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,

$$A^{Z_A} + B^{Z_B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [X^{\#}]^{(Z_A+Z_B)} \xrightarrow{k_2} \text{Products}$$

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 $Z_A + Z_B$.

@ 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.

Again, $a_i = \frac{c_i \gamma_i}{c_0}$ ——(3)

γ_i is called the activity coefficient of the i^{th} species and

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

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

$$K^{\#} = \text{equilibrium constant} = \frac{a^{\#}}{a_A a_B} = \frac{\frac{[X^{\#}]}{c_0}\gamma^{\#}}{\frac{[A]}{c_0}\gamma_A \frac{[B]}{c_0}\gamma_B} = \frac{c_0[X^{\#}]\gamma^{\#}}{[A][B]\gamma_A\gamma_B} \quad \text{——} (4)$$

(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))

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

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

→ always 1 mol/L and it is a constant

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

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 $k_0 = \frac{k_2 k^{\#}}{C_0}$ ——— (7)

Now the effective rate constant becomes

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

(3) 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 (γ_i) of the ith 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°C and the aqueous solution it is $0.509\ L^{1/2}\ mol^{-1/2}$

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

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

$[X^{\#}]^{z_A + z_B}$

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

$$= \log_{10} k_0 + 2 A_0 z_A z_B \sqrt{I} \quad \text{——(11)}$$

For an aqueous solution at 25°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 an y-axis intercept equal to $\log_{10} k_0$ and slope is equal to $1.018 Z_A Z_B$.

Similar to $y = mx + c$

$c = \log_{10} k_0$

$m = 1.018 Z_A Z_B$

$y = \log_{10} k$

$x = \sqrt{I}$