fold, for each unit of $Z_1 Z_2$. This has been experi...
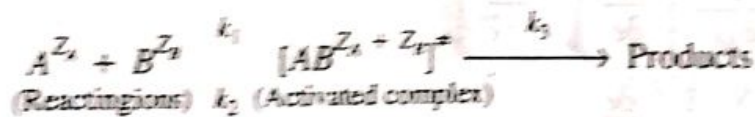
Salt Effects. In ionic reactions, due to electrostatic interactions between the reacting ions, the velocity constants of such reactions are greatly influenced by the charges of reacting ions and also ionic strength of solution. These effects of electrolyte in the ionic reactions are generally known as *salt effects*. The effects of the electrolytes (i.e., salt effects) are of two types :

1. *Primary Salt Effect*
2. *Secondary Salt Effect*

Both are discussed as under :

1. **Primary Salt Effect.** It is defined as the effect of ionic strength on the velocity of ionic reaction. **This effect is involved in non-catalytic reactions.** A very satisfactory and simple treatment of primary salt effect was made by Bjerrum.

Bjerrum postulated that the reacting ions first form an activated complex which is in equilibrium with the reactants. The activated complex subsequently decomposes in yield the products. The activated complex formed at any time has a small concentration. Therefore.

$$A^{Z_A} + B^{Z_B} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [AB^{Z_A + Z_B}]^{\neq} \xrightarrow{k_3} \text{Products}$$

(Reacting ions) (Activated complex)

where
$$Z_A \text{ and } Z_B = \text{Charges on the respective ions}$$
$$(Z_A + Z_B) = \text{Charge on the activated complex}$$
$$k_1, k_2, k_3 = \text{Velocity constants of respective steps}$$

According to law of mass action, the equilibrium constant K^* is given by

$$K^* = \frac{a^*}{a_A \, a_B} \quad \ldots (1)$$

$$K^* = \frac{k_1}{k_2} = \text{the equilibrium constant for the process}$$

$a^* = $ Activity of activated complex

a_A and $a_B = $ Activities of reacting ions A and B respectively

activity = Actual conc. × Activity coefficient

But

$$a = C \cdot \gamma$$

Hence replacing activities in equation (1), we get

$$K^* = \left(\frac{C_{AB}^*}{C_A C_B}\right)\left(\frac{\gamma_{AB}^*}{\gamma_A \gamma_B}\right)$$

$$C_{AB}^* = K^* \left(\frac{\gamma_A \gamma_B}{\gamma_{AB}^*}\right) C_A C_B \quad \ldots (2)$$

Now the rate of formation of products, *i.e.*, rate of reaction is

$$\frac{dC_P}{dt} = k_3 \, C_{AB}^*$$

$$= k_3 K^* \left(\frac{\gamma_A \gamma_B}{\gamma_{AB}^*}\right) C_A C_B$$

$$\frac{dC_P}{dt} = k_o \left(\frac{\gamma_A \gamma_B}{\gamma_{AB}^*}\right) C_A C_B \quad \ldots (3)$$

where

$$k_o = k_3 K^* = \text{Constant}$$

But for a bimolecular reaction between A and B ions, the *experimental rate* of reaction may be expressed as

$$\frac{dC_P}{dt} = k \, C_A \, C_B \quad \ldots (4)$$

where $k = $ Experimentally evaluated rate constant of the reaction

Comparing equations (3) and (4), we have

$$k = k_o \left(\frac{\gamma_A \gamma_B}{\gamma_{AB}^*}\right) \quad \ldots (5)$$

$$\log k = \log k_o + \log \left(\frac{\gamma_A \gamma_B}{\gamma_{AB}^*}\right) \quad \ldots (7)$$

$$\log k = \log k_o + \log \gamma_A + \log \gamma_B - \log \gamma_{AB}^* \quad \ldots (8)$$

Applying Debye-Huckel's relation, the activity coefficient may be expressed in terms of ionic strength μ,

$$\log \gamma = -0.509 \, Z^2 \, \sqrt{\mu} \quad \ldots (9)$$

$Z = $ Charge on the ion

$\mu = $ Ionic strength of the dilute solution

Hence for A, B and AB^x,

$$\log \gamma_A = -0.509\, Z_A^2\, \sqrt{\mu}$$

$$\log \gamma_B = -0.509\, Z_B^2\, \sqrt{\mu}$$

$$\log \gamma_{AB}^x = -0.509\, Z_{AB^x}^2\, \sqrt{\mu}$$

$$= -0.509\, (Z_A + Z_B)^2\, \sqrt{\mu}$$

Combining equations (8), (10), (11) and (12), we get

$$\log k = \log k_o - 0.509\, [Z_A^2 + Z_B^2 - (Z_A + Z_B)^2]\, \sqrt{\mu}$$

$$= \log k_o - 0.509\, [Z_A^2 + Z_B^2 - Z_A^2 - Z_B^2 - 2Z_A Z_B]\, \sqrt{\mu}$$

$$= \log k_o + 2 \times 0.509\, Z_A Z_B\, \sqrt{\mu}$$

$$\boxed{\log k = \log k_o + 1.018\, Z_A Z_B\, \sqrt{\mu}}$$

Equation (12) is known as **Bronsted-Bjerrum Equation.**

Discussion of equation (12). 1. This equation reveals that variation of rate constant with ionic strength (μ) depends upon the charges on the reacting ions.
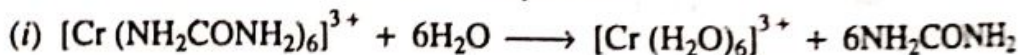
2. The plot of log (k/k_0) versus $\sqrt{\mu}$ would be linear, the slope of the line would be $Z_A Z_B$ and the line passes through the origin. This clear that the slope of the line depends on Z_A, Z_B, *i.e.*, charges of the reacting ions.

3. Three special cases of the equation (12) may arise :

Case 1. When $Z_A . Z_B = 0$, *i.e.*, one of the reactants is uncharged (*i.e.*, non-electrolyte), then equation (12) yields

$$\log k = \log k_o = \text{Constant}$$

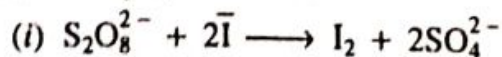*i.e., rate constant is independent of μ.* Examples are,

(i) $[Cr(NH_2CONH_2)_6]^{3+} + 6H_2O \longrightarrow [Cr(H_2O)_6]^{3+} + 6NH_2CONH_2$

(ii) $CH_2ICOOH + CN\bar{S} \longrightarrow CH_2(CNS)COOH + \bar{I}$

In these examples one reacting species is charged whereas the other is neutral so $Z_A Z_B = 0$.

Case 2. When $Z_A Z_B = +\text{ve}$, *i.e.*, Z_A and Z_B are of the same sign, then equation (12) is
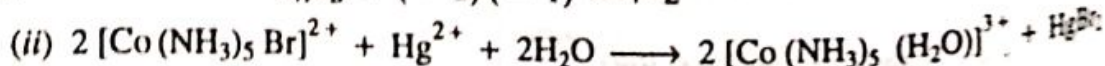
$$\log (k/k_o) = + 1.018\, Z_A Z_B\, \sqrt{\mu}$$

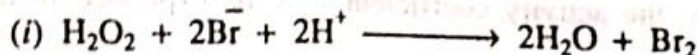*i.e.,* rate constant k would increase with $\sqrt{\mu}$.

For example,

(i) $S_2O_8^{2-} + 2\bar{I} \longrightarrow I_2 + 2SO_4^{2-}$

$\therefore \qquad Z_A Z_B = (-2)(-1) = +2$

(ii) $2[Co(NH_3)_5 Br]^{2+} + Hg^{2+} + 2H_2O \longrightarrow 2[Co(NH_3)_5(H_2O)]^{3+} + HgBr$

$\therefore \qquad Z_A . Z_B = (+2)(+2) = +4$

Case 3. When $Z_A . Z_B = -\text{ve}$, *i.e.*, Z_A and Z_B are of opposite sign, then the rate constant would decrease with $\sqrt{\mu}$. For example,

(i) $H_2O_2 + 2\bar{Br} + 2H^+ \longrightarrow 2H_2O + Br_2$

$\therefore \qquad Z_A . Z_B = (-1)(+1) = -1$

(ii) $[Co(NH_3)_5 Br]^{2+} + O\bar{H} \longrightarrow [Co(NH_3)_5 OH]^{2+} + Br^-$

$\therefore \qquad Z_A . Z_B = (+2)(-1) = -2$

The above predictions have been confirmed from experimental results. In Fig. 4.23, plots of $\log (k/k_o)$ against $\sqrt{\mu}$ are given for reactions of ions with different $Z_A Z_B$ values. The lines, passing through origin, indicate theoretical predictions from equation 12 and dots are the experimental data.
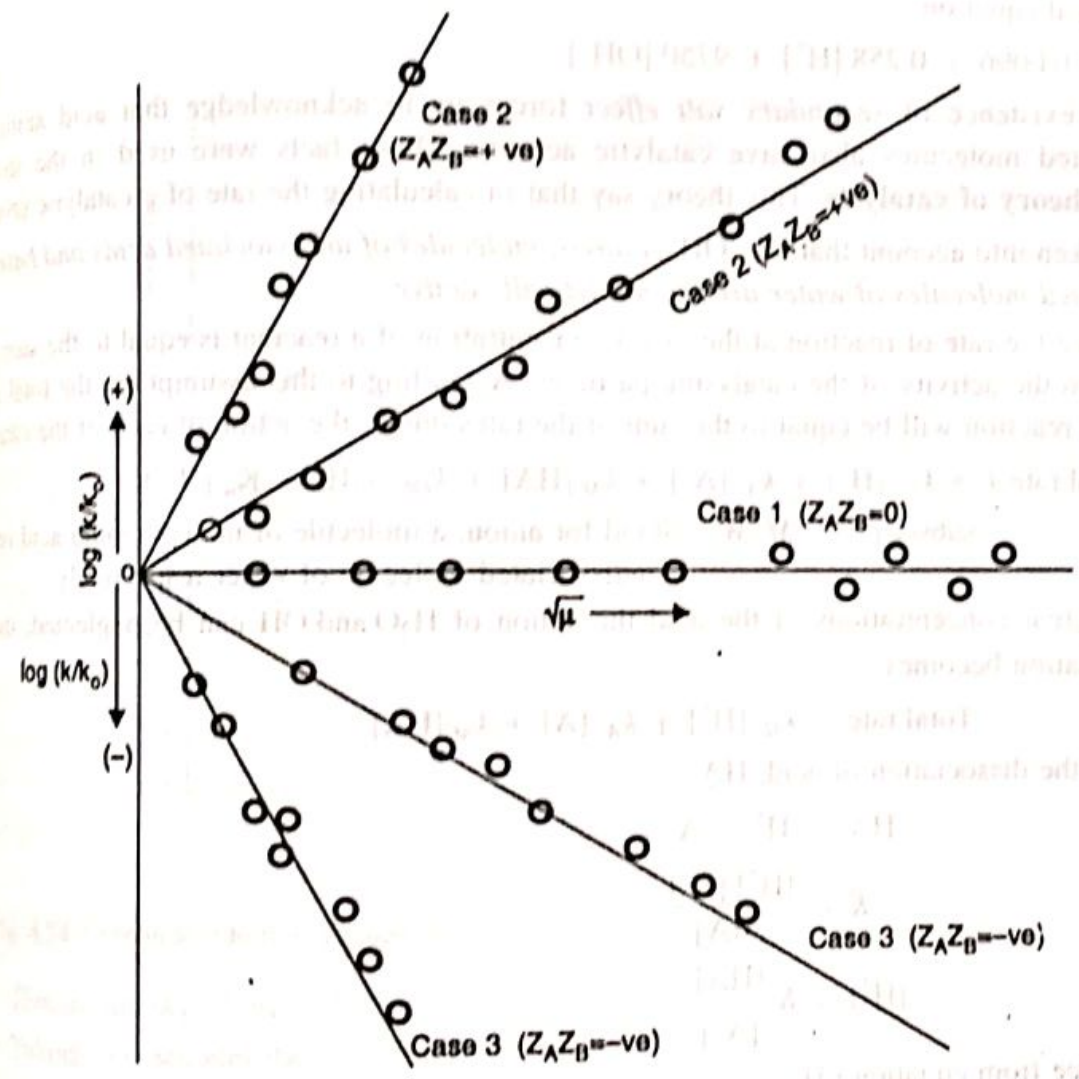

Fig. 4.23. Variation of rate constant with ionic strength.

(ii) Secondary Salt Effect. This salt effect arises when one of the reactants is a weak electrolyte ; the extent of ionization and, hence, the concentration of ions are then affected by the presence of salts. **The secondary salt effect is involved in catalytic reactions.**

Arrhenius discovered that when a salt of the acid catalysing a reaction is added to it, the catalytic effect not only does not decrease, but sometimes even grows. This phenomenon was named the *secondary salt effect*. Since the addition of a salt to a solution of its acid (*i.e.*, both acid and salt have anion in common) increases the concentration of the anion and undissociated acid (due to common-ion effect), the existence of the salt effect indicates that both the undissociated acid and its anions have a catalytic activity. Thus, *the reaction rate indirectly depends upon the amount of salt added in the catalysed reaction. This is called secondary salt effect. In other words, the secondary salt effect refers to the actual change in the concentration of reacting ions by the addition of electrolytes, in the catalysed reactions.*

Arrhenius also established that *the addition of a neutral salt having no common ion with the acid catalysing a reaction also sometimes leads to an increase in the catalytic action of the acid.*

This is the Primary Salt Effect. For example, the rate of inversion of cane sugar in presence acetic acid increases by 30% when 10% (mole) of NaCl is added.

In some cases, a reaction is accelerated catalytically only when an acid and a base simultaneously present in the solution. For example, the mutarotation of glucose. Depending concentration of introduced compounds (acid and base), the rate constant of the reaction the empirical equation

$$k_{mut.} = 0.0096 + 0.258 \, [H^+] + 9750 \, [OH^-]$$

The existence of *secondary salt effect* forces us to acknowledge that acid anions undissociated molecules also have catalytic activity. These facts were used in the so-**dualistic theory of catalysis**. This theory say that in calculating the rate of a catalytic process must be taken into account that H^+, OH^-, *anions, molecules of undissociated acids and bases undissociated molecules of water are all catalytically active.*

Hence the rate of reaction at the given concentration of a reactant is equal to the sum of rates due to the activity of the catalysing particles. According to this assumption, the total rate a catalytic reaction will be equal to the sum of the rates due to the action of each of the catalyst
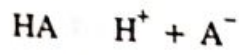
$$\text{Total rate } J = k_{H^+}[H^+] + k_{A^-}[A^-] + k_M[HA] + k_{OH^-}[OH^-] + K_w[H_2O]$$

where   subscripts A, M, W = Stand for anion, a molecule of undissociated acid or
undissociated molecule of water respectively.

At great concentrations of the acid the action of H_2O and OH^- can be neglected, then above equation becomes

$$\text{Total rate} = k_{H^+}[H^+] + k_{A^-}[\overline{A}] + k_M[HA]$$

For the dissociation of acid, HA

$$HA \quad H^+ + A^-$$

$$K = \frac{[H^+][A^-]}{[HA]}$$

$$\therefore \quad [H^+] = K\frac{[HA]}{[A^-]}$$

Hence from equation (3),

$$\therefore \quad \text{Total rate} = k_{H^+} \cdot K\frac{[HA]}{[A^-]} + k_{A^-}[A^-] + k_M[HA]$$

At high concentrations of the salt, the first and the last two terms of equation (2) may neglected. Hence

$$\text{Total rate, } J = k_{A^-}[A^-] + k_M[HA]$$

To take into consideration the action of water, let us introduce the notation

$$J_0 = k_{H^+}[H^+] + k_{OH^-}[OH^-] + k_w[H_2O]$$

Combining equations (2) and (6),

$$J = J_0 + k_{A^-}[A^-] + k_M[HA]$$

If, while measuring the rate, we consecutively dilute the system with water, the ratio

$$\frac{[HA]}{[A^-]} = q$$

will be constant.

Combining equations (7) and (8)

$$J = J_0 + k_{A^-}[A^-] + k_M \cdot q[A^-]$$

$$J = J_0 + (k_A^- + q\,k_M)\,[A^-] \qquad\qquad \dots (9)$$

the plot J vs $[A^-]$ will be a straight line having the slope $(k_A^- + q\,k_M)$, as shown in Fig. 4.24

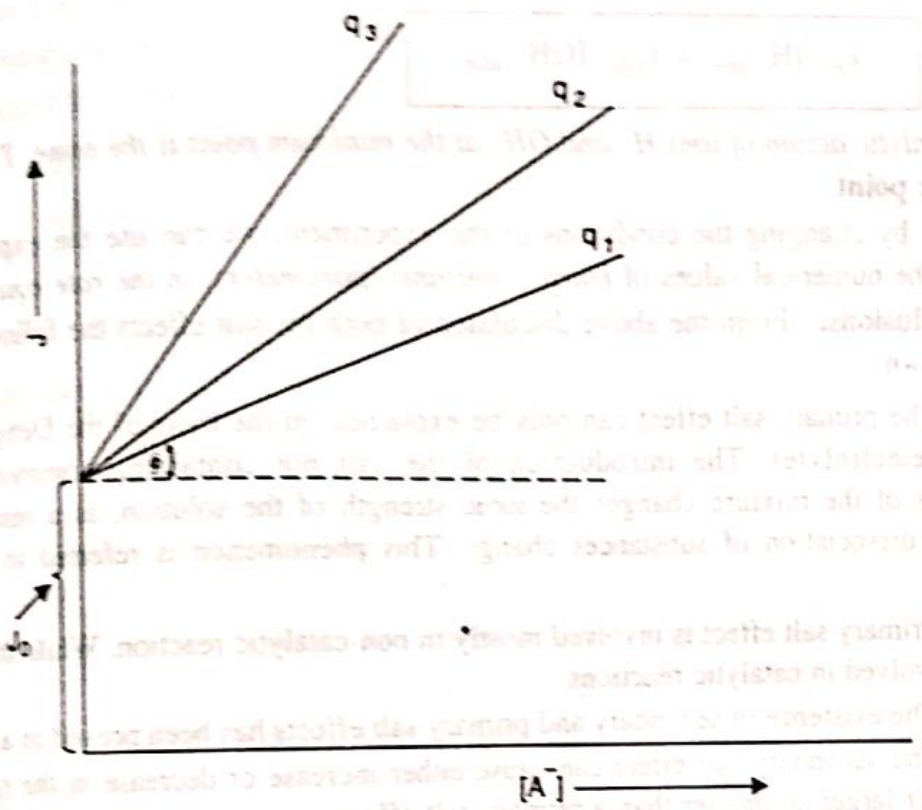Slope $= k_A^- + q\,k_M$

Intercept $= J_0$

Fig 4.24. Graphical solution of equation (9) $\tan\phi = $ slope $= (k_A^- + q_1\,k_M)$. Intercept on J-axis $= J_0$.

Thus J_0 and $(k_A^- + k_M \cdot q)$ are graphically evaluated.

Taking into account the ionic product of water

$$K_w = [H^+]\,[OH^-] \qquad\qquad \dots (10)$$

$$\therefore \quad [OH^-] = \frac{K_w}{[H^+]}$$

Combining equations (6) and (10)

$$J_0 = k_{H^+}\,[H^+] + \frac{k_{OH^-}\,K_w}{[H^+]} + K_w\,[H_2O] \qquad\qquad \dots (11)$$

Differentiating the equation (10) w.r.t. $[H^+]$ and equating of the derivative to zero yield.

$$\frac{dJ_0}{d\,[H^+]} = k_{H^+} - \frac{k_{OH^-}\,K_w}{[H^+]^2} = 0$$

$$\therefore \quad \frac{k_{OH^-}\,K_w}{[H^+]^2} = k_{H^+}$$

Hence

$$k_{OH^-} = \frac{K_{H^+}\,[H^+]^2}{K_w} \qquad\qquad \dots (12)$$

and
$$[H^+] = \left(\frac{k_{OH^-} K_w}{k_{H^+}} \right)^{1/2}$$

Combining equations (11) and (12), we get, the experimentally found minimum rate,
$$J_{0, min} = k_{H^+} [H^+]_{min} + k_{H^+} [H^+]_{min} + k_w [H_2O]$$
Comparing equation (14) with (6), we get

$$k_{H^+} [H^+]_{min} = k_{OH^-} [OH^-]_{min}$$

i.e., the catalytic action of ions H^+ and OH^- at the minimum point is the same. This point is cale **isocatalytic point**.

Thus, by changing the conditions of the experiment, we can use the experimental data determine the numerical values of *kinetic constants (parameters)* in the rate equation.

Conclusions. From the above discussion of both the salt effects the following conclusion may be drawn :

1. The primary salt effect can only be explained on the basis of the Debye-Huckel then of strong electrolytes. The introduction of the salt not containing common ions with t components of the mixture changes the ionic strength of the solution, as a result of which degrees of dissociation of substances change. This phenomenon is referred to as *primary effect*.

2. Primary salt effect is involved mostly in non-catalytic reaction. While the secondary effect is involved in catalytic reactions.

3. The existence of secondary and primary salt effects has been proved in a number of cae

4. The secondary salt effect can cause either increase or decrease in the rate constant a can be either larger or smaller than a primary salt effect.

5. In some instances both the primary and secondary salt effects occur at equal rate so th they cancel each other. Consequently, the rate of reaction remains independent of ionic strength

6. Sometimes these salt effects are so strong enough to even influence the mechanism the reaction.

7. For uncharged reactants (neutral molecules), the rate constant is independent of im strength.

8. For reaction between ions, the variation of rate constant of a reaction with the ic strength (maintained by adding so inert salt *i.e.*, the salt not having any ion common with reacting ions) of the medium is termed as *primary salt kinetic effector primary salt effect*.

(*iv*) **Significance of Primary and Secondary Salt Effects.** The existence of these s effects indicates the necessity for adequate control of ionic strength in a kinetic investigation Either the ionic strength must be kept low so that the effects are small or a series of measurements must be made and extrapolated to zero ionic concentrations. Another method is to add sm quantities of electrolytes in studying any reaction which may involve ions to see what the influe of ionic strength is. Some care must be taken to select substances whose ions may be regarde as acting only because of their charges.

The above discussion indicates that the ionic strength should be carefully controlled in a kinetic experiment. If the salt effects are observed, they must be interpreted with care in terms mechanism because of the many possible sources of these effects.