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INDUSTRIAL CHEMISTRY

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APPLICATION OF EMF TO ELECTROCHEMISTRY

**1. Determination of solubility of sparingly soluble salts and its solubility products**

There are salts that are sparingly soluble in water, whose solubility is difficult to be determined by other methods.

 ***Example*** : Silver chloride (AgCl)

The solubility of these sparingly soluble salts can be determined by the EMF measurement by constructing a concentration cell.

**Construction of the cell**

Ag(s) | AgCl(s) | KCl (0.01N) || AgNO3(0.01 N) | Ag(s)

 (unknown)

In this, one of the Ag electrodes is placed in contact with 0.01N AgNO3 solution and the other electrode is in contact with 0.01N KCl solution. The two solutions are connected through a salt bridge containing saturated solution of ammonium nitrate. A drop of AgNO3 solution is added to the KCl solution. This forms a small amount of AgCl which is sufficient to give a saturated solution.

**Working**

One of the electrodes of this cell thus is in contact with a solution of silver ions of **known concentration** (0.01N). The other electrode is in contact with a solution of **unknown concentration** of silver ions furnished by the ionisation of sparingly soluble silver chloride formed.

The EMF of the above cell is given as

 

 i.e., 

 

where, the only unknown factor is the “C”, the concentration of Ag+ ions furnished by AgCl in KCl solution. The emf of the cell can be measured and thus the concentration of AgCl “C” is calculated.

Multiplying the concentration of AgCl with the equivalent weight of AgCl (143.5), the solubility of AgCl is calculated in gm/litre.

(OR)

The solubility product of silver chloride is given by

Ksp(AgCl) = C × 0.01

The solubility (S) of the silver chloride is then given by

S = 

**2 Determination of the valency of an ion**

The valency of the ions could be determined from the EMF of the concentration cells.

**Example**

The valency of the mercurous ion could be obtained as follows

**Construction of the cell**

Mercury / Mercurous nitrate (C1) // Mercurous nitrate (C2) / Mercury

 solution solution

The salt bridge contains the saturated solution of ammonium nitrate.

The EMF of the cell is given by



C2 and C1 are known concentration of mercurous nitrate electrolyte. The emf is obtained experimentally.

Substituting these values in the above equation the “n” the valency of the mercurous ion is calculated.

**3. Determination of pH**

The pH could be obtained using any one of the indicator electrodes.

**Example :**

**Using a standard hydrogen electrode:**

**Construction**

A cell with a reference electrode and hydrogen electrode is constructed using a salt bridge.

Pt, H2(1atm), H+(c= unknown) // KCl(satd), Hg2Cl2(s), Hg

**Calculation**

The potential of the reference electrode i.e. calomel electrode is +0.2422 volts is known. The emf of the cell is obtained experimentally. Substituting the values in the following equation

Ecell = Eright­ – Eleft …(1)

Thus the potential of hydrogen electrode used is calculated as follows.

Eleft = Eright­ –Ecell …(2)

To obtain the pH, the potential of the hydrogen electrode calculated from eqn (2) is substituted in the following Nernst equation



By convention E0 of hydrogen is zero, therefore









Thus, substituting the value of the hydrogen electrode calculated from equation(2), the pH could be determined from the above equation.

 

**By using glass electrode**

 A cell with a reference electrode and glass electrode is constructed using a salt bridge as follows.

**Construction**

 Pt, HCl(0.1N) / glass / test soln // KCl(satd), Hg2Cl2(s), Hg(l)

The salt bridge consists of KCl solution.

**Calculation**

The potential of the reference electrode i.e. calomel electrode is 0.2422volts is known. The emf of the cell is obtained experimentally. Thus substituting the values in the following equation

Ecell = Eright­ – Eleft …(1)

The potential of a glass electrode used is calculated as follows.

Eleft = Eright­ – Ecell …(2)

To obtain the pH, the potential of the glass electrode obtained from eqn (2) is substituted in the equation (3) or (4).

EG = E0G + 0.0591 log[H+]

EG = E0G - 0.0591 pH

 …. (3)

(OR)  ..(4)

[ Where EG = Ecalomel – Ecell and glass electrode is anode].

Thus the pH is calculated using the glass electrode.

**4.Determination of standard free energy change and equilibrium constant**

The standard free energy change (ΔG0) of a reaction can be calculated from the using the standard emf from the following expression

 (– )ΔG0 = nFE0

Where,

 F = 96,500 coulombs

E0 = Standard emf of the cell

 n = number of electrons involved

The equilibrium constant k of a reaction can be calculated from the following equation:

 

Where,

 E0 is the standard EMF of the cell

k is the equilibrium constant

n is the number of electrons involved in the reaction.

APPLICATION OF EMF TO THERMODYNAMICS

When multiplied by an amount of charge *dQ* the emf ℰ yields a thermodynamic work term ℰ*dQ* that is used in the formalism for the change in [Gibbs energy](https://en.wikipedia.org/wiki/Gibbs_free_energy) when charge is passed in a battery:

{\displaystyle dG=-SdT+VdP+{\mathcal {E}}dQ\ ,}

where *G* is the Gibb's free energy, *S* is the [entropy](https://en.wikipedia.org/wiki/Entropy), *V* is the system volume, *P* is its pressure and *T* is its [absolute temperature](https://en.wikipedia.org/wiki/Absolute_temperature).

The combination ( ℰ, *Q* ) is an example of a [conjugate pair of variables](https://en.wikipedia.org/wiki/Conjugate_variables_%28thermodynamics%29). At constant pressure the above relationship produces a [Maxwell relation](https://en.wikipedia.org/wiki/Maxwell_relation) that links the change in open cell voltage with temperature *T* (a measurable quantity) to the change in entropy *S* when charge is passed [isothermally](https://en.wikipedia.org/wiki/Isothermally) and [isobarically](https://en.wikipedia.org/wiki/Isobarically%22%20%5Co%20%22Isobarically). The latter is closely related to the reaction [entropy](https://en.wikipedia.org/wiki/Entropy) of the electrochemical reaction that lends the battery its power. This Maxwell relation is:[[16]](https://en.wikipedia.org/wiki/Electromotive_force%22%20%5Cl%20%22cite_note-Finn-16)

{\displaystyle \left({\frac {\partial {\mathcal {E}}}{\partial T}}\right)\_{Q}=-\left({\frac {\partial S}{\partial Q}}\right)\_{T}}

If a mole of ions goes into solution (for example, in a Daniell cell, as discussed below) the charge through the external circuit is:

{\displaystyle \Delta Q=-n\_{0}F\_{0}\ ,}

where *n*0 is the number of electrons/ion, and *F*0 is the [Faraday constant](https://en.wikipedia.org/wiki/Faraday_constant) and the minus sign indicates discharge of the cell. Assuming constant pressure and volume, the thermodynamic properties of the cell are related strictly to the behavior of its emf by:[[16]](https://en.wikipedia.org/wiki/Electromotive_force%22%20%5Cl%20%22cite_note-Finn-16)

{\displaystyle \Delta H=-n\_{0}F\_{0}\left({\mathcal {E}}-T{\frac {d{\mathcal {E}}}{dT}}\right)\ ,}

where Δ*H* is the [enthalpy of reaction](https://en.wikipedia.org/wiki/Standard_enthalpy_of_reaction). The quantities on the right are all directly measurable.