

Akhilesh Kumar Singh

Chemistry department B.Sc (Hons) Part-I

Mob: 8750390927

□ Ostwald Isolation Method

This method is used to find out the order of complex reactions. If n_A , n_B and n_C molecules of substance A, when B and C are in excess, the order of reaction will be n_A .

When A and B are in excess, the order of reaction will be n_C .

When A and C are in excess, the order of reaction will be n_B .

Ex-34 When the initial concentration of a reaction was doubled, its half life become half, what should be the order of the reaction?

Sol. Rate law for product of a reaction is as follows!

$$\text{Rate} = k[A]^n \quad \text{and} \quad \frac{t_{0.5}}{t_{0.5}} = \left[\frac{2a}{a} \right]^{n-1}$$

$$2 = [2]^{n-1}; \quad n-1 = 2$$

$$n = 2$$

20. TEMPERATURE EFFECT:

The rate of reaction is dependent on temperature. This is expressed in terms of temperature coefficient which is a ratio of two rate constants differing by a temperature of 10. Generally the temperatures selected are 298K and 308K. It is mathematically expressed as,

$$\text{Temperature Coefficient} = \frac{\text{Rate Constant at } 308\text{K}}{\text{Rate Constant at } 298\text{K}}$$
$$= \frac{k_{t+10}}{k_t}$$

The value of temperature coefficient for most of the reactions lies between 2 to 3.

ARRHENIUS EQUATION:

Arrhenius derived a mathematical expression to give a quantitative relationship between rate constant and temperature. The expression

is
$$k = A \cdot e^{-E_a/RT}$$

(Here, A = frequency factor; E_a = activation energy, R = gas constant and T = temperature.)

If k_1 and k_2 are rate constants at temperature T_1 and T_2 then

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Ex. 35 Ethylene oxide is decomposed into CH_4 and CO . Rate constant for this reaction may be described by the equation

$$k (\text{s}^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T}$$

- (i) what will be the energy of activation of this reaction?
- (ii) what will be value of k at 670 K ?
- (iii) At what temperature will its half-life period be 25.6 minute?

Sol. (i) We know, $\log_{10} A = \frac{E_a}{2.303 RT}$ ——— (i)

Given, $\log k (\text{s}^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T}$ ——— (ii)

Comparing Eqs. (i) and (ii), we get

$$\frac{E_a}{2.303 R} = 1.25 \cdot 10^4$$

$$(ii) \quad E_a = 1.25 \cdot 10^4 \cdot 2.303 \cdot 8.314 \cdot 10^3$$

$$\therefore E_a = 239.339 \text{ kJ/mol}$$

Substituting the value of $T (670 \text{ K})$ in Eq. (ii),

$$\log k (s^{-1}) = 14.34 - \frac{1.25 \times 10^4}{670} = 4.3167$$

$$1. k = 4.82 \times 10^{-5} s^{-1}$$

$$(ii) k = \frac{0.693}{t_{1/2}} = \frac{0.693}{256 \times 60} = 0.000451 \text{ sec}^{-1}$$

$$\Rightarrow \log 0.000451 \text{ sec}^{-1}$$

$$= 14.34 - \frac{1.25 \times 10^4}{T} \Rightarrow T = 70679 \text{ K}$$