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Electrochemistry

Electrolytes

The substances which pass electricity through them, either in their aqueous solutions or in their molten form are called electrolytes.

When electrolytes are dissolved in water or melted they get splitted into ions. This phenomenon is called ionization or dissociation. For example,

$$NaCl\ (s) \xrightleftharpoons{\text{Water}} Na^+\ (aq) + Cl^-\ (aq)$$

$$NaCl\ (s) \xrightleftharpoons{\text{Melt}} Na^+ + Cl^-$$

The conduction of electricity through aqueous solutions or molten form of electrolytes is due to flow of ions.

All acids (e.g. HCl, H_2SO_4, HNO_3, CH_3COOH etc.), bases (e.g. NaOH, KOH, NH_4OH, $Ba(OH)_2$ etc.) and salts (e.g. NaCl, KCl, NH_4Cl, K_2SO_4, CH_3COONa etc.) are electrolytes.

Types of Electrolytes

Depending upon the degree of dissociation or ionization, the electrolytes may be of following two types-

(1) Strong electrolytes- Such electrolytes which dissociate almost completely in their aqueous solutions are called strong electrolytes. For example,

(i) All strong acids- e.g. HCl, H_2SO_4, HNO_3, $HClO_4$ etc.

(ii) All strong bases- e.g. NaOH, KOH, $Ba(OH)_2$ etc.

(iii) Salts of strong acids and strong bases- e.g. NaCl, KCl, Na_2SO_4, K_2SO_4, $NaNO_3$, KNO_3 etc.

(iv) Salts of strong acids and weak bases- e.g. NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3, $CuSO_4$ etc.

(v) Salts of weak acids and strong bases- e.g. CH_3COONa, CH_3COOK, Na_2CO_3, K_2CO_3, NaCN, KCN etc.

(2) Weak electrolytes- Such electrolytes which dissociate very feebly or partially in their aqueous solutions are called weak electrolytes. For example,

(i) All weak acids- e.g. CH_3COOH, H_2CO_3, HCN etc.

(ii) All weak bases- e.g. NH_4OH, $Mg(OH)_2$, $Ca(OH)_2$ etc.

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(iii) Salts of weak acids and weak bases- e.g. CH_3COONH_4, $HCOONH_4$, $(NH_4)_2CO_3$, NH_4CN etc.

Degree of dissociation or Degree of ionization (α)

"The fraction of total number of molecules which remains dissociated at equilibrium is called degree of dissociation or degree of ionization of the electrolyte."

Mathematically, degree of dissociation,

$$\alpha = \frac{The\ number\ of\ molecules\ dissociated\ at\ equilibrium}{Total\ number\ of\ molecules}$$

Strong electrolytes (e.g. HCl, H_2SO_4, HNO_3, NaOH, KOH, $Ba(OH)_2$, NaCl, KCl, NH_4Cl, K_2SO_4, CH_3COONa etc.) are almost completely dissociated in their aqueous solutions. Hence, for these electrolytes, the degree of dissociation is almost equal to 1. Thus, for strong electrolytes,

$$\alpha \approx 1$$

On the other hand, weak electrolytes (e.g. CH_3COOH, H_2CO_3, HCN, NH_4OH, CH_3COONH_4, $(NH_4)_2CO_3$, NH_4CN etc.) are very feebly dissociated in their aqueous solutions at equilibrium. Hence, for these electrolytes the number of molecules dissociated at equilibrium is much lesser than total number of molecules and their degree of dissociation is very very less than 1. Thus, for weak electrolytes,

$$\alpha << 1$$

Differences between Metallic and Electrolytic Conductions-

	Metallic Conduction	Electrolytic Conduction
1	It is conduction of electricity through metals like Copper, Silver, Aluminium etc.	It is conduction of electricity through aqueous solution or molten form of electrolytes such as NaCl, KCl, H_2SO_4, K_2SO_4 etc.
2	It occurs due to flow of electrons.	It occurs due to flow of oppositely charged ions.
3	It does not involve mass flow.	It involves mass flow.
4	It does not involve a chemical change.	It involves a chemical change, where ions get discharged on electrodes.
5	It decreases with increase of temperature as resistance of metals increases with rise of temperature.	It increases with increase of temperature as mobility of ions increases with rise of temperature.

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Electrical Conductance

Ohm's Law

According to this law-"The strength of current passing through an electrolytic conductor is directly proportional to the potential difference applied across the two ends of the conductor".

Mathematically,

$$V \alpha I$$

or $$V = IR$$

Where, R is a proportionality constant called resistance of the conductor.

Resistance (R)

The obstructions to the flow of current through a conductor is called the resistance of the conductor.

The resistance of an electrolytic conductor is directly proportional to the length (l) of the conductor and is inversely proportional to the area of cross section (A) of the conductor. Thus,

$$R \alpha \frac{l}{A}$$

or $$R = \rho \frac{l}{A}$$

Where, ρ is a proportionality constant called specific resistance or resistivity of the conductor.

Specific resistance or Resistivity

Experimentally it has been found that, the resistance of an electrolytic conductor is directly proportional to the length (l) of the conductor and is inversely proportional to the area of cross section (A) of the conductor. Thus,

$$R \alpha \frac{l}{A}$$

or $$R = \rho \frac{l}{A}$$

Where, ρ is a proportionality constant called specific resistance or resistivity of the conductor. It depends upon the nature of the conductor.

If $l = 1$ cm

$A = 1$ cm^2

Then, $R = \rho$

Thus, "The resistance of an electrolytic solution present between two electrodes at 1 cm apart and having area of cross section 1cm^2 is called the specific resistance or resistivity of the conductor."

or

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"The resistance of $1cm^3$ of an electrolytic solution is called the specific resistance or resistivity of the solution."

Unit of resistivity is ohm-cm.

Conductance (C)

The reciprocal of the resistance of an electrolytic solution is called the conductance of the solution.

Mathematically, conductance,

$$C = \frac{1}{R}$$

It is the measure of the ease to which the current can flow through the conductor.

Its unit is ohm^{-1} or mho or Siemen.

Specific conductance or Conductivity (K)

The reciprocal of the specific resistance or resistivity of an electrolytic solution is called the specific conductance or conductivity of the solution.

Mathematically,

$$K = \frac{1}{\rho}$$

$$\because \quad \rho = R\frac{A}{l}$$

$$\therefore \quad K = \frac{l}{RA}$$

$$\text{or} \quad K = \frac{1}{R} \cdot \frac{l}{A}$$

$$\text{or} \quad K = C \cdot \frac{l}{A}$$

If $l = 1$ cm

$A = 1\ cm^2$

Then, $K = C$

Thus, "the conductance of an electrolytic solution present between two electrodes at 1 cm apart and having area of cross section $1cm^2$ is called the specific conductance or conductivity of the conductor."

or

"The conductance of $1cm^3$ of an electrolytic solution is called the specific conductance or conductivity of the solution."

Unit of conductivity is ohm^{-1}-cm^{-1} or mho-cm^{-1} or S-cm^{-1}.

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Molar conductance (Λ_m)

"The conductance of all the ions furnished by one mole of an electrolyte in the solution is called the molar conductance of the solution."

It is used for comparing the electrical conductance of different electrolytes.

Molar conductance is related with the specific conductance or conductivity of the solution as per the following equation-

$$\Lambda_m = \frac{1000\,K}{C}$$

Where, K = conductivity in S cm^{-1}

C = Conc. of solution in mole L^{-1}

Here, the unit of molar conductance, Λ_m is S cm^2 mol^{-1}.

- In SI system the conductivity is expressed in S m^{-1} and concentration of solution in mole m^{-3}. Here, we get following relation between molar conductance and conductivity of the solution-

$$\Lambda_m = \frac{K}{C}$$

Here, the unit of molar conductance, Λ_m is S m^2 mol^{-1}.

$\because$ 1 mole m^{-3} = 1000 L m^{-3} × Molarity (mol L^{-1})

$\therefore$ $$\Lambda_m = \frac{K\,(S\,m^{-1})}{1000 \times \text{Molarity}}$$

Here also, the unit of molar conductance, Λ_m is S m^2 mol^{-1}.

Experimental determination of electrical conductance

There is no apparatus for direct determination of conductance of the electrolytic solutions. Hence, it is determined indirectly by measuring the resistance of the solution, whose reciprocal gives the conductance of the solution.

$$C = \frac{1}{R}$$

The apparatus used for the experimental determination of resistance (conductance) is called **conductivity meter**. It is nothing but a combination of meter bridge and conductivity cell and operates on the principle of Wheatstone bridge.

The solution whose conductance is to be determined is taken in a conductivity cell and it is made the unknown arm of the meter bridge. A known resistance R is introduced in the known arm of the meter bridge and the apparatus is connected to an AC source of about 1500-2000 cps. Now the sliding contact (Jokey) is so adjusted by moving to and fro over the wire of meter bridge that minimum sound is heard in the head piece (H). This point corresponds to the no deflection point or null point.

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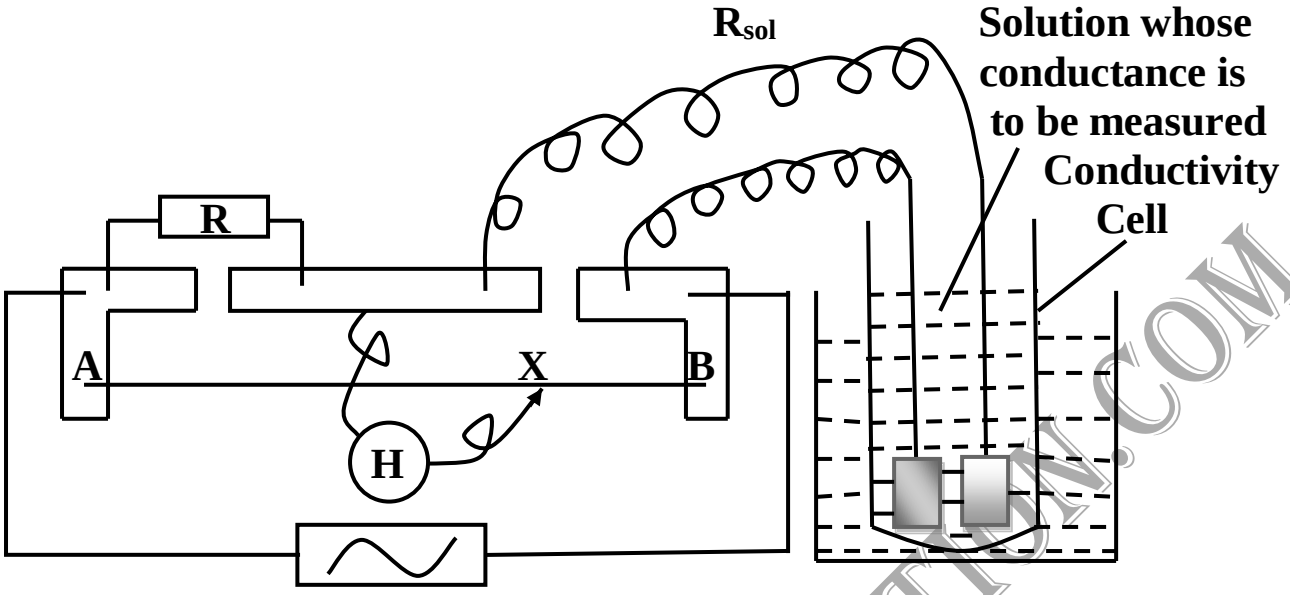


Fig.- Experimental determination of Conductance

Here, at null point (no deflation point), from the principle of Wheatstone bridge-

$$\frac{R}{R_{sol}} = \frac{Resistance\ of\ AX}{Resistance\ of\ BX}$$

$\because$ R α Length of conductor

$$\therefore \quad \frac{R}{R_{sol}} = \frac{Length\ of\ AX}{Length\ of\ BX}$$

$$\text{or} \quad R_{sol} = R \times \frac{Length\ of\ BX}{Length\ of\ AX}$$

The reciprocal of resistance R, thus obtained corresponds to the conductance of the solution.

- Here, DC current cannot be used because it would cause the electrolysis of the electrolytic solution. Hence, exact conductance would not be obtained.
- Since, AC current is being used, Galvanometer cannot be used for detection of null point.

Cell constant

For a given conductivity cell, the ratio of the distance between two electrodes and area of cross section of electrodes is always constant and it is called cell constant of the cell.

Mathematically, cell constant,

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$$G^* = \frac{l}{A}$$

If l is expressed in cm and A in cm^2, then unit of cell constant will be cm^{-1}.

Experimental determination of cell constant

We know that, conductivity,

$$K = \frac{1}{\rho}$$

$$\because \quad \rho = R\frac{A}{l}$$

$$\therefore \quad K = \frac{l}{RA}$$

$$\text{or} \quad K = \frac{1}{R}.\frac{l}{A}$$

$$\text{or} \quad K = C.\frac{l}{A}$$

or Conductivity = Observed Conductance × Cell constant

or $\text{Cell constant} = \frac{Conductivity}{Observed\ conductance}$

For experimental determination of the cell constant of a conductivity cell, a KCl solution of known conductivity is taken in this conductivity cell and its conductance is measured. Here, the ratio of conductivity and observed conductance of KCl solution corresponds to the cell constant of the conductivity cell.

Once the cell constant of the conductivity cell is known, it can be used further for experimental determination of conductivity of the other electrolytic solutions.

Experimental determination of conductivity

We know that, conductivity,

$$K = \frac{1}{\rho}$$

$$\because \quad \rho = R\frac{A}{l}$$

$$\therefore \quad K = \frac{l}{RA}$$

$$\text{or} \quad K = \frac{1}{R}.\frac{l}{A}$$

$$\text{or} \quad K = C.\frac{l}{A}$$

or Conductivity = Observed Conductance × Cell constant

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For experimental determination of the conductivity of a solution, it is taken in a conductivity cell of known cell constant and its conductance is measured. Here, the product of observed conductance and cell constant of the conductivity cell corresponds to the conductivity of the solution.

Effect of dilution on different types of conductances

(a) Effect of dilution on specific conductance or Conductivity

Strong electrolytes such as HCl, H_2SO_4, HNO_3, NaOH, KOH etc. are almost completely dissociated even in their concentrated solution. Hence, on dilution of the solutions of these electrolytes, the degree of dissociation of the electrolyte and therefore, number of ions in solution does not increase. However, on dilution the ions go farther from one another so that, the number of ions in unit volume of the solution gets decreased. Hence, the specific conductance or Conductivity of the solution gets decreased.

On the other hand, weak electrolytes such as CH_3COOH, NH_4OH, H_2CO_3 etc. are very feebly dissociated in their concentrated solution. On dilution the degree of dissociation of these electrolytes increases and therefore, number of ions in solution increases. However, the rate of the increase of the degree of dissociation of these electrolytes is much lesser than the rate of dilution. Hence, here also the number of ions in unit volume of the solution decreases and therefore, the specific conductance or Conductivity of the solution decreases.

Thus, the specific conductance or Conductivity of both strong and weak electrolytes decreases with increase of dilution.

(b) Effect of dilution on molar conductance

The conductance of an electrolytic solution mainly depends upon following two factors-

(1) No. of ions in the solution

(2) Mobility of the ions

On dilution molar conductance of both weak and strong electrolytes increases, but the principal cause of this increase is different for different types of electrolytes.

(i) Strong electrolytes such as HCl, H_2SO_4, HNO_3, NaOH, KOH etc. are almost completely dissociated even in their concentrated solution. Hence, degree of dissociation and therefore, number of ions does not increase on dilution of the solution of these electrolytes. However, on dilution the ions go farther from one another and inter-ionic attraction amongst oppositely

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charged ions gets decreased. It results in the increase in mobility of the ions and therefore, the increase of the molar conductance of the solution.

(ii) Weak electrolytes such as CH_3COOH, NH_4OH, H_2CO_3 etc. are very feebly dissociated in their concentrated solution. On dilution, the degree of dissociation of these electrolytes increases and therefore, number of ions in solution increases. Due to this increase in degree of dissociation i.e. number of ions in solution the molar conductance of the solution increases with dilution.

For strong electrolytes, molar conductance at a given concentration (Λ_m^C) varies with square root of the molar concentration of solution $\sqrt{C}$ as per the following relation-

$$\Lambda_m^C = \Lambda_m^0 - b\sqrt{C}$$

Where, Λ_m^0 is molar conductance of the electrolyte at infinite dilution and b is a constant which depends upon the nature of the electrolytes.

If molar conductance (Λ_m^C) of strong electrolytes are plotted against the square root of the molar concentration of solution $\sqrt{C}$, straight lines having intercept equal to Λ_m^0 and slope equal to -b are obtained.

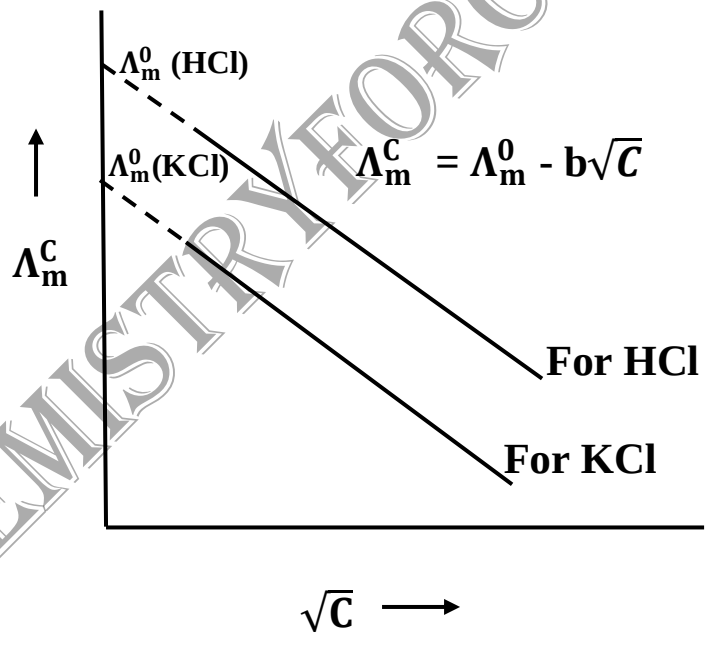


Fig.- Variation of Λ_m of strong electrolytes with $\sqrt{C}$

Here, on extrapolation, the straight lines touch the Λ_m^C axis. This point of intersection corresponds to the molar conductance of the solution at infinite dilution

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(Λ^0_m). Thus, molar conductance of the strong electrolytes at infinite dilution can easily be determined experimentally.

On the other hand, if molar conductance (Λ^C_m) of weak electrolytes are plotted against the square root of the molar concentration of solution $\sqrt{C}$, rectangular hyperbola curves are obtained.

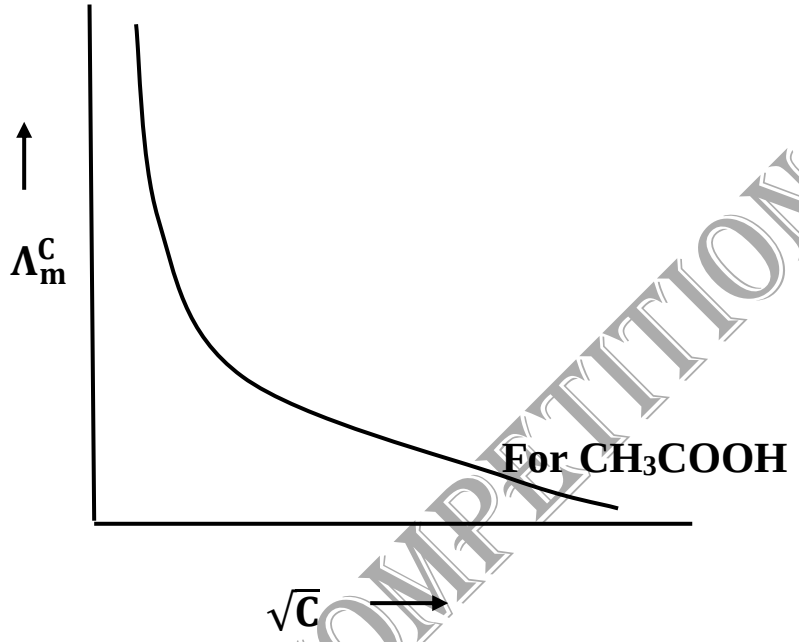


Fig.- Variation of Λ^C_m of weak electrolytes with $\sqrt{C}$

Here, on extrapolation, the curve does not touch the Λ^C_m axis. Thus, molar conductance of the weak electrolytes at infinite dilution (Λ^0_m) cannot be determined experimentally. Hence, it is determined indirectly using Kohlrausch law.

Kohlrausch law of independent migration of ions

According to this law, "At infinite dilution, when the electrolyte is completely dissociated and inter-ionic attraction has completely vanished, all the ions become free from their co-ions and migrate independently to give a definite contribution to the total conductance of the solution."

Thus, "at infinite dilution, the molar conductance of an electrolytic solution is equal to the sum of the ionic conductances of its constituent ions."

Mathematically,

$$\Lambda^0_m = \Lambda^0_m(\text{cation}) + \Lambda^0_m(\text{anion})$$

Where, Λ^0_m is molar conductance of the electrolyte at infinite dilution while, Λ^0_m(cation) and Λ^0_m(anion) are the ionic conductance of cations and anions at infinite dilution respectively.

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For example, for acetic acid,

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
$$\Lambda_m^0[CH_3COOH] = \Lambda_m^0[CH_3COO^-] + \Lambda_m^0[H^+]$$

Similarly, for $BaCl_2$,

$$BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$$
$$\Lambda_m^0[BaCl_2] = \Lambda_m^0[Ba^{2+}] + 2 \times \Lambda_m^0[Cl^-]$$

Applications

(i) Determination of degree of dissociation of weak electrolytes

Degree of dissociation (α) of weak electrolytes is given by following expression-

$$\alpha = \frac{\Lambda_m^C}{\Lambda_m^0}$$

Where, Λ_m^C = Molar conductance at a given conc.

Λ_m^0 = Molar conductance at infinite dilution

Here, the value of Λ_m^C can be determined experimentally and that of Λ_m^0 can be obtained using Kohlrausch law. Hence, the degree of dissociation (α) can be calculated.

(ii) Determination of molar conductances of weak electrolytes at infinite dilution

Molar conductance of the weak electrolytes at infinite dilution (Λ_m^0) cannot be determined experimentally. However, it can be determined indirectly using Kohlrausch law.

For example, if molar conductance of strong electrolytes, CH_3COONa, HCl, and NaCl are known then that of weak electrolyte, CH_3COOH can be calculated as under-

$$\Lambda_m^0[CH_3COOH] = \Lambda_m^0[CH_3COO^-] + \Lambda_m^0[H^+]$$
$$= \{\Lambda_m^0[CH_3COO^-] + \Lambda_m^0[Na^+]\} + \{\Lambda_m^0[H^+] + \Lambda_m^0[Cl^-]\} - \{\Lambda_m^0[Na^+] + \Lambda_m^0[Cl^-]\}$$
$$= \{\Lambda_m^0[CH_3COONa] + \Lambda_m^0[HCl]\} - \{\Lambda_m^0[NaCl]\}$$

Similarly, if molar conductance of strong electrolytes, NH_4Cl, NaOH and NaCl are known then that of weak electrolyte, NH_4OH can be calculated as under-

$$\Lambda_m^0[NH_4OH] = \Lambda_m^0[NH_4^+] + \Lambda_m^0[OH^-]$$
$$= \{\Lambda_m^0[NH_4^+] + \Lambda_m^0[Cl^-]\} + \{\Lambda_m^0[Na^+] + \Lambda_m^0[OH^-]\} - \{\Lambda_m^0[Na^+] + \Lambda_m^0[Cl^-]\}$$
$$= \{\Lambda_m^0[NH_4Cl] + \Lambda_m^0[NaOH]\} - \{\Lambda_m^0[NaCl]\}$$

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