

Kinetic of a reaction.

principle of and technique used to the
kinetics of ordinary reactions:

principle:

The change in some properties of the reactants or products are measured at various intervals of time and from them the rate constant can't be calculated.

i) Volumetry:

principle:

In this technique the change in volume of the reactions or the products is determined.

Kinetics of decomposition of H_2O_2 :

This can be studied by the technique in the presence of platinum black. H_2O_2 decompose into water & oxygen.



The progress of the reaction can be follow in two ways.

1. By cooling the oxygen gas evolved during the decomposition and measuring its volume at definite intervals of time. Let V_t be the volume of oxygen evolved at time $t = V_\infty$. Amount reacted after $t = x = V_t$.

Concentration to the volume at the end of the reaction, then the initial concentration after time $t = (a-x) = V_{\infty} - V_t$

$$k = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_t}$$

2. Equal portion of H_2O_2 are titrated against std. $Kmno_4$ solution at regular intervals. The titre values gives the amount of Hydrogen peroxide which remains undecomposed. This method is more convenient. The experimental results show that the decomposition of H_2O_2 follows first order kinetics.

Calculation:

1. The volume of $Kmno_4$ required by a particular volume of H_2O_2 in the beginning of the experiment V_{∞} , the initial conc of $H_2O_2 = a$.

2. The volume of $Kmno_4$ required by the same volume of H_2O_2 after a time $t = t_x$ the conc of H_2O_2 remaining at the time $t = (a-x)$

The values of a and $(a-x)$ are subs in the first order rate equation.

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)} = \frac{2.303}{t} \log \frac{V_{\infty}}{V_t}$$

The value of k is found to be constant showing that the decomposition of H_2O_2 follows 1st order reaction.

Manometry:

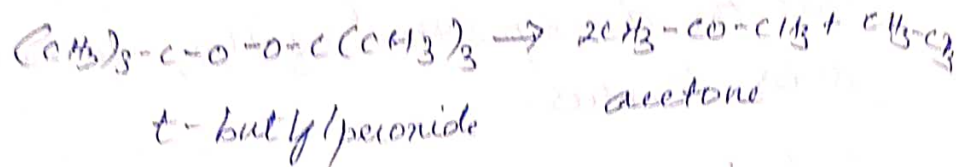
Principle:

Using ~~the~~ a manometer the presence of

of a reaction mixture can be measured at different intervals of time. From the pressure measurement at different intervals of time the rate constant can be calculated. This technique can be applied if both reactants & products are gases.

Experiment:

Tertiary butyl peroxide decompose to give acetone & ethane.



The above reaction is conducted in vapour state. The initial pressure of the reactant is measured as p_0 . One mole of t-butyl peroxide decomposes to give two moles of acetone & one mole of ethane. That is the pressure is increased three times. The final pressure of the product is $3p_0$, that is

$3p_0 - p_0 = 2p_0$. The value of $2p_0$ is directly proportional to the initial concentration of the peroxide.

$$\therefore 2p_0 \propto a$$

The pressure is measured at different intervals of time. If the pressure at time 't' is p_t , then $3p_0 - p_t$ will be directly proportional to the conc.

of peroxide ce.

$$(3p_0 - pt) \propto a - x$$

Subs these values in the first order rate equation - we get.

$$k = \frac{2.303}{t} \log \frac{2p_0}{3p_0 - 2pt}$$

The value of pressure recorded at different time is substituted in the above equation and the value of k is found to be constant. \therefore the above reaction follows the first order kinetics.

Polarimetry:

In measuring optical ~~rotat~~ relation- plane, polarised light travels down a long tube containing the sample. If it is a liquid the sample may be placed in the tube as a pure liquid. Usually the sample is dissolved in a solvent and the resulting solution is placed in the tube.

In summary.

$$[\alpha]_D^t = \frac{\alpha}{c \cdot l}$$

α - Specific rotation.

- * α is the measured optical rotation.
- * c is the sample conc in grams per decilitre ($1 \text{ dl} = 10 \text{ ml}$);
- * That is $c = m/v$ (mass $g = m$, $v = \text{Volume in dl}$);
- * l is the cell length in decimeters ($1 \text{ dm} = 10 \text{ cm} = 100 \text{ mm}$).

* The square brackets meant the optical rotation has been corrected for these variables.

Temperature dependence of reaction rates:

The rate equation & the value of the constants for a reaction are deduced from measurements of the reaction at a fixed temperature. Temperature has a considerable effects on the rate of chemical reaction. The rate of reaction generally increases with rise of temperature.

Temperature Coefficient:

Definition:

It is the ratio of rate const for a reaction at two different temp. separated by 10°C . The two temperature are generally taken as 35°C & 25°C .

Explanation:

Let the rate of a reaction at $t^\circ\text{C}$ be k_t . Let the rate const of the same reaction at $(t+10)^\circ\text{C}$ be k_{t+10} . Then the temperature co-efficient of this reaction will be (k_{t+10}/k_t) .

In most of the homogeneous gases reactions the value of temp. co-efficient lies between 2 & 3. It means that the specific reaction rate becomes 2 double of table for every 10°C rise in temperature.

Arrhenius equation of reaction rates:

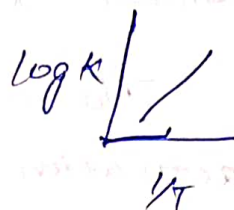
Arrhenius found that the rate or rate constant increases exponentially with temp. It is confirmed by plotting $\log k$ vs $1/T$. This gives a linear graph which shows that.

$$\log k \propto \frac{1}{T}$$

$$k \propto \frac{1}{T} \propto e^{\text{const}/T}$$

(or)

$$k = Ae^{-E_a/RT}$$



where A is a constant called the frequency factor; E' is the activation energy. Converting the equation to logarithmic form we get

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

$$2.303 \log k = 2.303 \log A - \frac{E_a}{RT}$$

$$\log k = \log A - \frac{E_a}{2.303 RT}$$

This equation is called the Arrhenius equation of reaction rates.

Arrhenius parameters & their calculation:

The Arrhenius eqn of reaction rates is constant & two important parameters A & E_a

A = frequency factor

E_a = Energy of activation.

The Activation energy:

The minimum energy necessary to permit a reaction to occur is called the activation energy E_a . This energy is necessary to

transfer the reaction into the activated complex.

All the molecules of a reactant do not take part in the chemical reaction. Only certain part in the number of molecules known as active molecules take part in the reaction, the other molecules are known as passive molecules.

The Arrhenius equation & hence the activation energy can be derived from the Van't Hoff equation. WKT Van't Hoff is close is given by

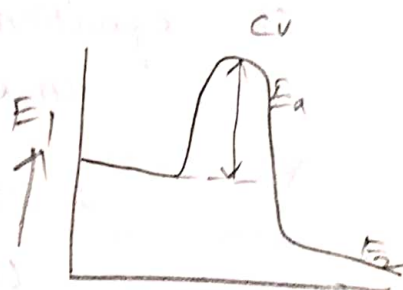
$$\frac{d \log k}{dT} = \frac{\Delta E}{RT^2}$$

$$\frac{d \log k_1/k_2}{dT} = \frac{E_1 - E_2}{RT^2}$$

The equation can be split

$$\frac{d \log k_1}{dT} = \frac{E_1}{RT^2} + C$$

$$\frac{d \log k_2}{dT} = \frac{E_2}{RT^2} + C$$



$E = \text{Energy vs}$

$E_a = \text{Activation energy.}$

$E_2 = \text{Energy of product}$

$E_1 = \text{Energy of reactant}$

$R = \text{Reaction co-ordinate.}$

C is a constant & has been shown to be independent of temp & is equal to zero.

So $\frac{d \log k_1}{dT} = \frac{E_1}{RT^2}$ & $\frac{d \log k_2}{dT} = \frac{E_2}{RT^2}$

In general

$$\frac{d \log k}{dT} = \frac{E}{RT^2}$$

$$d \cdot \log k = \frac{E}{RT^2} dT$$

on integration

$$\int d \log k = \frac{E}{R} \int \frac{1}{T^2} dT$$

$$\log k = \frac{E}{RT} + A$$

where A is constant

$$k = Ae^{-E_a/RT}$$

E - activation energy

R - measured calories

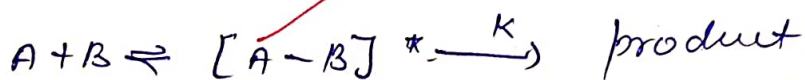
A = constant (frequency factor)

It is also called the collision no. or proportional factor.

Theories of reaction rates:

The ultimate goal of theoretical chemical kinetics is the calculation of the rate of any reaction from a ~~know~~ knowledge of the fundamental properties of the reacting molecules. properties such as the masses, diameter, moment of inertia, vibrational frequencies, binding energies & no. of approaches are given here for this purpose.

Thermodynamic derivation of Arrhenius:



By statistical mechanics

$$k = \frac{RT}{Nh} k^* \quad \text{--- (1)}$$

By T.P

$$\Delta G^\circ = -RT \ln K \quad \text{--- (2)}$$

T - Absolute temp
 n - Avogadro no
 h - plank constant
 R - gas constant

$$\Delta G^\circ = \Delta H^\circ - T\Delta S \quad \text{--- (3)}$$

For std complex:

Equ (3) convert into exponential

$$K = e^{-\Delta G^\circ / RT} \quad \text{--- (4)}$$

sub ΔG° in equ (4)

$$-\Delta H^\circ / RT + \Delta S / R$$

$$K = e$$

For activation complex

$$K^\ddagger = e^{-\Delta H^\ddagger / RT} e^{\Delta S^\ddagger / R} \quad \text{--- (5)}$$

$\therefore \Delta H^\circ =$ heat change
enthalpy
 $S =$ enthalpy
 $\Delta G =$ Gibbs free energy

put equ (5) in (1)

$$K = \frac{RT}{N\eta} e^{-\Delta H^\ddagger / RT} e^{\Delta S^\ddagger / R} \quad \text{--- (6)}$$

Equ (6) rearranges as Arrhenius's equ

$\Delta H^\ddagger =$ activation energy

$$K = \frac{RT}{N\eta} e^{-E_a / RT} e^{\Delta S^\ddagger / R} \quad \text{--- (7)}$$

Arrhenius

$$K = A e^{-E_a / RT} \quad \text{--- (8)}$$

compare equ (7) & (8)

$$A = \frac{RT}{N\eta} e^{\Delta S^\ddagger / R}$$

Completed
24/11/23