Chemistry 102

CHAPTER 14

Chemical Kinetics

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Chapter 13
Chemical Kinetics
Speed of an event: Change in a given period of time

Rate of a reaction: Change in the concentration of a reactant or product in a certain amount of time.

Units of Rate: M/s or mol/L s.

$$2NO_2 \rightarrow 2NO + O_2$$

Average rate of consumption of NO_2 (v_{NO2}):

$$v_{NO2} = \frac{-\Delta[NO_2]}{\Delta t}$$

$$\Delta[NO_2] = [NO_2]_{final} - [NO_2]_{initial}$$

Instantaneous rate of consumption of NO_2 (v_{NO2}):

$$v_{NO2} = \frac{-d[NO_2]}{dt}$$

Average rate of appearance of NO (v_{NO}):

$$v_{NO} = \frac{\Delta[NO_2]}{\Delta t}$$

Instantaneous rate of appearance of NO (v_{NO}):

$$v_{NO} = \frac{d[NO\ ]}{dt}$$

Initial Rate of reaction: the rate of reaction at t = 0

Initial rate ≈ instantaneous rate

Reaction Rate and Stoichiometry:

$$A \rightarrow B$$

$$\frac{-\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

$$v_A = v_B$$

$$A + 2B \rightarrow 3C$$

$$\frac{-d[A]}{dt} = \frac{1}{2}\frac{-d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt}$$

$$v_A = \frac{1}{2}v_B = \frac{1}{3}v_c$$

In general:

$$aA + bB \rightarrow cC + dD$$

$$\frac{1}{a}v_A = \frac{1}{b}v_B = \frac{1}{c}v_C = \frac{1}{d}v_D$$

Example: For the reaction A + 2B → 3C, the rate of consumption of B is 2×10^{-3} M/s. Calculate the rate of production of C.

$$v_A = \frac{1}{2}v_B = \frac{1}{3}v_c$$

$$v_C = \frac{3}{2}v_B$$

$$v_C = \frac{3}{2} \times 2 \times 10^{-3} = 3 \times 10^{-3} \; M/s$$

Factors Affecting Reaction Rate:
    1. Physical states of reactants.
    2. Concentration of Reactants.
    3. The Temperature of the reactants.
    4. The presence of a catalyst.

Concentration of Reactants:
Rule: Reaction rate increases as the concentration of reactants is increased.

$$aA + bB + cC \rightarrow products$$

$$rate = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma} \cdots$$

k : rate constant.
α: order of reaction in reactant A.
β: order of reaction in reactant B.
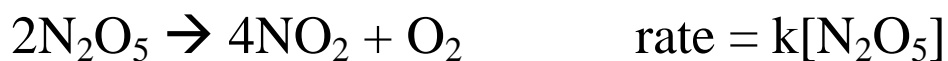γ: order of reaction in reactant C.
$\alpha + \beta + \gamma + \ldots.$= overall order of reaction.

Rule: α, β, γ, .. are empirical constants.
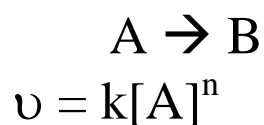
If $\alpha = 0$, the reaction is zero order in A.
If $\alpha = 1$, the reaction is first order in A.
If $\alpha = 2$, the reaction is second order in A.

$2N_2O_5 \rightarrow 4NO_2 + O_2$ rate $= k[N_2O_5]$

$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$ rate $= k[CHCl_3][Cl_2]^{1/2}$

$H_2 + I_2 \rightarrow 2HI$ rate $= k[H_2][I_2]$

Units of Rate Constant:

Rule: Units of Rate Constant depend on the overall order of reaction.

$$A \rightarrow B$$
$$\upsilon = k[A]^n$$

$$k = \frac{\upsilon}{[A]^n} = \frac{M\ s^{-1}}{M^n} = M^{(1-n)}s^{-1}$$

$$k = M^{(1-n)}s^{-1}$$

For first order reaction k $= s^{-1}$.
For second order reaction k $= M^{-1}\ s^{-1}$.
For zero order reaction k $= M\ s^{-1}$.

Determination of Rate Law:
1. Initial Rate Method:

Zero order Reaction: Changing the concentration of reactant has no effect on the rate.

First Order reaction:
$$Rate = k[A]$$
If the concentration is doubled, rate doubles.
If the concentration is tripled, rate will triple.

Second order reactions:
$$Rate = k[A]^2$$
Doubling the concentration, rate increase by a factor of 4
Tripling the concentration, rate increase by a factor of 9

Example: Given the following kinetic, determine the rate law for the reaction A + B → C.

Experiment number	[A] (M)	[B](M)	Initial rate (M/s)
1	0.10	0.10	$1.23\text{x}10^{-3}$
2	0.10	0.20	$2.46\text{x}10^{-3}$
3	0.20	0.10	$4.92\text{x}10^{-3}$

$$rate = k[A]^{\alpha}[B]^{\beta}$$

Order in A: From experiments 1 and 3, Doubling the concentration of A, increases the rate by a factor of 4.

$$\alpha = 2$$

Order in B: From experiments 1 and 2, Doubling the concentration of A, increases the rate by a factor of 2.

$$\beta = 1$$

Calculation of k:

$$rate = k[A]^{2}[B]$$

From experiment 1:

$$1.23\text{x}10^{-3} = k \text{ x } 0.1^{2} \text{ x } 0.1$$

$$k = \frac{1.23 \times 10^{-3}}{0.1^{3}} = 1.23 \, M^{-2}s^{-1}$$

2. Change of Concentration with Time:
A. First order Reactions

$$A \rightarrow B$$

If the reaction is first order in A:

$$\frac{-d[A]}{dt} = k[A]$$

The concentration of A at time = t is given by:

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

or

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

or

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

$$y = a - bx$$

Rule: For 1st order, reaction, plot of $\ln[A]_t$ versus time must be straight line.

B. Second Order Reactions

$$A \rightarrow B$$

If the reaction is first order in A:

$$\frac{-d[A]}{dt} = k[A]^2$$

The concentration of A at time = t is given by:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$y = ax + b$$

Rule: For 2nd order, reaction, plot of $\dfrac{1}{[A]_t}$ versus time must be straight line.

Half-Life of Reactions:
Half-Life of Reactions ($t_{1/2}$): the time needed for the concentration of a reactant to drop to one half of its initial concentration.

$$[A]_{t1/2} = \frac{1}{2}[A]_0$$

1. for 1ˢᵗ order reactions:

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

at $t_{1/2}$, $[A]_{t1/2} = \frac{1}{2}[A]_0$

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln \frac{\frac{1}{2}[A]_0}{[A]_0} = -kt_{1/2}$$

$$\ln 0.5 = -kt_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

3. For 2ⁿᵈ order reactions:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

Example: The reaction A→ B at 500 K is first order with rate constant of 6.8×10^{-4} s^{-1}. if the initial concentration of A is 0.135 M, calculate:

A .The concentration of A after 1420 s.

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

$$\ln[A]_t = \ln 0.135 - 6.8 \times 10^{-4} \times 1420 = -2.97$$

$$[A]_t = e^{-2.97} = 0.051 \, M$$

B. the half-life of the reaction.

For 1st order reactions:

$$t_{1/2} = \frac{\ln 2}{k}$$

$$t_{1/2} = \frac{0.693}{6.8 \times 10^{-4}} = 1019 \, s$$
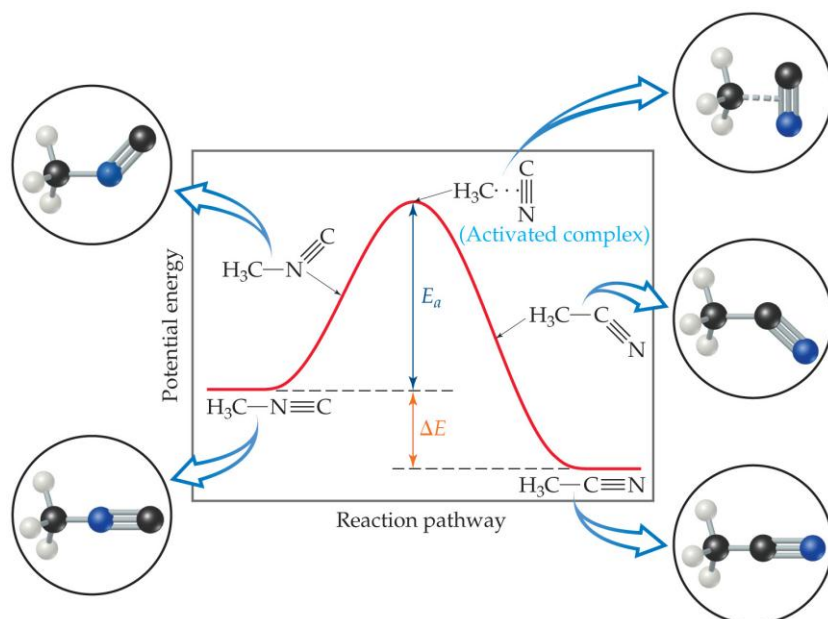
5. **Effect of Temperature:**

Rule: Rates of chemical reaction increases as temperature is increased.

The Collision Theory:
$$A + B \rightarrow C$$
1. Molecules must collide to react.
2. The colliding molecules must have enough energy.
3. Colliding molecules must have a suitable orientation.

The Activation Energy:

$$CH_3 NC \rightarrow CH_3 CN$$

Activation Energy (E_a): the minimum amount of energy reacting molecules must process in order react.

| Reactant | → | Activated complex | → | Products |

Rule: The rate of the reaction decreases as the activation energy increases. The lower the activation energy, the faster the reaction.

The Arrhenius Equation:

$$k = Ae^{\frac{-Ea}{RT}}$$

or

$$\ln k = \ln A - \frac{-Ea}{RT}$$

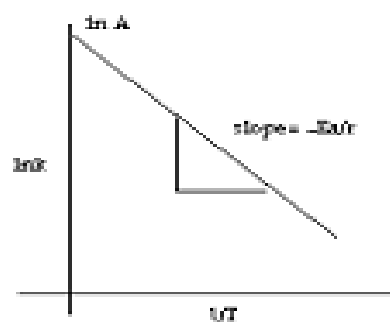Where Ea: the activation energy.

A: the frequency factor.

Determination of Activation Energy:

Method (1)

$$\ln k = \frac{-Ea}{RT} + \ln A$$

$$\ln k = \frac{-Ea}{R}(\frac{1}{T}) + \ln A$$

$$y = \quad -ax \quad + \quad b$$

Methode (2)

$$\ln k_1 = \frac{-Ea}{RT_1} + \ln A$$

$$\ln k_2 = \frac{-Ea}{RT_2} + \ln A$$

Subtract the first equation from the second:

$$\ln k_2 - \ln k_1 = \frac{-Ea}{RT_2} - \frac{-Ea}{RT_1}$$

$$\ln \frac{k_2}{k_1} = \frac{Ea}{R}(\frac{1}{T_1} - \frac{1}{T_2})$$

Example: The rate constant for a reaction is 1×10^{-9} s^{-1} at 320 K and 3×10^{-8} s^{-1} at 340 K. Calculate the activation energy and the frequency factor for this reaction.

1. Calculation of Ea:

$$\ln \frac{k_2}{k_1} = \frac{Ea}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{3 \times 10^8}{1 \times 10^{-9}} = \frac{Ea}{8.314} \left(\frac{1}{320} - \frac{1}{340} \right)$$

$$3.40 = \frac{Ea}{8.314} \times 1.83 \times 10^{-4}$$

$$Ea = \frac{3.40 \times 8.314}{1.83 \times 10^{-4}} = 153775 \, J = 153.8 \, kJ$$

6. Calculation of A

$$\ln k = \frac{-Ea}{RT} + \ln A$$

$$\ln 1 \times 10^{-9} = \frac{-153775}{8.314 \times 320} + \ln A$$

$$-20.7 = -57.8 + \ln A$$

$$\ln A = 57.8 - 20.7 = 37.1$$

$$A = e^{37.1} = 1.3 \times 10^{16} \, s$$