

Single-Sphere Activated Complex

single-sphere activated complex model.

In the single-sphere activated complex model, the reactant ions are merged into one single sphere when the activated complex is formed and it has a charge equal to the algebraic sum of the charges on the ions.

The schematic single-sphere activated complex is schematically represented in fig. Initially there are two ions (A & B) of charges $z_A e$ & $z_B e$ ^{at infinite distance} respectively. Let the ~~inter~~ ionic radii are r_A & r_B respectively. In the activated complex form total charges are $(z_A + z_B)e$ and radius is r_f .

The rate equation for this case can be obtained derived based on the ~~assu~~ expression obtained by Born for the energy of charging an ion in solution.

At first we are considering the process of charging a conducting sphere of radius 'r' from an initial charge of zero to a final charge equal to ze . Let the process is carried out by transport method from an infinite distance. ~~or~~ If a parameter ' λ ' varies from 0 to z , then small increments of charge equal to $e d\lambda$. At any time the charge on the sphere can be written as λe . If at a given instant the increment of charge is at a distance x from the ion, the force acting on it is

$$df = \frac{\lambda e x e d\lambda}{4\pi\epsilon_0 \epsilon x^2}$$

$$\text{or, } df = \frac{\lambda e^2 d\lambda}{4\pi\epsilon_0 \epsilon x^2} \longrightarrow (14)$$

Therefore, the work done of moving the increment from x to $(x-dx)$ is

$$dw = - \frac{\lambda e^2 d\lambda dx}{4\pi\epsilon_0 \epsilon x^2} \longrightarrow (15)$$

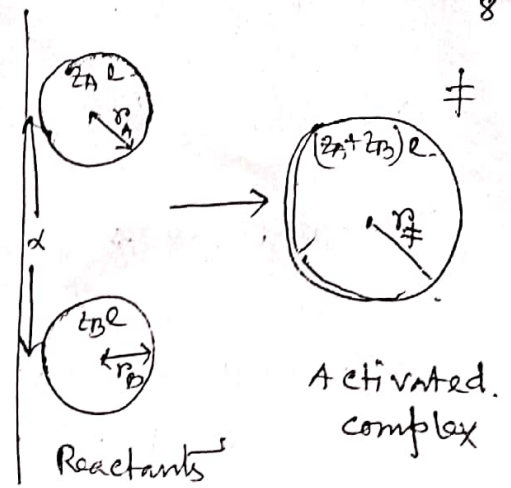
The total work of charging is thus thus.

$$W = \frac{-e^2}{4\pi\epsilon_0 \epsilon} \int_0^z \int_{\infty}^r \frac{\lambda d\lambda dx}{x^2} \longrightarrow (16)$$

$$w = -\frac{e^2}{4\pi\epsilon_0\epsilon} \int_0^z \lambda d\lambda \int_{\infty}^r \frac{dx}{x^2}$$

$$w = \frac{e^2}{4\pi\epsilon_0\epsilon} \cdot \frac{z^2}{2} \cdot \frac{1}{r}$$

$$w = \frac{z^2 e^2}{8\pi\epsilon_0\epsilon r} \longrightarrow (17)$$



This work is the electrostatic contribution to the Gibbs energy of the ion,

$$G_{\text{es}}^0 = \frac{z^2 e^2}{8\pi\epsilon_0\epsilon r} \longrightarrow (18)$$

From the fig, the electrostatic contributions to the Gibbs energies of the reactant ions and the activated complex are

$$G_{\text{es}}^0(A) = \frac{z_A^2 e^2}{8\pi\epsilon_0\epsilon r_A} \quad \left. \vphantom{G_{\text{es}}^0(A)} \right\} \longrightarrow (19)$$

$$G_{\text{es}}^0(B) = \frac{z_B^2 e^2}{8\pi\epsilon_0\epsilon r_B}$$

$$G_{\text{es}}^0(\ddagger) = \frac{(z_A + z_B)^2 e^2}{8\pi\epsilon_0\epsilon r_{\ddagger}} \longrightarrow (20)$$

The change in the electrostatic contribution $\Delta^{\ddagger} G_{\text{es}}^0$ is

$$\Delta^{\ddagger} G_{\text{es}}^0 = \frac{N e^2}{8\pi\epsilon_0\epsilon} \left[\frac{(z_A + z_B)^2}{r_{\ddagger}} - \frac{z_A^2}{r_A} - \frac{z_B^2}{r_B} \right]$$

If the non-electrostatic contribution is $\Delta^{\ddagger} G_{\text{es}}^0$; then rate constant

$$k = \frac{k_B T}{h} e^{-\Delta^{\ddagger} G_{\text{es}}^0 / RT}$$

$$\text{or, } k = \frac{k_B T}{h} e^{-\Delta^{\ddagger} G_{\text{es}}^0 / RT} \exp \left[\frac{N e^2}{8\pi\epsilon_0\epsilon RT} \left\{ \frac{(z_A + z_B)^2}{r_{\ddagger}} - \frac{z_A^2}{r_A} - \frac{z_B^2}{r_B} \right\} \right]$$

Taking natural logarithm on both sides

$$\ln k = \ln \frac{k_B T}{h} - \frac{\Delta^{\ddagger} G_{\text{es}}^0}{RT} - \frac{e^2}{8\pi\epsilon_0\epsilon k_B T} \left[\frac{(z_A + z_B)^2}{r_{\ddagger}} - \frac{z_A^2}{r_A} - \frac{z_B^2}{r_B} \right]$$

$$\text{or, } \ln k = \ln k_0 - \frac{e^{\ddagger}}{8\pi f_0 t k_B T} \left[\frac{(z_A + z_B)^2}{r_{\ddagger}^2} - \frac{z_A^2}{r_A^2} - \frac{z_B^2}{r_B^2} \right] \quad \text{--- (21)}$$

The equations (8) for ^{obtaining} rate constant according to double-sphere activated complex [eqn (8)] and single-sphere activated complex [eqn (9)] are identical if the radii r_A , r_B and r_{\ddagger} are all equal.

Influence of ionic strength

Experimentally it has been observed that the rates of the second order reactions between charged species are affected strongly by the ionic strength of the solution which relates with the concentration of each ion present (C_i) in present in the solution and charge number (Z_i) of each ion as

$$I = \frac{1}{2} \sum_i C_i Z_i^2 \quad \longrightarrow (22)$$

~~When~~ It has been observed that when the reacting species are of the same sign, the rate of the reaction increases with an increase in ionic strength and vice versa. To explain this phenomena the term activity coefficients

~~is~~ has introduced into the rate equations. According to Bronsted the rate of the reaction between two species A & B should be expressed as

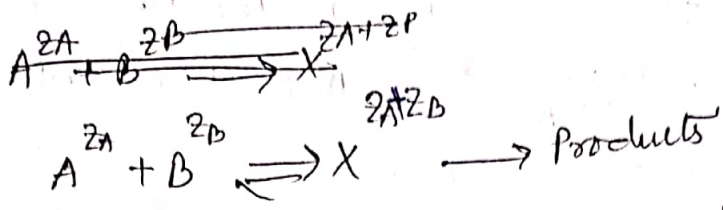
$$v = K_0 [A][B] \frac{Y_A Y_B}{Y_X} \quad \longrightarrow (23)$$

where K_0 is the ~~rate~~ constant at a given temp^o, Y_A & Y_B are the activity co-efficients of the reactants, and Y_X is the that of collision complex formed when A & B come together. The quantity $Y_A Y_B / Y_X$ is known as the kinetic activity factors. Again according to Debye-Hückel theory, the activity co-efficient of ~~an ion~~ Y_i of an ion i , is related to the ionic strength by the equation

$$\log Y_i = -A Z_i^2 \sqrt{I} \quad \longrightarrow (24)$$

where z_i is the charge number of the ion and A is a quantity whose value can be calculated from the Debye-Hückel equations.
 ~~$A \approx 0.51$~~ $A \approx 0.51 \text{ dm}^{-3/2} \text{ mol}^{-1/2}$ for aqueous solution at 25°C .

Now let us consider a reaction proceeds as follows



The second-order rate constant 'k' is

$$k = \frac{v}{[A][B]}$$

$$\text{or, } k = k_0 \frac{y_A y_B}{y_X} \longrightarrow (25)$$

Taking logarithm on both sides.

$$\log k = \log k_0 + \log y_A + \log y_B - \log y_X \longrightarrow (26)$$

$$\text{or, } \log k = \log k_0 - A [z_A^2 + z_B^2 - (z_A + z_B)^2] \sqrt{I} \longrightarrow (27)$$

(using ~~from~~ eqⁿ (24))

$$\text{or, } \log k = \log k_0 + 2Az_A z_B \sqrt{I} \longrightarrow (28)$$

For an aqueous solution at 25°C , eqⁿ (28) becomes

$$\log k = \log k_0 + 1.02 z_A z_B \sqrt{I}$$

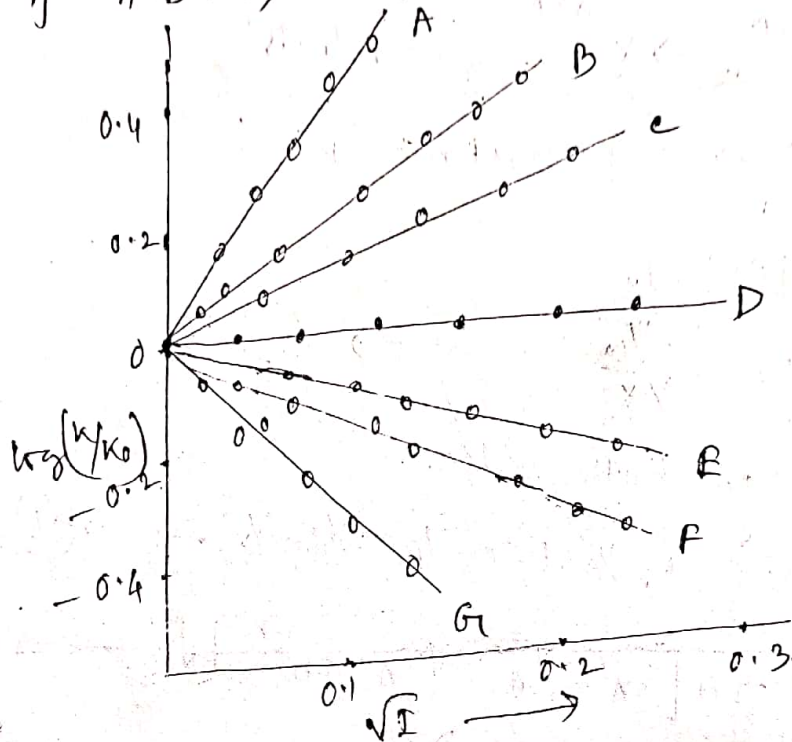
$$\text{or, } \log \frac{k}{k_0} = 1.02 z_A z_B \sqrt{I} \longrightarrow (29)$$

where 'k₀' is the rate constant extrapolated to zero concentration. According to the eqⁿ (29) a plot of log k as a function of \sqrt{I} will give a straight line with slope $1.02 z_A z_B$ and intercept $\log k_0$.

If one of the reactants is a neutral molecule, $z_A z_B = 0$ and

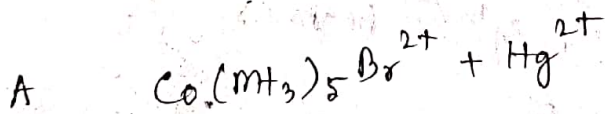
the rate constant should be independent of ionic strength. If $z_A z_B = -ve$, the rate constant decreases with increase in ionic strength. and if $z_A z_B = +ve$, the rate constant increases with the ionic strength.

In the following graph plot of $\log(k/k_0)$ vs \sqrt{I} , the examples of $z_A z_B = 0$, $z_A z_B = -ve$ & $z_A z_B = +ve$ are shown.

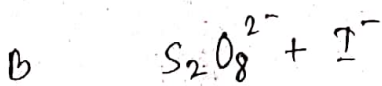


Plots of $\log(k/k_0)$ vs \sqrt{I} .

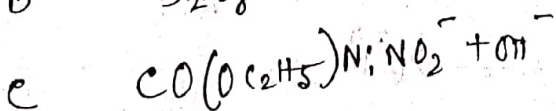
The reactants are



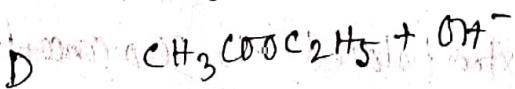
$(z_A z_B = +1)$



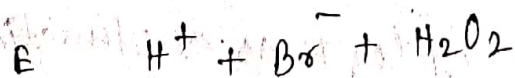
$(z_A z_B = +2)$



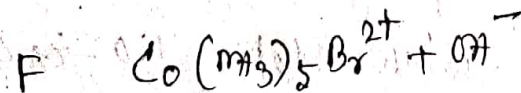
$(z_A z_B = +1)$



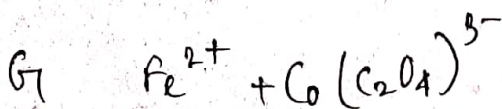
$(z_A z_B = 0)$



$(z_A z_B = -1)$



$(z_A z_B = -2)$



$(z_A z_B = -6)$