

Chapter 12

Chemical Kinetics

Introduction:

Thermodynamics, change in enthalpy or entropy considers only the initial and final states.

Kinetics considers what happens between these initial and final states.

Factors Involved:

- 1.) Rate of Reaction, $\Delta[A]/\Delta \text{time}$ (speed of reaction)
 - a.) Temperature
 - b.) Concentration
 - c.) Surface Area
 - d.) Catalysis
- 2.) Collision Theory.
Molecules must collide with proper orientation in order to react.
- 3.) Mechanism
Steps involved to convert reactants into products

Reaction Mechanisms can never be known for certain.

12.1 Reaction Rates

Information about reaction rates can give information about the steps in a chemical process. (i.e what molecules collide, their orientation, sequence.) Rate (tangent of slope) varies with time.

Study of the rate of chemical changes. Change in concentration per unit time. Usually of a reactant as:

$$\text{Rate} = \frac{\Delta[A]}{\Delta T} = \frac{\text{Conc.}t_2 - \text{conc.}t_1}{t_2 - t_1}, [A], \text{ refers to concentration in mol/L}$$

Reaction rates are expressed as positive values with units of mol/Ls

Instantaneous Rate: Value of a rate at a particular time. Slope of the tangent drawn at particular time.

Coefficients:

In $2\text{NO}_{2(g)} \longrightarrow 2\text{NO}_{(g)} + \text{O}_{2(g)}$, NO_2 and NO are lost and formed at the same rate. However, how does the rate of O_2 formed compare to the rate of NO formed? Ans: $\frac{1}{2}$ the rate of NO .

12.2 Rate Laws: An Introduction

Rates are studied at a point where the reverse reaction can be negated, that is how *the rate depends only on the concentration of the reactant(s)*. The reactant as close to time 0 as possible. This is the Differential Rate Law.

$$\text{Rate} = k[\text{NO}_2]^n$$

k = proportionality constant, the rate constant

n = order of the reactant (determined ONLY experimentally). Can be an integer, 0, or a fraction

$2\text{NO}_{2(g)} \longrightarrow 2\text{NO}_{(g)} + \text{O}_{2(g)}$, therefore k constant for NO_2 , $k' = 2x k$ for O_2

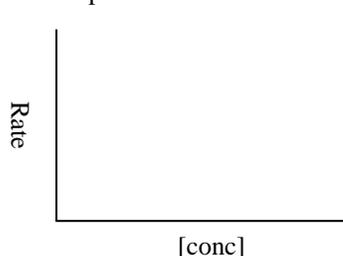
Differential rate Law or Rate Law (an expression that gives the rate as a function of concentration).

$$\text{Rate} = \frac{\Delta \text{mol} / \text{L}}{\Delta t} = k[A]^n [B]^m [C]^p$$

Types of Rate Laws: Once one form is known, the other can be determined.

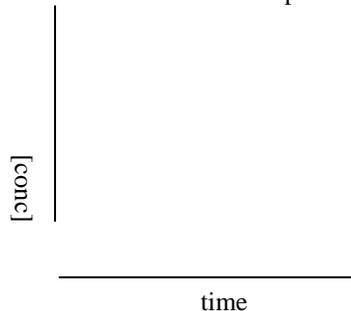
Data Differential Rate Law lends itself to:

Rate depends on concentration



Data of Integrated Rate Law

Concentration depends on time



#19 (Ans. $P_4 = 0.0024 \text{ mol/L} \cdot \text{s} / 4 = 6.0 \times 10^{-4} \text{ mol/L} \cdot \text{s}$, $H_2 = 0.0036 \text{ mol/L} \cdot \text{s}$)

#20. NH_3 is produced $2/3^{\text{rd}}$ rate of disappearance of H_2 .

#21. a.) $\frac{0.500 \text{ mol/L}}{2.16 \times 10^4 \text{ s}} = 2.31 \times 10^{-5} \text{ mol/L s}$ Production of $\text{O}_2 = (1/2 \text{ H}_2\text{O}_2) = 1.16 \times 10^{-5} \text{ mol/L s}$

b.) $\frac{0.500 - 0.250 \text{ mol/L}}{4.32 \times 10^4 - 2.16 \times 10^4 \text{ s}} = 1.16 \times 10^{-5} \text{ mol/L s}$ Production of $\text{O}_2 = (1/2 \text{ H}_2\text{O}_2) = 5.80 \times 10^{-6} \text{ mol/L s}$

#23. a.) mol/L s

b.) mol/L s $\text{Rate} = k[\text{A}]$ or $\frac{\text{mol}}{\text{L s}} = k \left(\frac{\text{mol}}{\text{L}} \right)$ or $\frac{\text{mol L}}{\text{mol L s}} = \frac{1}{\text{s}} = \text{s}^{-1}$

c.) $1/\text{s}$ or s^{-1}

d.) L/mol s

e.) $\text{L}^2/\text{mol}^2 \text{ s}$