

$$\begin{aligned}\text{Slope} &= \frac{\Delta Y}{\Delta X} \\ &= \frac{\Delta[\text{product or reactant}]}{\Delta T}\end{aligned}$$

-reaction rates change with time(due to $\Delta[]$) and is also dependent on the stoichiometry of the reaction.

12.2 Rate Laws: An Introduction

$$\text{rate} = k[\text{reactant}]^n \quad (k = \text{rate constant, } n = \text{order})$$

-**rate law** is an expression which shows how the rate depends solely on the concentrations of the reactants(**different rate law**)

-**integrated rate law** expresses how the concentrations depend on time.

-the use of either one of the two rate laws is dependent on experimental convenience rate laws are important in yielding information about different steps in a reaction thus far,

$$\text{rate} = \frac{-\Delta[\text{reactant}]}{\Delta T} = k[\text{reactant}]^n$$

12.3 Determining the Form of the Rate Law

-to understand a given reaction we must first determine its “form” (or figure out the order and rate constant).

-initial rate is the instantaneous rate of a reaction before the concentration of reactants change significantly.

- sample exercise 12.1



$$\text{Rate} = k[\text{BrO}_3^-]^n[\text{Br}^-]^m[\text{H}^+]^p$$

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{(1.6 \times 10^{-3} \text{ mol/L x S})}{(1.0 \times 10^{-4} \text{ mol/L x S})} = \frac{k(.20 \text{ mol/L})^n(.10 \text{ mol/L})^m(.10^k)}{k(.10 \text{ mol/L})^n(.10 \text{ mol/L})^m(.10^k)}$$

$$2.0 = \frac{((.20 \text{ mol/L}))^n}{((.10 \text{ mol/L}))^n}$$

$$\frac{\text{Rate 3}}{\text{Rate 2}} = \frac{3.2 \times 10^{-3}}{1.6 \times 10^{-3}} = \frac{((.20))^m}{((.10))^m}$$

$$2.0 = (2.0)^m \rightarrow m = 1$$

$$\frac{\text{Rate 4}}{\text{Rate 1}} = \frac{3.2 \times 10^{-3}}{8.0 \times 10^{-4}} = \frac{((.20))^p}{((.10))^p}$$

$$4.0 = (2.0)^p \rightarrow p = 2$$

so, rate = $k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$

$$8.0 \times 10^{-4} = k(.10)(.10)(.10)^2$$

$$8.0 \times 10^{-4} \text{ mol/L x S} = k$$

$$1.0 \times 10^{-4} \text{ mol/L} = k$$

$$8.0 \text{ L}^3/\text{mol}^3 \text{ x S} = k$$

12.4 The Integrated Rate Law

1st Order Rate Laws

[A]-conc. at time t

$$\ln[A] = -kt + \ln[A]_0$$

t = time

[A]₀ - conc. at t=0

-a reaction is first order in A if a plot of ln[A] vs. t is a straight line.

*sample ex. 12.2

$$\text{slope } \frac{-\Delta y}{\Delta x} = \frac{\Delta \ln[p]}{\Delta t}$$

Half-Life of a First-Order Reaction- the time required for a reactant to reach half its original concentration.

*sample ex. 12.4

A certain first-order reaction has a half-life of 20 minutes.

- Calculate the rate constant for this reaction.
- How much time is required for this reaction to be 75% complete?

a) Solving Equation 12.3 ($t_{1/2} = \frac{.693}{k}$) for k gives

$$k = \frac{.693}{t_{1/2}} = \frac{.693}{20 \text{ min.}} = 3.47 \times 10^{-2} \text{ min}^{-1}$$

b) We use the integrated rate law in the form $\ln\left(\frac{[A]_0}{[A]}\right) = kt$

If the reaction is 75% complete, 75% of the reactant has been consumed, leaving 25% in the original form: $\frac{[A]}{[A]_0} \times 100 = 25$

This means that $\frac{[A]_0}{[A]} = \frac{1}{.25} = 4.0$ Then, $\ln(4.0) = kt = \frac{(3.47 \times 10^{-2})t}{(\text{min})}$

and $t = \frac{\ln(4.0)}{3.47 \times 10^{-2}} = 40 \text{ min.}$
min

Integrated second-order rate law has the form $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$

Integrated rate law for a zero-order reaction is $[A] = -kt + [A]_0$

12.6 Reaction Mechanisms – series of steps that occur in chemical reactions

intermediate- a species that is neither a reactant nor product but formed and consumed in the reaction series

rate determining step- slowest step in a reaction sequence.

Elementary step- a reaction whose rate law can be written based on its molecularity.

Molecularity- # of species that must collide to produce the reaction in a particular step

→ unimolecular step – involves one molecule

→ bimolecular step – involves two molecules

→ termolecular step – involves three molecules

- a series of elementary steps must satisfy two requirements.
 1. The sum of the elementary steps must give the overall balanced equation for the reaction.
 2. The mechanism must agree with the experimentally determined rate law.

12.7 A Model for Chemical Kinetics

Collision Model- reactions occur due to the collision of molecules

Activation Energy- threshold energy(min. energy required to produce a chemical reaction)

Activated complex-transition state(top of energy barrier)

-rate depends on the size of the activation energy of a particular reaction

Factors that effect reaction rates:

1. Concentration (rate laws)

2. **Temperature- effective collisions increase exponentially with temperature.**
3. **Molecular orientations – refers to the orientation of molecules at the point of collision**

12.8 Catalysis

Enzyme- increases the rate of biological reaction

Catalyst- substance that speeds up a reaction without being consumed(creates a lower energy pathway)

Homogenous catalyst- they are in the same phase as the reacting molecules.

**Heterogeneous catalyst- they are in a different phase (usually solid) ex:
hydrogenation of ethene**

-they provide a surface for reactants to bind to , activate, react, and escape.