# Kohlraush's Law

F .W. Kohlraush (1875) determined the values of equivalent conductivity at infinite dilution for a large number of electrolytes and observed that the difference between the equivalent conductivity at infinite dilution of pairs of salts, having either a cation or anion in common, is constant at constant temperature.

For example, the difference between $\lambda_\infty$ at 25°C for K and Na salts having a common anion is always found to be $23.41 omh^{-1} cm^2 equiv^{-1}$ and that for chloride and bromide having a common cation is always $2.06 ohm^{-1} cm^2 equiv^{-1}$. It is clear from the following table:

| Electrolyte | A∞ at $25^0$C | Difference |
|---|---|---|
| NaBr<br><br>NaCl | 128.51<br><br>126.45 | 2.06 |
| KBr<br><br>KCl | 151.92<br><br>149.86 | 2.06 |
| LiBr<br><br>LiCl | 117.09<br><br>115.03 | 2.06 |
| KBr<br><br>NaBr | 151.92<br><br>128.51 | 23.41 |
| KCl<br><br>NaCl | 149.86<br><br>126.45 | 23.41 |
| $KNO_3$<br><br>$NaNO_3$ | 144.66<br><br>121.25 | 23.41 |

From the study of above table, it may be pointed out that at infinite dilution, each ion makes a definite contribution towards the equivalent conductivity of electrolyte, irrespective of the nature of the other ion with which it is associated in solution. This important generalisation, called the law of independent **migration of ions**(also called (**Kohlraush's law**, after the discoverer) is strictly true at infinite dilution only where there is no mutual interaction between the different ions.

It may be stated as:

*"The equivalent conductivity of an electrolyte at infinite dilution is the sum of two values, one depending only on the cation and the other only on the anion".*

Mathematically, $\lambda_\infty = \lambda_a + \lambda_c$

where ka and kc are the ionic mobilities or ionic conductivities of the anion and cation respectively. By the term ionic mobility of an ion we mean*, 'the conductivity of one equivalent of the ion when the solution containing that quantity of the ion is placed between two electrodes 1 cm apart.'*

**Applications:**

(i) In calculating the equivalent conductivity at infinite dilution of weak electrolyte.

(ii) In explaining the independent motion of ions assumed in Arrhenius theory.

(iii) In calculating the absolute velocity of ion.

(iv) In calculating the ionic product of water.

(v) In determining the degree of dissociation of electrolytes.

(vi) In finding out the solubility of sparingly soluble salts.

**Determination of equivalent conductivity of weak electrolytes at infinite dilution, $\lambda_\infty$:**

In the case of weak electrolytes (e.g., $CH_3COOH \text{and} NH_4OH$) specific conductivity measurement method can not be applied to determine the equivalent conductivity at infinite dilution because a limited value of equivalent conductivity is not reached as they go on ionising even at a very high dilution and do not, therefore, dissociate completely. In such cases Kohlraush's law helps a lot in determining $\lambda_\infty$ by an indirect method.

According to this law, $\lambda_\infty = \lambda_a + \lambda_c$

Thus $\lambda_\infty$ for $CH_2COOH = \lambda CH_3COO^- + \lambda H^+$

It can be calculated provided the ionic mobilities for acetate and hydrogen ions are known.

In order to determine equivalent conductivity at infinite dilution for a weak electrolyte, we choose strong electrolytes containing the ions of weak electrolyte and determine their equivalent conductivity at infinite dilution experimentally.

By the application of Kohlraush's law, $\lambda_\infty$ for weak electrolyte is then calculated.

Thus for $CH_3COOH$, following salts may be taken:

$\lambda_\infty$ for $HCl = \lambda H^+ + \lambda Cl^- = a \cdots (1)$

$$\lambda_\infty \text{for} \quad CH_3COONa = \lambda CH_3COO^- + \lambda Na^+ = b \cdots (2)$$
$$\lambda_{infty} \text{for} \quad Nacl = \lambda Na^+ + \lambda Cl^- = C \cdots (3)$$

Adding (1) to (2) and subtracting (3), we get

$$\lambda H^+ + \lambda Cl^- + \lambda CH_3COO^- + \lambda Na^+ - Na^+ - \lambda Cl^- = a + b - c$$

$$or \quad \lambda CH_3COO^- + \lambda H^+ = a + b - c$$

$$or \quad \lambda_\infty \text{for} CH_3COOH = a + b - c$$

Since a, b and c quantities