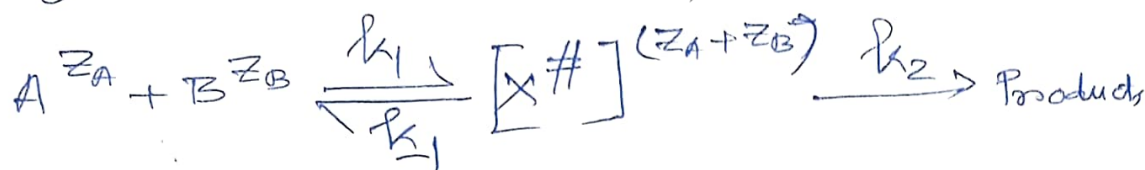


# ① Influence of Ionic Strength on the Rates of Ionic Reactions. The Salt Effects

\* Ionic strength of a solution can considerably affect the rates of reactions. Consider a general reaction involving ions in solution,



where  $Z_A$  and  $Z_B$  are the charges on the reactants A and B and the charge on the activated complex is equal to  ~~$Z_A + Z_B$~~   $Z_A + Z_B$ .

① Rate of reaction is

$$v = k_2 [X^\#] \quad \text{--- ①}$$

The equilibrium between the activated complex and the reactants is

$$K^\# = \frac{a^\#}{a_A a_B} \quad \text{--- ②}$$

Note: an electrolytic solution is much deviated from ideality.

$$\text{Again, } a_i = \frac{c_i \gamma_i}{c_0} \quad \text{--- ③}$$

$\gamma_i$  is called the activity coefficient of the  $i^{\text{th}}$  species and

$c_0$  is the standard concentration (1 mole/L).

Inserting Eq. (3) into Eq. (2), we obtain

$$\begin{aligned} K^\# &= \text{equilibrium constant} \\ &= \frac{a^\#}{a_A a_B} = \frac{\frac{[X^\#] \gamma^\#}{c_0}}{\frac{[A] \gamma_A}{c_0} \frac{[B] \gamma_B}{c_0}} = \frac{c_0 [X^\#] \gamma^\#}{[A] [B] \gamma_A \gamma_B} \quad \text{--- ④} \end{aligned}$$

② from Eq. (4), we get

$$K^\# = \frac{C_0 [X^\#]}{[A][B]} \frac{\gamma^\#}{\gamma_A \gamma_B}$$

$$[X^\#] = K^\# \frac{\gamma_A \gamma_B}{\gamma^\#} \frac{[A][B]}{C_0} \quad \text{--- (5)}$$

Now the rate of the reaction (putting Eq. (5) in Eq. (1))

$$v = k_2 [X^\#]$$

$$= k_2 K^\# \frac{\gamma_A \gamma_B}{\gamma^\#} \frac{[A][B]}{C_0}$$

$$v = k [A][B]$$

where the effective rate constant  $k$  is

$$k = k_2 K^\# \frac{\gamma_A \gamma_B}{\gamma^\# C_0} \quad \text{--- (6)}$$

Note: If the reactants are neutral and concentration is not too high then it can be assumed to be an ideal or ideally dilute solution, i.e.,

$\gamma_A = \gamma_B = \gamma^\# = 1$ , then the rate constant is  $k_0 = \frac{k_2 K^\#}{C_0}$

Now the effective rate constant becomes

$$k = k_0 \frac{\gamma_A \gamma_B}{\gamma^\#} \quad \text{--- (8)}$$

always  
1 mol/L and  
it is a constant

② Now taking logarithm

$$\log_{10} k = \log_{10} k_0 + \log_{10} \gamma_A + \log_{10} \gamma_B - \log_{10} \gamma^{\#} \quad \text{--- (9)}$$

From the Debye-Hückel limiting law, we know that the activity coefficient ( $\gamma_i$ ) of the  $i$ th species having charge  $z_i$  is related to the ionic strength ( $I$ ) of the solution as

$$\log_{10} \gamma_i = -A_0 z_i^2 \sqrt{I} \quad \text{--- (10)}$$

Where  $A_0$  is the Debye-Hückel limiting law constant. At  $25^\circ\text{C}$  and the aqueous solution it is  $0.509 \text{ L}^{1/2} \text{ mol}^{-1/2}$

Therefore, from equations (8) and (9), we get

$$\log_{10} k = \log_{10} k_0 - A_0 z_A^2 \sqrt{I} - A_0 z_B^2 \sqrt{I}$$

$$+ A_0 (z_A + z_B)^2 \sqrt{I}$$

$$\rightarrow \boxed{X^{\#}}^{z_A + z_B}$$

$$= \log_{10} k_0 + A_0 z_A^2 \sqrt{I} - A_0 z_B^2 \sqrt{I}$$

$$+ A_0 z_A^2 \sqrt{I} + A_0 z_B^2 \sqrt{I} + 2 z_A z_B \sqrt{I}$$

$$= \log_{10} k_0 + 2 A_0 z_A z_B \sqrt{I}$$

$$\text{--- (11)}$$



① For an aqueous solution at  $25^\circ\text{C}$  this equation becomes

$$\log_{10} k = \log_{10} k_0 + 1.018 z_A z_B \sqrt{I}$$

→ Brönsted-Bjerrum equation. — (12)

Only the nature of the equation is important.

Remember the equation (11) or (12).

~~If we plot  $\log_{10} k$  vs  $\sqrt{I}$ , we get a straight line with a y-axis intercept equal to  $\log_{10} k_0$  and slope is equal to  $1.018 z_A z_B$ .~~

~~Similar to  $y = mx + c$~~

~~$c = \log_{10} k_0$~~

~~$m = 1.018 z_A z_B$~~

~~$y = \log_{10} k$~~

~~$x = \sqrt{I}$~~

