ELECTRO-CHEMISTRY

Electrolytes are categorized into **two** main types based on their behavior in solution:

Strong Electrolytes: These substances completely dissociate into ions when dissolved in water. Examples include soluble salts like sodium chloride ($NaCl$) and strong acids like hydrochloric acid (HCl).

Weak Electrolytes: These substances partially dissociate into ions when dissolved in water. Examples include weak acids like acetic acid (CH_3COOH) and weak bases like ammonia (NH_3).

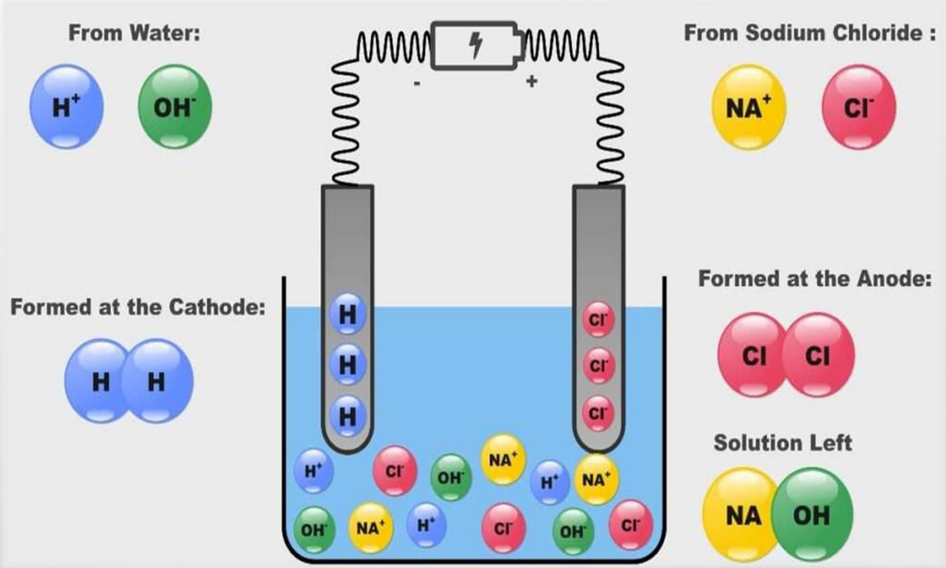
Electrolytes

Electrolytes are substances that break apart into ions (charged particles) when dissolved in water or another solvent or in molten stage.

When certain compounds like salts, acids, or bases dissolve in water, they dissociate into positively and negatively charged ions. These ions can move freely in the solution and carry electrical current. For example, table salt (sodium chloride) dissolves in water to form sodium ions (Na^+) and chloride ions (Cl^-), both of which can conduct electricity.

Mechanism of Electrolytic Conduction

The mechanism of electrolytic conduction involves the movement of ions through a solution or a molten electrolyte under the influence of an electric field. This movement of ions is what allows the electrolyte to conduct electricity.
When an electric field is applied across the electrolyte (for example, by connecting the electrolyte to a battery), the positive ions are attracted to the negative electrode (cathode), while the negative ions are attracted to the positive electrode (anode). This movement of ions towards oppositely charged electrodes is called migration.



Salt Bridge: A salt bridge is a component of an electrochemical cell that helps maintain electrical neutrality by allowing the flow of ions between the half-cells without allowing mixing of the electrolyte solutions.

The transport number (t_i) for a particular ion can be calculated using the ratio of the change in concentration of that ion to the total change in concentration of all ions. Mathematically, it can be expressed as:

$$t_i = (\Delta C_i / \sum \Delta C)$$

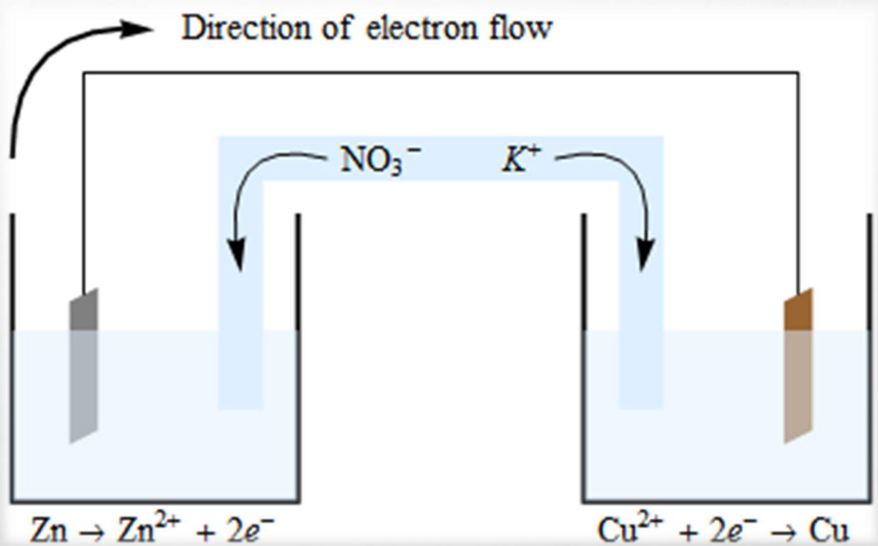
Where:

ΔC_i is the change in concentration of the specific ion.

$\sum \Delta C$ is the total change in concentration of all ions.

Salt Bridge Electrolytic Conduction Mechanism

All ionic salts can be used as electrolyte in a Salt Bridge. But some salts are used as electrolyte in salt bridge which transport number of constituent ions is 1:1. Some salts having 1:1 transport number are KCl, $NaNO_3$, NH_4NO_3, KNO_3 etc.



Considering a reaction as:

$$M + N^{n+} \xrightarrow{ne^-} M^{n+} + N$$

$$\text{So, } E_{cell} = E^{o}_{cell} - (0.059 / n)*\log [\, M^{n+} \,] / [\, N^{n+} \,]$$

Where,

$$RT/F = 0.059$$

EMF Electromotive force refers to the voltage or electrical potential difference generated by a cell or battery when it's supplying current. It represents the driving force that pushes electric charge around a circuit. In an idealized scenario, this EMF would be constant regardless of the current drawn from the cell. However, in real-world situations, factors like internal resistance and chemical reactions within the cell can cause the actual voltage output to vary. The EMF of a cell is typically measured in volts (V).

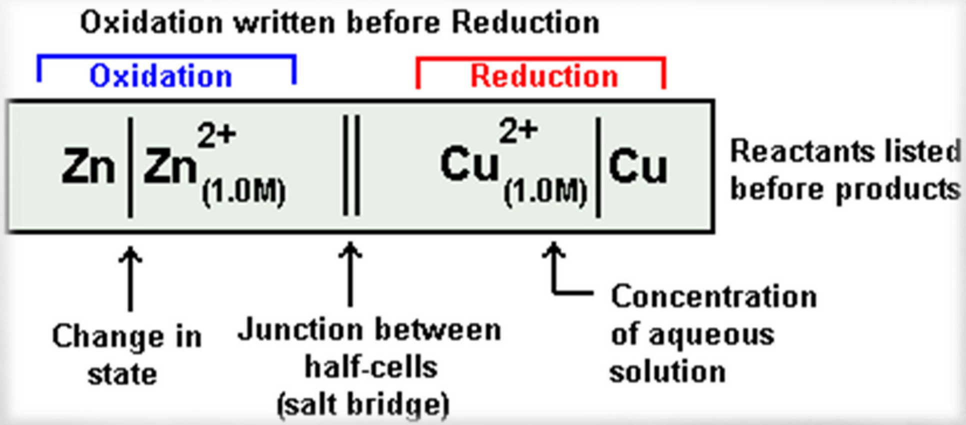
To calculate the electromotive force (EMF) of a cell formed by two different metal electrodes in electrolytic solutions, you can use the **Nernst equation.** The Nernst equation describes the potential difference between two half-cells in an electrochemical cell. Here's the equation:

$$E = E^{\circ} - RT/nF\ln(Q)$$

How to remember the Reactivity Series?

Please	Potassium	Most reactive
Stop	Sodium	
Calling	Calcium	
Me	Magnesium	
A	Aluminium	
Careless	(Carbon)	
Zebra	Zinc	
Instead	Iron	
Try	Tin	
Learning	Lead	
How	(Hydrogen)	
Copper	Copper	
Saves	Silver	
Gold	Gold	Least reactive

How to represent a cell using salt bridge?



CHEMICAL KINETICS AND CHEMICAL EQUILIBRIUM

Factors Determining the Rate: Several factors influence the rate of a chemical reaction. Here are some of the key factors:

Nature of Reactants: Different substances react at different rates. For example, reactions involving highly reactive substances like alkali metals tend to occur very quickly, while reactions involving stable molecules may proceed more slowly.

Concentration of Reactants: Generally, increasing the concentration of reactants leads to an increase in the rate of reaction. This is because higher concentrations result in more collisions between reactant molecules, increasing the likelihood of successful collisions.

Temperature: Increasing the temperature usually increases the rate of reaction. This is due to the fact that higher temperatures provide more kinetic energy to the molecules, resulting in more frequent and energetic collisions between reactant molecules.

Rate of a Reaction:

The rate of a chemical reaction is the speed at which reactants are converted into products. It's typically expressed as the change in concentration of a reactant or product per unit of time.

The general form of a rate equation for a reaction:

$$aA + bB \rightarrow cC + dD$$

So the Rate = $k\ [A]^m[B]^n$

Surface Area: For reactions involving solids, increasing the surface area of the solid reactant can increase the rate of reaction. This is because more surface area allows for more contact between reactant particles, increasing the frequency of collisions.

Catalysts: Catalysts are substances that increase the rate of reaction by providing an alternative reaction pathway with a lower activation energy. They do not get consumed in the reaction and can be used repeatedly.

Presence of Light: In some reactions, particularly photochemical reactions, the presence of light can increase the rate of reaction by providing energy to drive the reaction.

Pressure (for gas-phase reactions): For reactions involving gases, increasing the pressure can increase the rate of reaction. This is because higher pressure increases the concentration of gas molecules, leading to more frequent collisions.

Law of Mass Action:

The law of mass action is a fundamental principle in chemical kinetics that describes the relationship between the concentrations of reactants and the rate of a chemical reaction.

The law of mass action states that the rate of a chemical reaction is directly proportional to the product of the concentrations of the reactants, each raised to the power of their respective stoichiometric coefficients in the balanced chemical equation.

Mathematically, it can be expressed as follows:

For a reaction:

$$aA + bB \rightarrow cC + dD$$

$$\text{Rate} \propto [A]^a [B]^b$$

Where:

$[A]$ and $[B]$ are the concentrations of reactants A and B, respectively.

a and b are the stoichiometric coefficients of reactants A and B, respectively.

If we introduce a proportionality constant (k), we get the rate equation:

$$\text{Rate} = k\,[A]^a [B]^b$$

This equation shows that the rate of reaction is directly proportional to the product of the concentrations of the reactants, each raised to the power of its coefficient in the balanced chemical equation.

The law of mass action provides a conceptual framework for understanding how changes in the concentrations of reactants affect the rate of a reaction and is foundational to the study of chemical kinetics. It forms the basis for rate equations and rate laws that are used to describe and predict the rates of various chemical reactions.

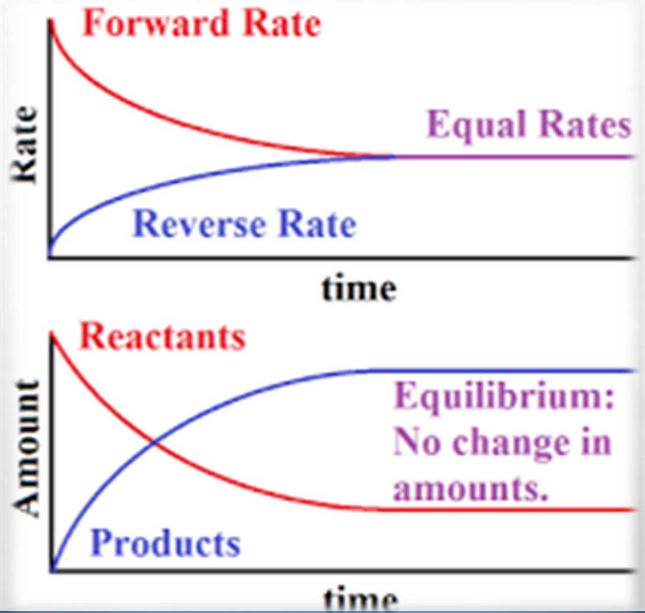
Equilibrium Constant of Reaction

The equilibrium constant (K_{eq}) of a chemical reaction is a key parameter that quantifies the extent of a chemical reaction at equilibrium. It relates the concentrations of reactants and products at equilibrium and helps to predict the direction in which a reaction will proceed under given conditions.

Definition: The equilibrium constant **(K_{eq})** for a reaction **$aA+bB \rightleftharpoons cC+dD$** is defined as the ratio of the concentrations of products to the concentrations of reactants, each raised to the power of its stoichiometric coefficient, at equilibrium:

$$\mathbf{K_{eq}} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Expression: The expression for the equilibrium constant depends on the balanced chemical equation for the reaction. It reflects the stoichiometry of the reaction and is independent of the initial concentrations of reactants and products.
Units: The equilibrium constant does not have units since it is a ratio of concentrations, and concentrations are expressed in moles per liter (M). However, partial pressure units (atm, bar) are used when dealing with gases.
Magnitude: The magnitude of the equilibrium constant provides information about the relative amounts of products and reactants at equilibrium. A large value of K_{eq} (much greater than 1) indicates that the equilibrium favors the formation of products, while a small value (much less than 1) indicates that the equilibrium favors the reactants. A value close to 1 suggests that significant amounts of both reactants and products are present at equilibrium.



Reaction Quotient Comparison: The reaction quotient (Q) can be compared to the equilibrium constant (Keq) to determine the direction in which a reaction will proceed to reach equilibrium. If $Q < K_{eq}$, the reaction will proceed in the forward direction (towards products) to reach equilibrium, while if $Q > K_{eq}$, the reaction will proceed in the reverse direction (towards reactants) to reach equilibrium.

Temperature Dependence: The value of K_{eq} is temperature-dependent. Changes in temperature can alter the equilibrium constant according to the principles outlined in Le Chatelier's Principle.

Equilibrium Position: The equilibrium constant provides information about the position of equilibrium for a given reaction. It does not provide information about the rate at which equilibrium is reached, only about the relative amounts of reactants and products present at equilibrium.

Le Chatelier's Principle:

Le Chatelier's Principle is a fundamental concept that describes how a system or a reaction at equilibrium responds to changes in its conditions. **It states that** if a system at equilibrium is subjected to a change in temperature, pressure, concentration of reactants or products, or volume, the equilibrium will shift in a direction that tends to counteract that change.

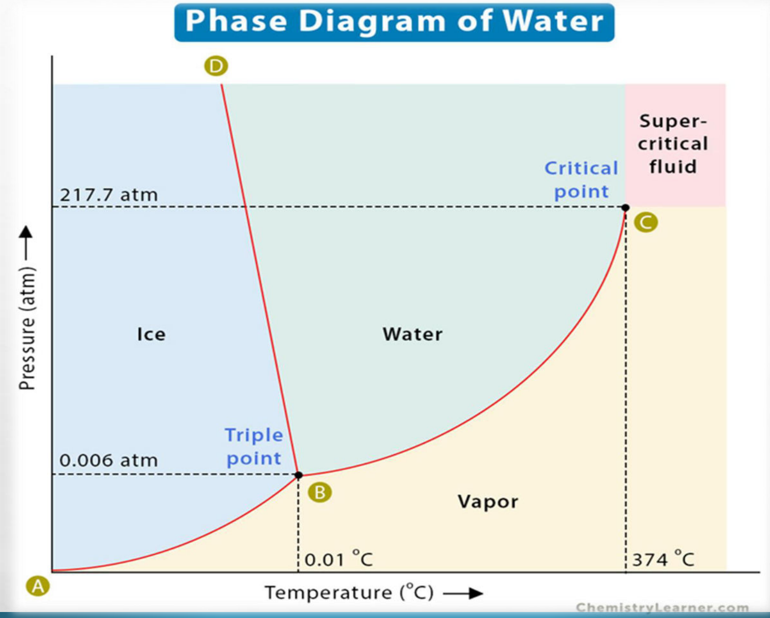
Effect of Concentration Changes: If the concentration of a reactant or product is increased, the equilibrium will shift in the direction that consumes the added substance, effectively reducing its concentration. Conversely, if the concentration of a reactant or product is decreased, the equilibrium will shift in the direction that replenishes the decreased substance.

Effect of Pressure Changes (for gas-phase reactions): If the pressure of a system containing gases at equilibrium is increased, the equilibrium will shift in the direction that reduces the total number of moles of gas. If the pressure is decreased, the equilibrium will shift in the direction that increases the total number of moles of gas.

Effect of Temperature Changes: Changes in temperature can affect the equilibrium position of a reaction depending on whether the reaction is exothermic or endothermic. If the temperature is increased in an exothermic reaction (heat is a product), the equilibrium will shift in the direction that consumes heat (the reactants side) to counteract the increase. Conversely, if the temperature is increased in an endothermic reaction (heat is a reactant), the equilibrium will shift in the direction that produces heat (the products side). The opposite is true if the temperature is decreased.

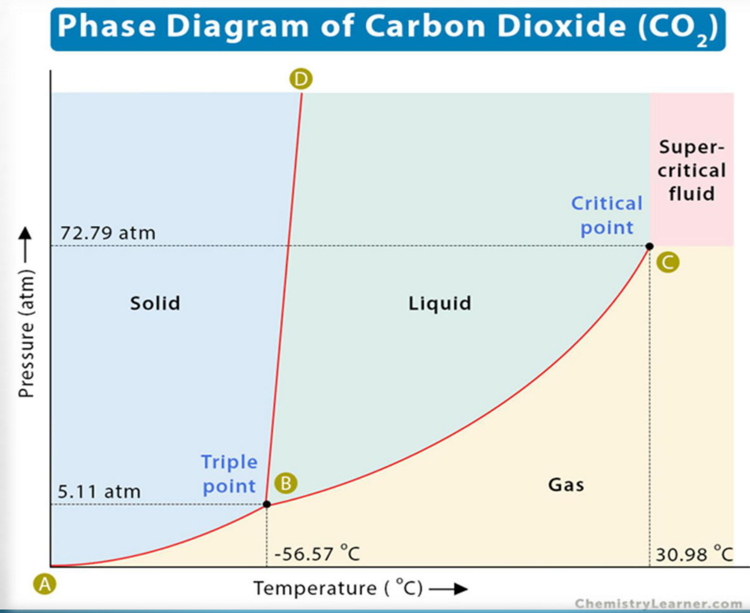
PHASE RULE AND PHASE DIAGRAM OF MONO-COMPONENT SYSTEM

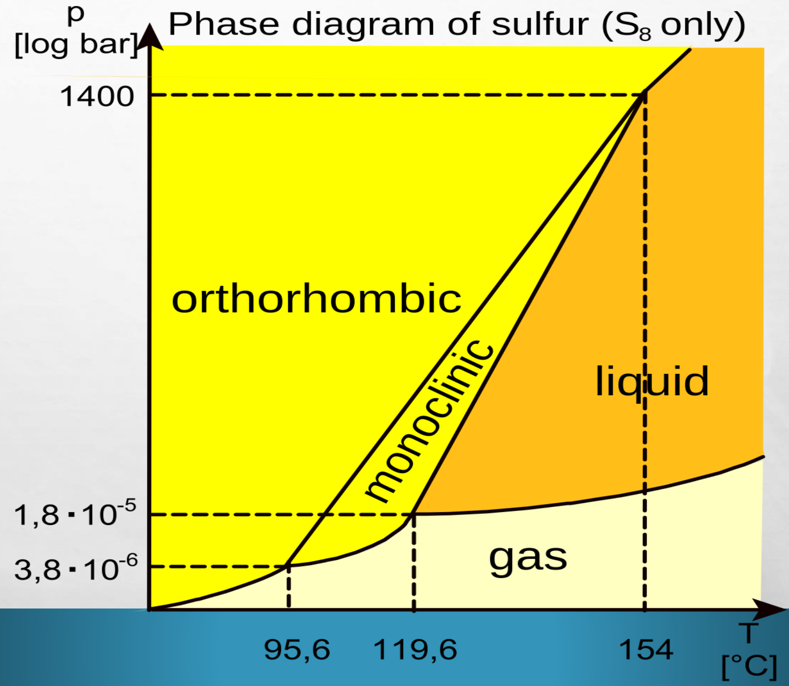
PROPERTIES OF COMPOUNDS WITH TEMPERATURE & PRESSURE



PHASE DIAGRAM

A phase diagram is a graphical representation that shows the equilibrium phases of a substance under different conditions of temperature and pressure. In a phase diagram, the phases typically represented are solid, liquid, and gas. The lines on the diagram represent the conditions at which two phases coexist in equilibrium, such as the melting point or boiling point. Phase diagrams are important tools in understanding the behavior of substances, especially in fields like chemistry, physics, and materials science. They help scientists predict how a substance will behave under various conditions and provide insights into processes like melting, freezing, vaporization, and sublimation.





Gibbs Phase Rule

Named after the American scientist Josiah Willard Gibbs, <u>is a fundamental principle in thermodynamics that relates the number of phases, degrees of freedom, and components in a system at equilibrium.</u> It provides a mathematical framework to understand the conditions under which different phases of matter coexist and the number of variables that can be independently varied while maintaining equilibrium.

The phase rule is expressed as:

$$\mathbf{F = C - P + 2}$$

Where:

F is the degrees of freedom (the number of intensive variables, such as temperature and pressure, that can be independently varied without changing the number of phases in equilibrium).

C is the number of components (chemically independent constituents) in the system.

P is the number of phases in equilibrium.

Degrees of Freedom (F): These represent the number of variables that can be independently varied while still maintaining equilibrium. For example, in a closed container of water (a two-component system - hydrogen and oxygen), the degrees of freedom could be temperature and pressure.

Components (C): These are the chemically independent constituents of the system. For example, a mixture of water and ethanol has two components: water and ethanol.

Phases (P): Phases refer to the distinct forms of matter that are homogeneous in composition and distinct from one another, such as solid, liquid, and gas phases. For example, ice and liquid water represent two phases of water.

Phase Diagrams: The Gibbs phase rule is fundamental in the construction and interpretation of phase diagrams, which graphically represent the equilibrium phases of a substance as a function of temperature, pressure, and composition. Phase diagrams are extensively used in material science, metallurgy, geology, and chemistry to understand phase transitions and predict the behavior of materials under different conditions.

Chemical Equilibrium: In chemical systems involving multiple phases, the Gibbs phase rule helps in determining the number of degrees of freedom and predicting the equilibrium conditions. This is particularly useful in chemical reactions involving multiple phases, such as heterogeneous catalysis and reactions involving gas-liquid or solid-liquid equilibria.

Uses of Gibbs Phase Rule

Engineering Applications: In engineering, the Gibbs phase rule is applied in various processes involving phase transitions, such as distillation, crystallization, and phase separation. Understanding the equilibrium conditions using the phase rule helps engineers optimize processes, design efficient separation units, and control reaction conditions.

Material Design and Processing: In materials science, the Gibbs phase rule is essential for understanding the phase transformations and microstructural evolution in materials during processing, heat treatment, and alloy design. By manipulating temperature, pressure, and composition within the constraints of the phase rule, engineers can tailor material properties to meet specific performance requirements.

Geological Studies: The Gibbs phase rule finds applications in geology for understanding phase equilibria in geological processes such as metamorphism, magma crystallization, and mineral formation. Phase diagrams derived from the phase rule help geologists interpret the conditions under which different mineral assemblages are stable and infer the thermal history of geological formations.

Biological Systems: The principles of the Gibbs phase rule are also applied in biological systems, such as the study of lipid bilayer phase transitions in cell membranes, protein folding, and the behavior of biological fluids under different conditions. Understanding phase equilibria in biological systems is crucial for elucidating cellular processes and designing drug delivery systems.