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Physical chemistry

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Chemical Kinetics

Chemical Kinetics is concerned with the rates of reactions and the mechanisms by which reactions occur. A mechanism is a series of elementary reactions that accounts for the kinetics of the overall reaction. To learn about the mechanism of a reaction, the changes in rate due to variations of concentrations of reactants, products, and catalysts are studied. Important information may also be obtained from studies of the effect on rate of changing the temperature, pressure, solvent, electrolyte concentration, or isotopic composition. Since a mechanism is a hypothesis to explain experimental facts.

Rate equation

A rate equation gives the dependence of the rate on concentrations of reactants, products, and other substances, such as catalysts, which do not appear in the stoichiometric equation for the reaction. For many reactions, the rate is proportional to integer powers of the concentrations of these substances.

\[
\frac{d[CA]}{dt} = k[CA_1][CA_2]
\]
The proportionality constant $K$ is referred to as the rate constant. The exponent of a species' concentration is referred to as the order of the reaction with respect to that species. If $n = 1$, the reaction is said to be first order in $A_1$, and if $n = 2$ the reaction is said to be second order in $A_1$. For a rate equation of this simple form the total reaction order is the sum $\sum n_i$ of the exponents.

First-order Reactions

The rate equation for a first-order reaction:

$$-\frac{d[A]}{dt} = k_1 [A]$$

Conc. of $A$ at $t = 0$ equals $a$
Conc. of $A$ react at $t$ time equals $x$
Conc. of $A$ remaining after $t$ time equals $(a-x)$

$$-\frac{d(a-x)}{dt} = k_1 (a-x)$$

$$-\frac{da}{dt} + \frac{dx}{dt} = k_1 (a-x)$$

$$\frac{da}{dt} = 0$$

$$\frac{dx}{dt} = k_1 (a-x)$$

$$\int (a-x) = K_1 \ dt$$
\[
\int_0^x \frac{dx}{(a-x)} = k_1 \int_0^t dt = t \quad (6)
\]

\[
\frac{\ln a}{(a-x)} = k_1 \times t \quad (7)
\]

\[
\ln(a-x) = \ln a - k_1 t \quad (8)
\]

\[
k_1 = \frac{2.303}{2} \log \frac{a}{(a-x)} \quad (9)
\]

The last form indicates that the rate constant \( k_1 \) may be calculated from a plot of \( \log (a-x) \) versus \( t \); the slope of the line in such a plot is \( \frac{-k_1}{2.303} \).

The half-life \( (t_1/2) \) of a reaction is the time required for half of the reactant to disappear. For a first-order reaction, the half-life is independent of the initial concentration. The relation between the half-life and the rate constant is obtained from equation (9),

\[
k_1 = \frac{2.303}{t_{1/2}} \log \frac{a}{(a-x)}
\]

\[
k_1 = \frac{2.303}{t_{1/2}} \log 2
\]

\[
t_{1/2} = \frac{0.693}{k_1}
\]

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Second-ORDER REACTIONS

A reaction is second-order if the rate is proportional to the square of the concentration of one reactant or is proportional to the product of the concentrations of two reactants.

If the rate is proportional to the square of the concentration of one reactant as follows:

\[ 2A \rightarrow \text{products} \]

The rate law may be integrated after arranging it in the form:

\[ -\frac{d[CA]}{[CA]^2} = k_2 \, dt \]

If the concentration of A at \( t=0 \) is \( a \), if the reactant at A after \( t \) time is \( x \), and the remaining of A after \( t \) time is \( (a-x) \),

\[ \frac{dx}{dt} = k_2 (a-x)^2 \]

\[ \int_0^t \frac{dx}{(a-x)^2} = k_2 \int_0^t dt \]

\[ k_2 = \frac{1}{a^2} \cdot \frac{x}{a(a-x)} \]
Thus a plot of \( \frac{1}{(a-x)} \) versus \( t \) is linear for such a second-order reaction, and the slope is equal to the second-order rate constant. This integrated rate equation also applies if the rate is given by \( k_2 A C \), the stoichiometry is represented by \( A + B \rightarrow \text{products} \), and \( A \) and \( B \) are initially at the same concentration. As may be seen from equation (4), the half-life for such a second-order reaction is given by:

\[
    t_{1/2} = \frac{1}{k_2 \cdot a}
\]

Thus the half-life is inversely proportional to the initial concentration.

A different integrated rate law for a second-order reaction is obtained if the rate is given by \( k_2 A C \) and the stoichiometry is given by:

\[
aA + bB \rightarrow \text{products}
\]

The rate constant is defined by:

\[
    -\frac{1}{a} \frac{dC_A}{dt} = -\frac{1}{b} \frac{dC_B}{dt} = k_2 \cdot C_A \cdot C_B
\]

If the reactants are not in stoichiometric proportion [i.e., \( bA \neq aB \)], then the integrated rate equation is:

\[
    k_2 = \frac{2.303 \log \frac{b(a-x)}{a(b-x)}}{t(a-b)}
\]

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Thus for a second-order reaction in which the reactants are not in stoichiometric proportions, a plot of \( \log(a-x)/b-x \) versus \( t \) is linear. The rate constant for a second-order reaction has the units (concentration)\(^{-1}\) \( \text{s}^{-1} \).

**Third-order Reactions**

A reaction is third-order if the rate is given by \( k[A]^3 \), \( k[A]^2[B] \), or \( k[A][B][C] \). If the reactants are in stoichiometric proportions, these three rate laws all lead to the same integrated equation:

\[
\frac{dx}{dt} = k_3 (a-x)^3
\]

\[
\int_0^x \frac{dx}{(a-x)^3} = k_3 \int_0^t dt
\]

\[
\frac{1}{2(a-x)^2} - \frac{1}{2a^2} = k_3 t
\]

or

\[
K_3 = \frac{1}{2t} \left[ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right]
\]

\[
t \frac{1}{2} = \frac{3}{2K_3a^2}
\]
Zero-order Reactions

These are reactions in which the rate is unaffected by changes in the concentrations of one or more reactants because it is determined by some limiting factor other than concentration, such as the amount of light absorbed in a photochemical reaction or the amount of catalyst in a catalytic reaction. Then

\[- \frac{dC_a}{dt} = K_0 \]

A catalytic reaction might be first order in catalyst and zero-order in reactant. Integration of equation (1) yields:

\[ \frac{dX}{dt} = K_0 \quad \text{2,} \]

\[ K_0 \int_0^t dt = \int_0^X dx \quad \text{3,} \]

\[ K_0 t = X \quad \text{4,} \]

\[ K_0 = \frac{X}{t} \quad \text{5,} \]

The value of $K_0$ calculated using this equation may be a function of the intensity of light or the concentration of catalyst.

\[ t_{1/2} = \frac{a}{2K_0} \]
Effect of Temperature on Reaction Rate

The dependence of rate constants on temperature can usually be represented by an empirical equation proposed by Arrhenius:

\[ K = A e^{-\frac{E_a}{RT}} \quad (1) \]

where \( A \) is the preexponential factor and \( E_a \) is the activation energy.

Equation (1) may be written in logarithmic form:

\[ \frac{d \ln K}{dT} = \frac{E_a}{RT^2} \quad (2) \]

\[ \log K = -\frac{E_a}{2.303RT} + \log A \quad (3) \]

According to this equation, a straight line should be obtained when the logarithm of the rate constant is plotted against the reciprocal of the absolute temperature.

![Graph showing logarithmic relationship]

\[ \text{slope} = \frac{-E_a}{2.303R} \]

\[ \text{intercept} = \log A \]

and integrating between limits,

\[ \log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_2 T_1} \right] - 10 \]
Activation Energy

The molecules must have a certain amount of energy, \(E_a\), in order to react. Generally, molecules have to be activated before they can react.

For the simple reaction \(A \rightarrow B\) the activated complex \(X^*\) can be represented by:

\[ A \rightarrow X^* \rightarrow B \]

In order for \(A\) to be converted to \(B\), it is necessary for it to be activated to \(X^*\) and similarly \(B\) can be converted to \(A\) only through this activated complex.

Both the forward and reverse reactions go through the same intermediate structure. If a bond is in the process of being broken in \(X^*\) for the reaction \(A \rightarrow B\), the bond is in the process of being formed in \(X^*\) for the reaction \(B \rightarrow A\)

The relative energies of \(A\), \(X^*\) and \(B\) are indicated in Fig. below:

\[ \text{Reaction Coordinate} \]
\[ \Delta E = E_a - E_r \]

If \( E_a > E_r \)

\[ \Delta E = (+) \text{ is positive} \]
The reaction is \textit{Endothermic}

and If \( E_a < E_r \)

\[ \Delta E = (-) \text{ is negative} \]
The reaction is \textit{Exothermic}

**Complex Reactions**

1. **Parallel Reactions**
2. **Consecutive Reactions**
3. **Reversible Reactions**

**Parallel First-order Reactions**

\[
A \stackrel{K_1}{\rightarrow} B \\
A \stackrel{K_2}{\rightarrow} C
\]

Parallel first-order reactions which compete for
the reactant are often encountered because many
products may be possible according to the laws of
thermodynamics. For example, in the nitration of
bromobenzene, o-, m-, and p-nitro bromobenzene
are obtained. Under certain conditions the yields
are indicated by.

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often such yields do not indicate the equilibrium concentration of the products but indicate the different rates with which the various products are formed.

The rate equation for A is

\[
\frac{dx}{dt} = (k_1 + k_2) C_A
\]

The rate equation for B and C is:

\[
\frac{dB}{dt} = k_1 C X
\]

\[
\frac{dC}{dt} = k_2 C X
\]

\[
\frac{dB}{dC} = \frac{k_1}{k_2}
\]

2. Consecutive First-order Reactions

Consecutive reactions occur when the product of a reaction undergoes further reaction.

Two consecutive first-order reactions may be represented by:

\[
A \xrightarrow{k_1} B \xrightarrow{k_2} C
\]
In order to determine the way in which the concentration of the compounds in such a mechanism depend upon time, the rate equation are first written down for each substance. It is necessary to obtain the solution of these simultaneous differential equations. For the above reactions the rate equations are as follows:

The rate equation for A is

\[ \frac{dx}{dt} = k_1 (a-x) \quad \text{(1)} \]

The rate equation for B is: The rate equation for C is:

\[ \frac{dx}{dt} = k_2 (x-y) \quad \text{(2)} \]

after integration:

\[ C_A = (a-x) = a e^{-k_1 t} \quad \text{(3)} \]

\[ C_B = (x-y) = \frac{a k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \]

\[ C_C = \frac{a}{k_2 - k_1} \left[ (k_2 - k_1 e^{-k_1 t})(k_1 - k_2 e^{-k_2 t}) \right] \]

The concentrations of A, B and C are shown as follows:

[Diagram showing concentrations over time]
Reversible First-order Reactions

The integrated rate equation for a reversible first-order reaction

\[ A \xrightleftharpoons[\text{K}_2]{\text{K}_1} B \]

may readily be derived. The rate equation is:

\[ \frac{dx}{dt} = k_1 (a-x) - k_2 x \]

At equilibrium the rates of the forward \( k_1(a-x) \) and reverse reaction \( k_2 x \) are equal.

\[ k_1(a-Xe) = k_2 Xe \]

\[ k_2 = \frac{k_1(a-xe)}{Xe} \]

\[ \frac{dx}{dt} = k_1(a-x) - \frac{k_1(a-xe)}{Xe} \]

\[ \frac{dx}{dt} = \frac{k_1a(Xe-x)}{Xe} \]

\[ \frac{k_1a}{Xe} \cdot \frac{1}{t} \ln \frac{Xe}{Xe-X} \]
Problems

1. How does the time required for a first-order reaction to go to 99.9% completion relate to the half-life of the reaction?

2. The gas-phase reaction \( \text{NO}_3 \rightarrow \text{NO}_2 + \frac{1}{2} \text{O}_2 \) is second order with respect to \( \text{NO}_3 \). At a temperature of 20°C and initial concentration of \( \text{NO}_3 \) equal to 0.05 mol\( \text{L}^{-1} \), the concentration after 60.0 min is equal to 0.0358 mol\( \text{L}^{-1} \). Find the value of the forward rate constant.

3. For the gas-phase reaction at 30°C
   \[ \text{Gt}^4 \rightarrow \frac{1}{2} \text{Ct} \text{t} \text{H}_8 \]
   The following data on the concentration of \( \text{Gt}^4 \) were taken. Using the half-life method,
   \[
   t_\frac{1}{2} \text{ min} : 250 \quad 500 \quad 1000 \quad 2000
   \]
   \[
   \text{initial conc.} / \text{M} : 0.05 \quad 0.025 \quad 0.0125 \quad 0.00625
   \]
   Determine the order of reaction?

4. The gas-phase reaction between nitric oxide and oxygen is third-order. The following rate constants have been measured:
   \[
   T/\text{K} \quad 800.0 \quad 1430.0 \quad 2280.0 \quad 3000.0 \quad 4130.0
   \]
   \[
   K \times 10^9 / \text{cm}^3 \text{mol}^{-1} \text{s}^{-1} \quad 4.18 \quad 2.02 \quad 1.01 \quad 0.71 \quad 0.40
   \]
   Determine the activation energy.
5- The hydrolysis of methyl acetate in (0.05 M) hydrochloric acid at 25°C. The data are as follows:

\[ t \text{(sec)}: \begin{array}{cccc}
0 & 1200 & 4500 & 7140 \\
\text{Initial NaOH(mol)}: & 24.36 & 25.85 & 29.32 & 31.72 & 47.15
\end{array} \]

a. What is the order of the reaction?
b. What is the value of the rate constant?

6- The results of decomposition of an organic compound are as follows:

\[ \begin{array}{cccc}
\text{C}_2 \text{(M)}: & 2.48 & 1.1 & 0.5 \\
\text{t}_1/2 \text{(sec)}: & 174 & 880 & 4280
\end{array} \]

a. What is the order of reaction?
b. What is the value of rate constant?

7- The rate constant of trichloroacetic acid at 25°C is \((4.0 \times 10^{-5}) \text{ min}^{-1}\) and \((8.0 \times 10^{-5}) \text{ min}^{-1}\) at 45°C. Calculate the activation energy of this reaction.

8- The following specific reaction rates were obtained for the first-order decomposition of acetic dianhydride acid in aqueous solution:

\[ \begin{array}{cccc}
\text{Temp, } \degree C: & 0 & 20 & 40 & 60 \\
K \times 10^5, \text{ sec}^{-1}: & 2.46 & 47.5 & 576 & 5480
\end{array} \]

Calculate the energy of activation?
9. At 700 K, what is the half-life of SiH4? The equation for the first-order rate constant for decomposition is \[ K = (2 \times 10^{13} \text{s}^{-1}) e^{-0.16 \cdot \frac{E_a}{RT}} \], where the activation energy is in J/mol.

10. The reaction: \( \text{SO}_2\text{Cl}_2 = \text{SO}_2 + \text{Cl}_2 \) is first order with a rate constant of \( 2.2 \times 10^{-5} \text{s}^{-1} \) at 320°C. What percentage of \( \text{SO}_2\text{Cl}_2 \) is decomposed after being heated at 320°C for 2 hrs?
Catalysis

Catalyst is defined as a substance, a small amount of which alters (increases or decreases) the velocity of a chemical reaction by its mere presence, without itself undergoing any change in mass and composition at the end of the reaction. This phenomenon of altering the velocity of chemical reaction by the presence of a catalyst is called catalysis.

When a catalyst accelerates the speed of the reaction, it is called a positive catalyst, e.g., MnO₂ in the decomposition of KClO₃ into KCl and O₂, platinum black in the oxidation of SO₂ by the atmospheric oxygen. On the other hand, if the catalytic substance retards the chemical reaction, it is called a negative catalyst, e.g., alcohol retards the oxidation of chloroform to poisonous phosgene.

Classification of Catalysis

a. Homogeneous Catalysis are those catalytic reactions in which the catalyst as well as the reacting substances are present in the same physical phase, i.e., if the reactants are solids, the catalyst is also solid; if the reactants are liquids or gases, the catalyst is also a liquid or gas respectively, e.g., citric
oxide (NO) vapour, the catalyst in the oxidation of SO₂ by oxygen.

\[ 2 \text{SO}_2 + \text{O}_2 \rightarrow \text{NO}_3 \rightarrow 2 \text{SO}_3 \]

6. Heterogeneous catalysis are those catalytic reactions in which the catalyst is of different physical phase than the reactants, e.g. oxidation of SO₂ to SO₃ in presence of platinum catalyst (solid) in contact process as follows:

\[ 2 \text{SO}_2 + \text{O}_2 \rightarrow \text{Pt}_5 \rightarrow 2 \text{SO}_3 \]

**Characteristics of Catalysis**

1. A catalyst remains unchanged in mass and chemical composition at the end of the reaction.

2. A small amount of catalyst is sufficient to bring about an appreciable change in the velocity of the reaction.

3. A catalyst can exert a selective action.

4. A catalyst can only alter the speed of the reaction, but does not affect the final state of the equilibrium.

5. Catalyst can not start a reaction, but can only decrease or increase its rate.
6. A catalyst is most active at a particular temperature called the optimum temperature.

7. The addition of a small amount of foreign substances, which are not themselves catalytically active, sometimes, increase the activity of the catalyst. Such substances, which catalyse the catalyst, are called promoters, e.g., in the nitric manufacture by Haber's process finely divided Fe acts as Catalyst; while molybdenum (or a mixture of Al2O3 + K2O) acts as a promoter.

8. The activity of a catalyst is inhibited or completely destroyed by the presence of even minute trace of certain substances called catalytic poisons or anti-catalysts. For example, in the manufacture of H2SO4 by the contact process, a trace of As2O3 destroys the catalytic efficiency of spongy platinum.

**Auto-Catalysis**

When a product formed in the course of reaction enhances the velocity of the reaction (or acts as catalyst), the phenomenon is called auto-catalysis. Thus, the hydrolysis of an ester by water is an auto-catalytic process since the acid liberated,

\[ RCOO^+ + H_2O \rightarrow RCOOH + ROH \]

as a result of hydrolysis catalyses the reaction.
Enzymes Catalysis

Enzymes are highly complex, non-living, nitrogenous organic substances produced by living animals and plants. They possess the incredible capacity in bringing about many complex chemical reactions like hydrolysis, oxidation, reduction, etc. They are highly specific and each enzyme can catalyse a specific reaction. The catalytic activity of enzymes, like catalysts, is due to their capacity to lower the activation energy for a particular reaction. For example:

Starch is catalysed by diastase:

\[
2 \left( \text{C}_6\text{H}_{10}\text{O}_5 \right)_n + \text{nH}_2\text{O} \xrightarrow{\text{Diastase}} \text{nC}_2\text{H}_{2}\text{O}_1\text{1}
\]

\text{starch} \quad \text{Maltose}

\[
\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{Maltase}} 2 \text{C}_6\text{H}_{12}\text{O}_6
\]

\text{Maltose} \quad \text{Glucose}
**Mechanism of Enzyme Catalysis**

The Mechanism of Enzyme Catalysis was first explained by Michaelis and Menten as follows:

\[ E + S \xrightarrow{K_1} ES \xrightarrow{K_2} E + P \]

Here, E and S are the enzyme and substrate, ES is an activated complex, and P is the product. \( K_1, K_2 \) and \( K_3 \) are the rate constants.

The rate equations:

\[ \frac{d[ES]}{dt} = K_1[E][S] - K_2[ES] = K_3[ES] \quad (2) \]

\[ \frac{d[ES]}{dt} = K_1[E][S] - K_2[ES] - K_3[ES] \quad (3) \]

The concentration \([E]\) that appears in this equation is the concentration of the free enzyme, and it may be very much less than the total concentration \([E]_0\) of enzyme. Since much of the enzyme may be in the form of ES, the total concentration is given by:

\[ [E]_0 = [E] + [ES] \quad (4) \]

\[ \frac{d[ES]}{dt} = K_1([E]_0 - [ES])[S] + K_2[ES] - K_3[ES] \quad (5) \]

\[ = K_1[E]_0[S] - (K_1[S] + K_2 + K_3)[ES] \quad (6) \]
At steady state:

\[
\frac{d[ES]}{dt} = 0
\]

\[
0 = K_1 [E_0][S] - (K_1[ES] + K_2 + K_3) [ES] - (7)
\]

\[
[ES] = \frac{K_1 [E_0][S]}{K_1[S] + K_2 + K_3} - (8)
\]

\[
[ES] = \frac{[E_0]}{1 + \frac{K_2 + K_3}{K_1[ES]} - (9)
\]

\[
\frac{d[P]}{dt} = K_3 [ES]
\]

\[
\frac{d[P]}{dt} = \frac{K_3 [E]}{1 + \frac{K_2 + K_3}{K_1[S]} - (10)
\]

\[
\frac{K_2 + K_3}{K_1} \text{ (Michaelis constant)}
\]
Electrochemical Cell

In an electrolytic cell an external source of voltage is used to bring about a chemical change. In such a case when an electrical potential is applied, the flow of electrons is forced in particular direction from the negative pole to the positive pole of the battery. In the solution, however, the electrolyte exists already in the ionic form, and the applied electrical potential causes these ions to move the positive ions in the direction of cathode, while the negative ions towards the anode. The cation on reaching the cathode acquires electrons (which are available at this electrode) thereby its charge is neutralized. Similarly, when an anion reaches the anode, the electrons are removed, leaving behind the discharged atom or group of atoms.

In such a manner different products are liberated at the two electrodes.

On the other hand, electrochemical cell a device used to convert chemical energy released in a redox reaction taking place indirectly into electrical energy. Thus, electric current in an electrochemical cell results from oxidation and reduction reactions occurring simultaneously at two electrodes, which are separated from each other by partition such as porous vessel.
Redox Reactions

Oxidation:

A process which involves the loss of electrons by a substance, while reduction is a process which involves the gain of electrons by a substance. It is quite apparent that if a substance loses electrons, some other substance must be involved in the reaction to accept these electrons. On the other hand, if a substance accepts electrons, some other substance must be involved in the reaction to supply these electrons.

In other words, oxidation and reduction must always go side by side. Thus, if we place a zinc metal in a solution of copper sulphate, immediately precipitation of copper takes place.

\[ \text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s) \]

In this change, the zinc atom (Zn) is oxidised to zinc ion (Zn^{2+}) since it loses electrons, while the copper ion (Cu^{2+}) is reduced to copper atom, since it gains electrons.

\[ a- \quad \text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^- \quad \text{(oxidation)} \]
\[ b- \quad \text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s) \quad \text{(reduction)} \]

\[ \text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s) \quad \text{(redox)} \]
The overall reaction obtained by adding (a) and (b) is called redox or oxidation-reduction reaction. Each of these reactions is known as half-reaction. The reaction (a), in which loss of electrons take place is called oxidation half-reaction, while the other reaction (b), in which gain of electrons takes place is called reduction half-reaction.

**Electrical Energy From A Redox Reaction**

A redox reaction is usually spontaneous. However, if we arrange for the electrons that are transferred in the redox reaction to pass through a metallic conductor, we can utilize the redox reaction as a source of producing electrical energy. But this can be achieved only if the oxidation and reduction reactions are not allowed to come into direct contact with each other. All this may be achieved by using a set up shown in Fig-1.

![Figure 1: An electrochemical cell](image)

**Fig-1** - An electrochemical cell
Here a zinc rod is partially immersed in 1M ZnSO₄ solution and a copper rod is partially immersed in 1M CuSO₄ solution. The two solutions are then interconnected by a salt bridge which is U-tube containing concentrated KCl or NH₄NO₃ solution in agar-agar gel. The salt bridge, thus, provides a contact between the two compartments. If the zinc and copper rods are connected (from outside), electrons flow from the Zn to the Cu as Zn²⁺ ions are oxidised and Cu⁺ ions are reduced. The flow of electrons is indicated by voltmeter (or ammeter), placed in the circuit, the driving force is the decrease in free energy for the reaction.

\[
\text{Zn}^{2+}_{(aq)} + \text{Cu}^{+}_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + \text{Cu}^{+}_{(aq)}
\]

For instance, the value of ΔG for this reaction is \(-223.8 \text{ kJ mol}^{-1}\) at 25°C. This free energy available is, thus, utilized in get electrical energy. Such a device in which a redox reaction is utilized to get electrical energy is known as electrochemical cell. The electrode where oxidation occurs is called anode; while the electrode where reduction occurs is called cathode. Thus, in the above cell zinc electrode is anode; while the copper electrode is cathode.
The practical application of an electrochemical cell is the Daniel cell. It consists of zinc electrode dipping in ZnSO4 solution, where oxidation takes place and copper electrode, dipping in CuSO4 solution, where reduction takes place. In other words, each electrode may be regarded as half-cell. The two solutions are separated by a porous pot. The two solutions can seep through the pot and so come in contact with each other automatically. Thus porous partition acts as a salt bridge. The electrode reactions in Daniel cell are:

At anode: \[ \text{Zn} \rightarrow \text{Zn}^{+2} + 2\text{e}^- \]

At cathode: \[ \text{Cu}^{+2} + 2\text{e}^- \rightarrow \text{Cu} \]

Cell reaction: \[ \text{Zn} + \text{Cu}^{+2} \rightarrow \text{Zn}^{+2} + \text{Cu} \]

The tendency of Zn to form Zn\(^{+2}\) is greater than the tendency the Zn\(^{+2}\) to get deposited in the electrode; therefore, Zn will go into solution forming Zn\(^{+2}\); thereby the Zn metal will acquire a negative charge. On the other hand, tendency of copper to get into solution is less than the tendency of copper to get deposited and hence copper electrode will become positively charged.
Electrode potential

A metal \( M \) consist of metal ions \( M^{m+} \) with the valency electrons that binds them together. Now if a metal is in contact with a solution of its own salt, the positive ions in the metal comes into equilibrium with those in the solution, leaving behind equivalent number of electrons on the metal. Thus, the metal acquires a negative charge since it is now left with excess of electrons and lesser number of metallic positive ions.

\[
\begin{array}{c|c|c}
\text{Zinc ion moving} & \text{Zn in solution} & \text{Zn}^{2+} \text{ions} \\
\text{from Zn metal} & \text{leaving behind free electrons} & \\
\text{to solution leaving} & \text{on Zn} & \\
\end{array}
\]

De-electronation

The following reaction take place when metal \( M \) is in contact with its salt Solution:

\[
M \rightarrow M^{m+} + n\overline{e}
\]

when \( n \) electrons are left behind on the metal \( M \) and the rate of this reaction depends on a- the nature of metal.
b. the concentration of metal ions in solution.
c. the temperature.

A difference of potential is, consequently, set up between the metal and the solution. This potential difference will persist as long as the charge is allowed to remain on the metal; and this will prevent the further passing of the positive ions from or to the metal. At equilibrium, the potential difference between the metal and solution remains a constant value. The equilibrium potential difference so established is called the (electrode potential) of the metal. Thus, electrode potential of the metal is the measure of tendency of a metallic electrode to lose or gain electrons when it is in contact with a solution of its own salt at unit molar concentration at 25°C. Consequently, the tendency of an electrode to lose electrons is a direct measure of its tendency to get oxidised; and this tendency is called oxidation potential. Similarly, the tendency of an electrode to gain electrons is a direct measure of its tendency to get reduced; and as such this tendency is known as reduction potential. Thus, if the oxidation of potential of an electrode is $(+x)$ volt, its reduction potential will have a value $(-x)$ volt.
Nernst equation for electrode potential

Consider a general reaction:

\[ M \rightarrow M^{+n} + n\bar{e} \]

Now for a reversible reaction, the free energy change (\(\Delta G\)) and its equilibrium constant (\(K\)) are inter-related as:

\[ \Delta G = \Delta G^0 + RT \ln K \]

where \(\Delta G^0\) is known as a standard free energy change.

In a reversible reaction, the electrical energy is produced as the expense of the free energy decrease:

\[ -\Delta G = nFE \]
\[ \Delta G = -nFE \quad \Delta G^0 = -nFE^0 \]

where \(E\) is the electrode potential.
\(E^0\) is the standard electrode potential.
\(F\) = Faraday (96,500 coulombs).

Consequently, the above expression takes the form:

\[ [-nFE = -nFE^0 + RT \ln K] = (nF) \]

\[ E = E^0 - \frac{RT}{nF} \ln K \]

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\[ E = E^0 - \frac{0.0591}{n} \log K \]

Standard hydrogen electrode (SHE)

A platinum electrode in contact with 1 M H\(^+\) ion concentration and hydrogen gas at atmospheric pressure is constantly bubbled over it as follows:

Normal hydrogen electrode

Standard hydrogen potential has been arbitrarily fixed at zero; and all other electrode potentials are expressed in comparison with this value.
This is represented as:

\[ \text{Pt, H}_2 (1 \text{ atm}) + H^+ (1 \text{ M}) \]

and either of the following reactions may take place at this electrode:

\[ H^{+}_{(aq)} + e^- \rightarrow \frac{1}{2} \text{H}_2 (g), \quad \text{(1)} \]

\[ \frac{1}{2} \text{H}_2 (g) \rightarrow H^+_{(aq)} + e^- \quad \text{(2)} \]

\[ E_{H_2} = E_{H^2}^{0} - \frac{0.0591}{n} \log K \]

\[ = 0 - \frac{0.0591}{n} \log K \]

\[ E_{H_2} = -\frac{0.0591}{n} \log K \]

For reaction (1):

\[ E_{H_2} = -\frac{0.0591}{n} \log \frac{[H_2]^{1/2}}{[H^+]} \]

\[ E_{H_2} = -\frac{0.0591}{n} \log \frac{1}{[H^+]} \]

\[ E_{H_2} = -0.0591 \log \frac{1}{[H^+]} \]  

(Activity of hydrogen gas at 1 atm = 1)
Reference Electrodes

It is impossible to measure the value of single electrodes potential by using voltmeters or potentiometers. Therefore, it is necessary to assemble first a cell by coupling the given electrode with another electrode, whose potential is either arbitrarily fixed or is exactly known. This type electrode of standard electrode with which we can compare the potentials of all other electrodes is called a reference electrode. Thus, by knowing the (e.m.f) of the assembled cell and the electrode potential of reference electrode, important reference electrodes are:

1. Hydrogen electrode
2. Calomel electrode
3. Glass electrode
4. Quinhydrone electrode

Determination of pH

$$pH = \frac{E_{cell} - E_{calomel}}{0.0591}$$
Concentration cell

The electrical energy in a concentration cell arises from the transfer of a substance from the solution of a high concentration around one electrode to solution of lower concentration around the other electrode. A concentration cell is thus made up of two half-cells having identical electrodes and identical electrolyte, except that the concentration of the reactive ions at the two electrodes are different. The two half-cells may be joined by a salt bridge - one such cell is represented below:

\[ \text{Ag} \mid \text{AgNO}_3 (C_1) \mid \text{Salt bridge} \mid \text{AgNO}_3 (C_2) \mid \text{Ag} \]

In this case, both the electrodes are of the same metal (Ag) and these are in contact with solutions of the same ions (Ag\(^+\)) however, the concentration of active ions (Ag\(^+\) ions) around the two electrodes are different.

\[ E_{\text{cell}} = E^\circ + \frac{0.0591}{n} \log \frac{C_2}{C_1} \]

\[ E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1} \]
The lead storage cell

The lead storage cell consists of an electrode of lead and an electrode of lead oxide immersed in sulfuric acid. Each plate has a rough surface exposing a large area, and the two are held close together in rigid frames. The cell reaction is:

\[ \text{Pb} + \text{H}_2\text{SO}_4 = \text{PbSO}_4(s) + 2\text{e}^- + 2\text{H}^+ \text{ Anode} \]
\[ \text{PbO}_2 + \text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e}^- = \text{PbSO}_4 + 2\text{H}_2\text{O} \text{ Cathode} \]
\[ \text{pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O} \text{ Cell reaction} \]

Oxidation - Reduction Cells

Oxidation-reduction cells known as redox cells, in which both the oxidized and reduced species are in solution; their interconversion is effected by an inert electrode such as one of platinum. Consider, for example, the cell:

\[ \text{Pt} | \text{H}_2/\text{H}^+(1\text{m}) || \text{Fe}^{+3}, \text{Fe}^{+2} / \text{Pt} \]

\[ \frac{1}{2} \text{H}_2 \rightarrow \text{H}^+ + \text{e}^- \quad \text{anode} \]

\[ \text{Fe}^{+3} + \text{e}^- \rightarrow \text{Fe}^{+2} \quad \text{Cathode} \]

\[ \text{Fe}^{+3} + \frac{1}{2} \text{H}_2 \rightarrow \text{Fe}^{+2} + \text{H}^+ \quad \text{Cell reaction} \]
The Corrosion of Metals

The role of the exchange currents in determining the corrosion rate can be seen by considering the case of iron in contact with an acidic solution. Thermodynamically, the iron can be oxidized by hydroxyl group to form FeOH₂⁺. A model of the corrosion system is:

\[ O_2 + H_2O + 4e^- \rightarrow 4OH^- \]

![Corrosion diagram](image)

This model shows that a corrosion system is really a short-circuited electrochemical cell, the electrodes being (Fe, Cu), the electrolyte the water droplet, and the circuit completed by the contact of (Fe, Cu).

Several techniques for inhibiting corrosion:
1. Coating the surface with some impermeable layer, such as paint, may prevent the access of damp air.
2. Coating the iron with zinc (galvanizing).
3. Change the potential of the object by pumping in electrons.
Electrochemistry

IS the study of the various chemical effects of electricity. It deals with (a) the study of chemical changes produced by the passage of direct electric current, and (b) the production of direct electricity from chemical changes.

Conductors and Insulators

Electric Current is a flow of electrons generated by a battery when the circuit is completed. A substance which allows electric current to pass through it is called a conductor, e.g., all metals, graphite, fused salts, aqueous solution of acids, bases and salts; while insulators is a substance which does not conduct the electric current, i.e., which does not allow the passage of electric current through it.

The conductors are of two type:

1. Metallic Conductors
2. Electrolyte

Electrolyte is a substance which, in aqueous solution in molten state, releases ions and allows electric current to pass through, thereby resulting in its chemical decomposition, e.g., acids, bases and electrovalent salts.
Faraday's laws of Electrolysis

First law: According to it "during electrolysis the amount of substance deposited or evolved at any electrode is proportional to the quantity of electricity passed".

The quantity of electricity (Q) is equal to the product of the current strength and the time for which it is passed. In other words,

\[ Q = \text{Current strength} \times \text{time} \]

\[ Q = I \times t \]

\[ m = ZIT \]

where \( m \) is the amount of substance evolved.

\( I \) is current in amperes.

\( t \) is time in seconds for which current passed.

\( Z \) is a constant of proportionality and is known as the electrochemical equivalent of the substance.

Electrochemical equivalent may be defined as the weight of the substance deposited/evolved by the passage of 1 coulomb of electricity.

Second law: According to it "the amount of different substances evolved/deposited by the passage of same quantity of electricity are proportional to their chemical equivalent weights".

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Mathematically:

\[ W \times E \]

where \( W \) = net of the substance liberated or deposited.
\( E \) = equivalent weight of the substance.

Thus, if \( W_1 \) and \( W_2 \) are the weights of two different substances liberated by the passage of same amount of electricity and \( E_1 \), \( E_2 \) are their respective chemical equivalents then:

\[ \frac{W_1}{E_1} = \frac{W_2}{E_2} \]

**Conductivity of electrolytes**

The resistance of conductor is directly proportional to its length and inversely proportional to its cross-sectional area (ohm's law).

\[ R = \rho \frac{l}{a} \]

where \( R \) = resistance in ohms (\( R \))
\( \rho \) = specific resistance
\( l \) = length in cm
\( a \) = area in cm²

**The specific conductance \( K_s \):**

\[ K_s = \frac{1}{\rho} = \frac{1}{R} \cdot \frac{1}{a} \]

The unit of \( K_s \) is \( \text{S}^-1 \text{cm}^1 \).
Equivalent Conductivity \( (\Lambda) \): It represents to the conductance of all the ions present in 1 gram equivalent of the electrolyte in the solution at given dilution.

\[
\Lambda = \frac{1000 \text{ Ks}}{C}
\]

where \( \Lambda \) = equivalent conductance \( (\text{S} \cdot \text{cm}^2 \cdot \text{eq}^{-1}) \),

\( C \) = Concentration in gram equivalent per liter \( (\text{cm}^3) \).

Molecular Conductivity \( \mu \): The conductance of all the ions present in one mole of electrolyte in the solution.

\[
\mu = \frac{1000 \text{ Ks}}{C}
\]

where \( \mu \) = Molecular Conductance \( (\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}) \),

\( C \) = Molar Concentration.
Kohlrausch noticed that pairs of sodium and potassium salts with the same anion showed a constant difference in equivalent conductance at infinite dilution. Kohlrausch concluded that:

"At infinite dilution when dissociation is complete and all interionic effects vanish, each ion moves independently of its co-ion and contributes to the total equivalent conductance of an electrolyte a definite share, which depends only on its own nature and not at all on that of the ion with which it is linked. Thus, equivalent conductivity at infinite dilution of any electrolyte is equal to the sum of the equivalent conductance of its cation and anion. Since each ion contributes a definite amount to the total conductance of the electrolyte:

$$\lambda_o = \lambda_o^+ + \lambda_o^-$$

where \((\lambda_o^+, \lambda_o^-)\) are the ionic conductance at infinite dilution of cation and anion respectively."
Application of Kohlrausch's law

1. Determination of equivalent conductivity of weak electrolytes.
2. Determination of solubility of sparingly soluble salts.
3. Determination of degree of dissociation.

Conductometric titration

Conductometric titration is a method of volumetric analysis based on the change in conductance of the solution at the equivalent point (or end-point) during titration. In these titration advantage is taken of the facts that the electrical conductance of an aqueous solution containing an electrolyte depends upon:

1. Number of free ions in the solution.
2. The charge on the free ions.
3. Mobility or speeds of the ions.
Debye-Hückel Theory of strong Electrolytes

The Ostwald's dilution law is found to be valid only in case of weak electrolytes. The failure of the law in case of strong electrolytes has been satisfactorily explained both qualitatively as well as quantitatively by Debye-Hückel theory. According to it:

1. All strong electrolyte are completely ionised even in solid state.
2. On melting or dissolution the ions become mobile and mobility depends upon 1. viscosity of medium, 2. the extent of solvation.
3. The ratio $\lambda/\lambda_0$ for strong electrolyte does not represent the degree of ionisation.
4. The increase in $\Lambda$ of strong electrolyte solution on dilution, is due to increase in the mobility of ions.
5. The lower values of mobility of ions in concentrated solutions, in spite of complete dissociation, is due to the:
   a. Relaxation Effect.
   b. Electrophoretic Effect (ionic atmosphere)

\[
\Lambda = \Lambda_0 - (A + B \lambda_0) \sqrt{C}
\]