Chemical Kinetics

- Rates of reaction:

Change in concentration of any of the reactants or products in unit time.

- Expression: (for average rate of reaction)

For any reaction $A + B \rightarrow C + D$

The rate of reaction is $-\frac{\Delta A}{\Delta t} = -\frac{\Delta B}{\Delta t} = +\frac{\Delta C}{\Delta t} = +\frac{\Delta D}{\Delta t}$

For a reaction $xA + yB \rightarrow mC + nD$

The rate of reaction is $-\frac{\Delta A}{x\Delta t} = -\frac{\Delta B}{y\Delta t} = +\frac{\Delta C}{m\Delta t} = +\frac{\Delta D}{n\Delta t}$

- Expression: (for instantaneous rate of reaction)

For a reaction $xA + yB \rightarrow mC + nD$

The rate of reaction is $-\frac{dA}{xdt} = -\frac{dB}{ydt} = +\frac{dC}{mdt} = +\frac{dD}{ndt}$

- **Factors affecting the rate of reaction:**

1) Nature of reactants
2) Temperature- with increase in temperature the rate of reaction increases. For every 10 degree raise in temperature the RoR(Rate of reaction) nearly doubles.
3) Concentration- higher is the concentration of reactants higher would be the RoR.
4) Catalyst- the RoR increases in the presence of a catalyst
5) Surface area of reactants- larger the surface area, higher is the RoR

Rate law expressions:

For a reaction $xA + yB \rightarrow mC + nD$

The rate of reaction according to the rate law expression $\propto [C]^a * [D]^b$

$$= K * [C]^a * [D]^b$$

Where:

K= specific rate constant or velocity constant

And a & b need to necessarily be equal to the stoichiometric coefficients m & n.

- Reactions can be classified into 2 types:
    - Simple reactions and
    - Complex reactions

For a reaction $A_2 + B_2 \rightarrow 2AB$

Step-1: $A_2 \rightleftharpoons 2A\ (fast)$

Step-2: $A + B_2 \rightarrow AB + B\ (slow)$

Rate of reaction $\propto [A] * [B_2]$

But $[A] = \sqrt{K * [A_2]}$ (from laws of chemical equilibrium)

Hence rate of reaction is $\propto \sqrt{K * [A_2]} * [B_2]$

Order of a reaction:

If the rate of reaction is $\propto [C]^a * [D]^b$

Then the order of the reaction is **a+b**

Modification of Rate Law Expression:

For a reaction $xA + yB \rightarrow products$

Rate of reaction is $K * [A]^m * [B]^n$

Order of the reaction is m+n

But if one of the reactants, say, B; is taken in large quantity then its concentration is eliminated from the rate law expression (owing to the fact that the reaction will proceed only to that extent to which A is available)

Hence the rate of reaction can be written as $K * [A]^m$ And the NEW Order of the reaction would be= m

Integrated rate equations:

1) Zero order reaction:

$$K = \frac{[R]_0 - [R]}{t}$$

Where

$[R]_0$= concentration of the reactant at the beginning of the reaction

$[R]$= concentration of the reactant at time t

When we plot a graph of [R] vs t, we would get a straight line with slope=-K and intercept=$[R]_0$

2) 1st order reactions:

$$K = \left(\frac{2.303 \log \left(\frac{[R]_0}{[R]} \right)}{t} \right)$$

3) Half life of a reaction:

$$K = \left(\frac{[R]_0}{2} \right)$$

Hence half life of a first order reaction would be:

$$t_{\frac{1}{2}} = \left(\frac{0.693}{K}\right)$$

For an n-th order reaction:

$$t_{\frac{1}{2}} \propto \left(\frac{1}{[R]_0^{n-1}}\right)$$

Where: $[R]_0$ is the initial concentration of the reactant and n is the order of the reaction.

Amount of reactant left after n-th half life periods for a 1st order reaction:

Amount of reactant left=$(initial\ amount)/2^n$

Where: n is the number of half-lives.

Some examples of 1st order reactions are as follows:

- Decomposition of nitrogen pentoxide
- Decomposition of ammonium nitrite
- Decomposition of hydrogen peroxide
- Hydrolysis of ester in acidic medium
- Inversion of cane sugar

DETERMINATION OF ORDER OF REACTION:

- On the basis of units of K
- On the basis of relationship between $t_{\frac{1}{2}}$ and initial concentration of the reactants
- Graphical method
- Initial rate method

Molecular collisions are effective only when the following conditions are satisfied:

- Proper orientation
- Energy= certain minimum energy which is known as the threshold energy or critical energy.

E_a is the activation energy which is the additional energy required by the molecules of reactants, so that their energy becomes equal to threshold energy and they undergo effective molecular collision to give activated complex and then products.

In an EXOTHERMIC REACTION, E_a has a small value, ie, larger number of molecules will cross the energy barrier and the rate of reaction will be higher.

In an ENDOTHERMIC REACTION, E_a has a higher value, ie, lower number of molecules will cross the energy barrier and the rate of reaction will be slower.

ARRHENIUS EQUATION: This relates the effect of temperature to the rate of reaction.

Sample Examples

Temperature coefficient = $\frac{rate\ of\ reaction\ at\ T+10K}{rate\ of\ reaction\ at\ T\ K}$

The value of temperature coefficient is usually 2-3

The effect of change in temperature on the rate of reaction is given by: $K = Ae^{(\frac{-E_a}{RT})}$

Where:

E_a = activation energy

A= frequency factor

K= velocity constant

R= molar gas constant

T= temperature in Kelvin

This implies that $logK = logA - \left(\frac{E_a}{2.303RT}\right)$

- A first order reaction has a rate constant of 1.00 s^{-1}. What is the half life of the reaction?

Solution:

For a first order reaction, and for a **first order reaction only**, the half life is a constant and is proportional to the inverse of the rate constant. By definition, at the time $t = t_{1/2}$, the concentration is equal to exactly one half of what it was when you started, i.e. $[A] = [A]_0$. Thus, the relationship between the half life and the rate constant of a reaction can easiltybe derived for any type of rate law. In this case we have a first order reaction. Remembering the integrated rate law for a first order reaction:

$$[A] = [A]_0 e^{-kt}$$

Then

$[A]/[A]_0 = 1/2 = \exp(- k t_{1/2})$

taking the **ln** of both sides

$\ln(1/2) = - \ln 2 = - k\, t_{1/2}$

or

$t_{1/2} = (\ln 2) / k$

Thus, the halflife of the reaction is (ln 2)/1.00 seconds or

$t_{1/2} = 0.6931$ s

- An elementary reaction, **2 A + C --> D**, is second order in A and first order in C. The rate of this reaction is 2.5×10^{1} M/s when the concentrations of A, C, and D are all 1.00 mM. What is the rate constant for the reaction?

Solution:

The rate law for the reaction is

rate = $k [A]^2[C]$

Since we know the instantaneous rate of the reaction at known concentrations, we can directly evaluate the rate constant

2.5×10^{-1} M/s = $k (1.00 \times 10^{-3} \text{ M})^2 \ (1.00 \times 10^{-3} \text{ M})$

$k = 2.5 \times 10^{8} \text{ M}^{-2}\text{s}^{-1}$

This is the appropriate units of a rate constant for a reaction that is third order overall.