
INFLUENCE OF
IONIC STRENGTH
Ionic strength

The ionic strength of a solution is measure of electrical intensity due to the presence of ions in the solution.

It is given by "half of sum of all terms of multiplying the molarity of each ion by square of its valency"

$$\text{i.e } I = \tfrac{1}{2}\{m_1Z_1^2 + m_2Z_2^2 + \ldots\}$$

Consider a reaction molecule of A and B

$$A^{zA} + B^{zB} \leftrightarrow [X^{\neq}]^{zA+zB} \rightarrow \text{products}$$

$Z_A + Z_B$ is the ions in complex.

Z_A, Z_B are the charges on the reactants

Rate of the reaction depend on activated complex

$$R = k'[X^{\neq}] \qquad ...1$$

When the reacting species are of the same sign an increase in ionic strength increases the rate, when the ions are of opposite sign react, there is decrease in rate with increasing ionic strength.

- from eqn 2, the second order rate constant
- $k = r/[A][B]$
- $r = k[A][B]$ 3
- equating 2 &3
- $k = k_o \gamma_A \gamma_B / \gamma^*$

- Taking natural log
- $\ln k = \ln \{k_o \gamma_A \gamma_B / \gamma^*\}$ 4
- $\ln k = \ln k_o + \ln \gamma_A + \ln \gamma_B - \ln \gamma^*$ 5
- from DHLL for an electrolyte

$$\ln\gamma_i = -AZ_i^2\sqrt{I} \qquad \text{.....6}$$

where

$A \rightarrow$ constant~0.51 $dm^{-3/2}$

$Z \rightarrow$ charge number of the ion or valency

$I \rightarrow$ ionic strength

Substitute this eqn 6 in 5

$$\ln k = \ln k_o - A Z_A^2 \sqrt{I} -- A Z_B^2 \sqrt{I} + A (Z_A Z_B)^2 \sqrt{I} \quad ....7$$

$$\ln k = \ln k_{O^-} - A\sqrt{I} \{ Z_A^2 + Z_B^2 - (Z_A + Z_B)^2 \}$$

$$\ln k = \ln k_{O^-} - A\sqrt{I} \{ Z_A^2 + Z_B^2 - Z_A^2 - Z_B^2 - 2 Z_A + Z_B \}$$

$$\ln k = \ln k_{O^-} + 2AZ_AZ_B\sqrt{I} \quad .....8$$

at 25°C, the value of A is 0.5100

$$\ln k = \ln k_{O-} + (2 \times 0.51) Z_A Z_B \sqrt{I}$$

$$\ln k = \ln k_{O-} + 1.02\, Z_A Z_B \sqrt{I} \qquad \text{.....9}$$

$$\ln k - \ln k_O = 1.02\, Z_A Z_B \sqrt{I}$$

$$\ln (k/ k_O) = 1.02\, Z_A Z_B \sqrt{I} \qquad \text{.....10}$$

a plotting of results log k/k_o versus $\sqrt{I}$


Tan Q