35 Elementary Chemical Kinetics

Chemical reactions:
Reactants→Products

Essential treaties:
►Reaction rate and method to determine the reaction rate
►Concept of reaction mechanism in terms of elementary reaction

<u>Elementary reaction</u>

$A + B \rightarrow Product$
Reaction rate

$$Rate = -\frac{dn_A}{dt} = -\frac{dn_B}{dt} = k n_A^1 n_B^1$$

Rate of reaction is proportional the concentration (=Mass action)

Elementary reaction is described by
►Integrated rate law and
►Numerical method (when integration is not possible)

35.1 Introduction to Kinetics

►Transport phenomena: Chemical composition is not changed.
►Thermodynamics:
-Spontaneity determined by $\Delta G<0$
-Equilibrium composition of reactant and
 product determined by K

►Kinetics:
-How fast the reaction proceed?
-Time scale is described.
-Determine the rate of concentration change

(See Figure 1) in terms of temperature, pressure, concentration
→Elucidate the reaction mechanism

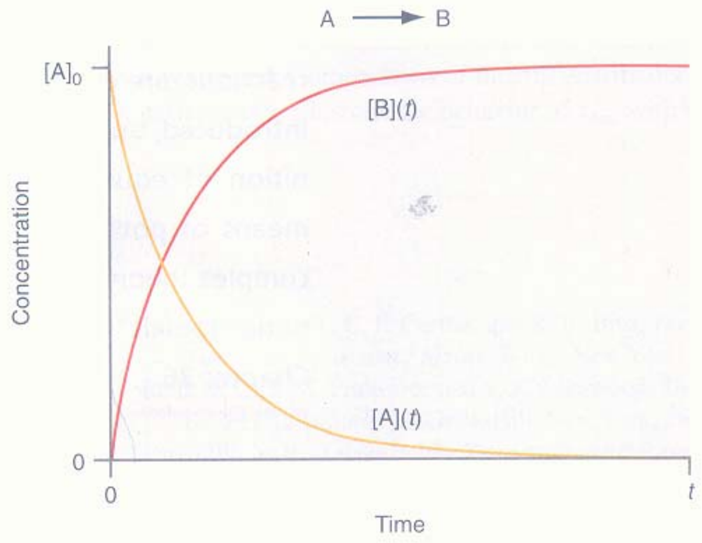

FIGURE 35.1

Concentration as a function of time for the conversion of reactant A into product B. The concentration of A at $t = 0$ is $[A]_0$, and the concentration of B is zero. As the reaction proceeds, the loss of A results in the production of B.

Figure 1

35.2 Reaction rate

$$aA + bB..... \rightarrow cC + dD + ... \qquad (1)$$

A, B....= Chemical species
LHS=Reactants, RHS=Products
a, b.. = Stoichiometric coefficient

Number of moles of a species i at any time is given by:

$$n_i = n_i^o + \nu_i \xi \qquad (2)$$

$n_i = Nmber\, of\, moles\, of\, species\ i\ at\ time\ t$

$n_i^o = Nmber\, of\, moles\, of\, species\ i\ at\ time\ t = 0$

$\xi = Advancement\ of\ reaction\ (Extent\ of\ reaction)$
$\quad = 0\ at\ t = 0$

$\nu_i < 0$ for $reactant$, > 0 for $product$

Change of moles of reactants and products are given by:

$$\frac{dn_i}{dt} = \nu_i \frac{d\xi}{dt} \tag{3}$$

Reaction rate is defined by

$$Rate = \frac{d\xi}{dt} \tag{4}$$

Then the rate of reaction wrt the change of moles of species, i

$$Rate = \frac{1}{\nu_i} \frac{dn_i}{dt} \tag{5}$$

<u>Example</u>

$$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g) \tag{6}$$

$$Rate = -\frac{1}{4}\frac{dn_{NO_2}}{dt} = -\frac{dn_{O_2}}{dt} = \frac{1}{2}\frac{dn_{N_2O_5}}{dt} \tag{7}$$

See the sign convention for reactant and product.

►Rate of conversion of NO_2 is four times of O_2.

►"Rate" is positive, even though the moles of reactant decreases w/ time, according to the sign convention!

►Rate as written is an extensive property since it depends on the system size (More n_{O_2} increases rate).

►Rate becomes intensive property by dividing (5) by the system volume:

$$R = \frac{Rate}{V} = \frac{1}{V}\left(\frac{1}{\nu_i}\frac{dn_i}{dt}\right) = \left(\frac{1}{\nu_i}\frac{d(n_i/V)}{dt}\right) = \frac{1}{\nu_i}\frac{dM_i}{dt} = \frac{1}{\nu_i}\frac{d[i]}{dt} \quad (8)$$

$$M_i = \frac{moles\ of\ i}{\ell\ of\ solution} = Molarity$$

$$(Note\ m_i = \frac{moles\ of\ i}{kg\ of\ solvent} = Molality)$$

NOTE

►R is an intensive property.

►Moles of species i per unit volume = molarity (M=moles/L)

→R has unit of M/t

►Eq (8) is the definition of rate of reaction at constant volume (Solution reaction).

►But it can also be used for gases as EXAMPLE 35.1.

EXAMPLE PROBLEM 35.1

The decomposition of acetaldehyde is given by the following balanced reaction:

$$CH_3COH(g) \rightarrow CH_4(g) + CO(g)$$

Define the rate of reaction with respect to the pressure of the reactant.

Solution

Beginning with Equation (35.2) and focus in on the acetaldehyde reactant, we obtain

$$n_{CH_3COH} = n^o_{CH_3COH} - \xi$$

Using the ideal gas law, the pressure of acetaldehyde is expressed as

$$P_{CH_3COH} = \frac{n_{CH_3COH}}{V}RT = [CH_3COH]RT$$

Therefore, the pressure is related to the concentration by the quantity RT. Substituting this result into Equation (35.8) with $\nu_i = -1$ yields

$$R = \frac{Rate}{V} = +\frac{1}{\nu_{CH_3COH}}\frac{d[CH_3COH]}{dt} = \frac{1}{-1}\frac{d[CH_3COH]}{dt}$$

$$= -\frac{1}{RT}\frac{dP_{CH_3COH}}{dt}$$

35.3 Rate Laws

Rate of reaction=f(T, P, Concentration)

Homogeneous reaction (single phase reaction)

vs heterogeneous reaction (Reactions on catalyst surface)

Rate law=Empirical:

Homogeneous reactions are treated in this chapter:

For the reaction (1) (Irreversible)

$$aA + bB..... \rightarrow cC + dD + ... \qquad (1)$$

$$R = k[A]^{\alpha}[B]^{\beta}..... \qquad (9)$$

$k = Reaction\ rate\ constant = f\ (T)\ but\ independent\ of\ concentration$

$[A], [B]..... = Concentration\, of\, A, B...$

$\alpha = reaction\ \text{order}\ wrt\ A, \quad \beta = Reaction\ \text{order}\ wrt\ B$

$\alpha + \beta..... = \ Overall\ reaction\ \text{order}$

$\alpha, \beta.....Determined\ \text{by experiment}$

$If\ \ \alpha = a\ \text{and}\ \beta = b\ \ \rightarrow\ \ Called\ \ elementary\ reaction$

$If\ \ \alpha \neq a\ \text{and}\ \beta \neq b\ \ \rightarrow\ \ Called\ \ non-elementary\ reaction$

<u>Example</u>

$4NO_2(g) + O_2(g) \rightarrow 2N_2O_2(g)$