

There are some acid or base catalysed reactions which are catalysed by  $H^+$  or  $OH^-$  ions and they are generated from the dissociation of weak acid or weak base.

Addition of salt (or electrolyte) influences the weak acid (or base) dissociation and hence the concentration of  $H^+$  and  $OH^-$ .

Since the rate of reaction depends on concentrations of  $H^+$  and  $OH^-$ , it will be affected by the addition of salt.

This is known as secondary kinetic salt effect.

In examination, write the below one for the derivation

Let us consider a reaction which is catalysed by  $H^+$  produced from a weak acid HA,



The dissociation constant of weak acid HA is

Equilibrium constant  $\leftarrow$   $K_a = \frac{a_{H^+} a_{A^-}}{a_{HA}}$

$$= \frac{\left(\frac{C_{H^+}}{C_0} \gamma_{H^+}\right) \left(\frac{C_{A^-}}{C_0} \gamma_{A^-}\right)}{\left(\frac{C_{HA}}{C_0} \gamma_{HA}\right)}$$

$$= \frac{C_{H^+} C_{A^-}}{C_{HA} C_0} \frac{\gamma_{H^+} \gamma_{A^-}}{\gamma_{HA}}$$

$$a_i = \gamma_i \frac{C_i}{C_0}$$

$$C_0 = 1 \text{ mol/L}$$

Some cases, we write as

$$a_i = \gamma_i C_i$$

$$② \quad C_{H^+} = K_a \left( \frac{C_{HA}}{C_{A^-}} \right) \times C_0 \frac{\gamma_{HA}}{\gamma_{H^+} \gamma_{A^-}}$$

$$= k_{eff} \frac{\gamma_{HA}}{\gamma_{H^+} \gamma_{A^-}} \quad \text{where } k_{eff} = K_a \left( \frac{C_{HA}}{C_{A^-}} \right) C_0$$

$k_{eff}$  is a constant for a given acid salt mixture at a particular temperature.

For a specific  $H^+$  ion catalysed reaction rate constant

$$k = k_{H^+} C_{H^+}$$

$k_{H^+}$  is the catalytic coefficient of  $H^+$

$$k = k_{H^+} k_{eff} \frac{\gamma_{HA}}{\gamma_{H^+} \gamma_{A^-}}$$

$$= k_0 \frac{\gamma_{HA}}{\gamma_{H^+} \gamma_{A^-}} \quad [k_0 = k_{H^+} k_{eff}]$$

$$\log_{10} k = \log_{10} k_0 + \log_{10} \gamma_{HA} - \log_{10} \gamma_{H^+} - \log_{10} \gamma_{A^-}$$

— (1)

Putting Debye-Hückel limiting law

$$\log_{10} \gamma_i = -A_0 z_i^2 \sqrt{I}$$

in the equation (1) we get

$$\log_{10} k = \log_{10} k_0 - A_0 z_{HA}^2 \sqrt{I} + A_0 \sqrt{I} z_{H^+}^2 + A_0 z_{A^-}^2 \sqrt{I}$$

$$\textcircled{3} \quad \log_{10} k = \log_{10} k_0 + A_0 \sqrt{I} + A_0 \sqrt{I}$$

$$= \log_{10} k_0 + 2A_0 \sqrt{I} \quad \text{---} \textcircled{2}$$

$$(A_0 \quad z_{HA} = 0, \quad z_{H^+} = +1, \quad z_{A^-} = -1)$$

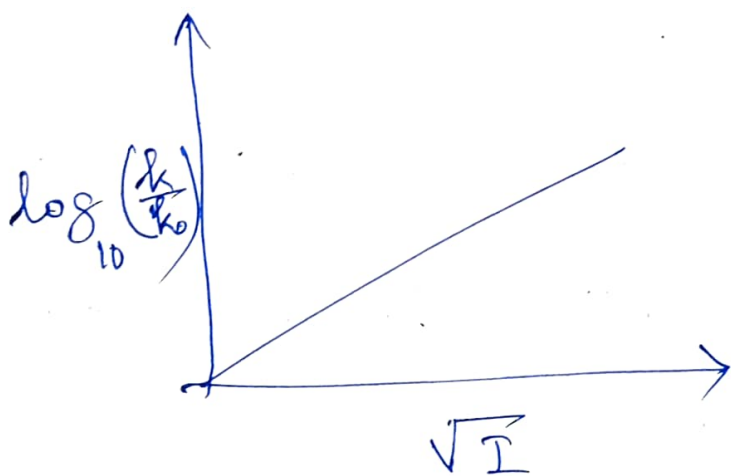
Here  $A_0$  is the Debye-Hückel limiting law constant,

For aqueous solution and at  $25^\circ\text{C}$ ,  
 $A_0 = 0.509 \text{ L}^{1/2} \text{ mol}^{-1/2}$

Hence the equation  $\textcircled{2}$  becomes

$$\log_{10} \left( \frac{k}{k_0} \right) = 1.018 \sqrt{I}$$

Therefore, for a specific acid catalysed reaction, rate of the reaction as well as rate constant increases with increase in ionic strength ( $I$ ) of the solution.



plot of  $\log \left( \frac{k}{k_0} \right)$  vs  $\sqrt{I}$ ,