Higher Secondary
First year
Chemistry Important Laws and Definitions

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Chemistry important laws

Avogadro's Number (NA)
The number of atoms in a 12-g sample of carbon - 12 is called Avogadro's number (to which we give the symbol NA). Recent measurements of this number give the value $6.0221367 \times 10^{23}$, which is $6.023 \times 10^{23}$.

mole
The mole may be defined as the amount of the substance that contains as many specified elementary particles as the number of atoms in 12g of carbon - 12 isotope

Molar mass
The molar mass of a substance is the mass of one mole of the Substance

Empirical Formula
"An empirical formula (or) simplest formula for a compound is the formula of a substance written with the smallest integer subscripts".

Steps for writing the molecular formula
i. Calculate the empirical formula
ii. Find out the empirical formula mass by adding the atomic mass of all the atoms present in the empirical formula of the compound.
iii. Divide the molecular mass (determined experimentally by some suitable method) by the empirical formula mass and find out the value of $n$ which is a whole number.
iv. Multiply the empirical formula of the compound with $n$, so as to find out the molecular formula of the compound.

Stoichiometry
Stoichiometry is the calculation of the quantities of reactants and products involved in the chemical reaction. It is the study of the relationship between the number of mole of the reactants and products of a chemical reaction.
7. In binary compounds of metal and non-metal the metal atom has positive oxidation number while the non-metal atom has negative oxidation number. Example. Oxidation number of K in KI is +1 but oxidation number of I is -1.

8. In binary compounds of non-metals, the more electronegative atom has negative oxidation number, but less electronegative atom has positive oxidation number. Example: Oxidation number of Cl in ClF3 is positive (+3) while that in ICl is negative (-1).

**Oxidation**

"A chemical process in which oxidation number of the element increases".

**Reduction**

"A chemical process in which oxidation number of the element decreases".

**Balancing Redox reaction by Oxidation Number Method**

The various steps involved in the balancing of redox equations according to this method are:

1. Write skeleton equation and indicate oxidation number of each element and thus identify the elements undergoing change in oxidation number.
2. Determine the increase and decrease of oxidation number per atom. Multiply the increase (or) decrease of oxidation number of atoms undergoing the change.
3. Equalise the increase in oxidation number and decrease in oxidation number on the reactant side by multiplying the respective formulae with suitable integers.
4. Balance the equation with respect to all atoms other than O and H atoms.
5. Balance oxygen by adding equal number of water molecules to the side falling short of oxygen atoms.
6. H atoms are balanced depending upon the medium in same way as followed in ion electron method

**Strength**

The Strength of a solution is defined as the amount of the solute in grams, present in one litre of the solution. It is expressed in g L⁻¹.

\[
\text{Strength} = \frac{\text{Mass of solute in grams}}{\text{Volume of solution in litres}}
\]

If X gram of solute is present in V cm³ of a given solution then

\[
\text{Strength} = \frac{X \times 1000}{V}
\]

**Molarity (M)**

Molarity of a solution is defined as the number of gram-moles of solute dissolved in 1 litre of a solution

\[
\text{Molarity} = \frac{\text{No. of moles of solute}}{\text{Volume of Solution in litres}}
\]

If `X` grams of the solute is present in `V` cm³ of a given solution, then,

\[
\text{Molarity} = \frac{X}{1000} \times \frac{\text{Mol. mass}}{V}
\]

Molarity is represented by the symbol M. Molarity can also be calculated from the strength as follows

\[
\text{Strength in grams per litre} = \frac{\text{Molarity}}{\text{Volume of Solution in litre}}
\]

\[
\text{Molarity} = \frac{\text{Strength in grams per litre}}{\text{Molecular mass of the solute}}
\]

**Normality**

Normality of a solution is defined as the number of gram equivalents of the solute dissolved per litre of the given solution.

\[
\text{Normality} = \frac{\text{Number of gram-equivalents of solute}}{\text{Volume of Solution in litre}}
\]
Molality (m)
Molality of a solution is defined as the number of gram-moles of solute dissolved in 1000 grams (or 1 kg) of a Solvent. Mathematically,
Number of moles of solute
Molality = _______________________
Mass of solvent in kilograms

Mole Fraction
Mole fraction is the ratio of number of moles of one component (Solute or Solvent) to the total number of moles of all the components (Solute and Solvent) present in the Solution.

Volumetric Analysis Law
"Equal volume of equinormal solutions exactly neutralise the other solution having same concentration and volume".
\[ V_1 \times N_1 = V_2 \times N_2 \]
V1, V2 - Volume of solutions.
N1, N2 - Strength of solutions.

Determination of equivalent masses of elements
Equivalent masses can be determined by the following methods:
1. Hydrogen displacement method
2. Oxide method
3. Chloride method
4. Metal displacement method

Zeeman effect:
If a substance which gives a line emission spectrum, is placed in a magnetic field, the lines of the spectrum get split up into a number of closely spaced lines. This phenomenon is known as Zeeman effect.

Stark effect:
If a substance which gives a line emission spectrum is placed in an external electric field, its lines get split into a number of closely spaced lines. This phenomenon is known as Stark effect.

Pauli’s exclusion principle
“it is impossible for any two electrons in a given atom to have all the four quantum numbers identical”

Hund’s rule of maximum multiplicity
no pairing occurs until all orbitals of a given sublevel are half filled.

Aufbau Principle
In the ground state of the atoms, the orbitals are filled in order of their increasing energies

Mendeleev’s Periodic Table
“the properties of the elements are the periodic function of their atomic weights”.

modern periodic law
The modern periodic law states that “the physical and chemical properties of the elements are periodic function of their atomic numbers

Shell
an electron in an atom is characterized by a set of four quantum numbers and the principal quantum number (n) defines the main energy level known as the Shell
The p-Block Elements comprise those belonging to groups 13 to 18 and together with the s-block elements are called the Representative Elements or Main Group Elements

atomic or ionic radius
The term atomic or ionic radius is generally defined as the distance between the centers of the nucleus and the outermost shell of electrons in an atom or ion.

Ionization enthalpy.
The energy required to remove an electron from an atom is known as ionization enthalpy (IE)
Electron affinity
In modern terminology, electron affinity is known as the electron gain enthalpy. Electron gain enthalpy is the amount of energy released when an isolated gaseous atom accepts an electron to form a monovalent gaseous anion. The magnitude of EA is influenced by a number of factors such as (i) Atomic size; (ii) Effective nuclear charge; and (iii) Screening effect by inner electrons.

Electronegativity
Electronegativity may be defined as the tendency of an atom in a molecule to attract towards itself the shared pair of electrons.

Uses of duetrium
(i) It is used as a radioactive tracer in chemical research.
(ii) It is used in nuclear fusion reactions.

Conversion of para into ortho hydrogen
Ortho hydrogen is more stable than para hydrogen. The para form is transformed into ortho form by the following methods.
(i) By treatment with catalysts like platinum or iron
(ii) By passing an electric discharge
(iii) By heating to 800°C or more.
(iv) By mixing with paramagnetic molecules like O2, NO, NO2.
(v) By mixing with nascent hydrogen or atomic hydrogen.

Uses of heavy water
1. As a neutron moderator, in nuclear reactors.
2. It is used as a tracer compound in the study of reactions occurring in living organisms.
3. It is used for the preparation of deuterium.

Uses of hydrogen peroxide
i) It destroys bacteria and hence it is used as an antiseptic and germicide for washing wounds, teeth and ears.
ii) It destroys the colour of some organic compounds and is used in bleaching delicate things like hair, wool, silk ivory and feathers.
iii) It is used as an oxidizing agent.
iv) It is also used as a propellant in rockets.

General characteristics of alkali metals
1. The alkali metals are shiny white and soft.
2. They can be readily cut with a knife.
3. They are extremely reactive metals and form strong alkaline oxides and hydroxides.
4. The last metal of this group, francium is radioactive.
5. Since the alkali metals are extremely reactive they occur only as compounds in nature.
6. All the alkali metals exhibit an oxidation state of +1. This is because the metals can easily lose their single outermost electron.
7. The alkali metals give characteristic colour in bunsen flame. The colours given by Li, Na and K are crimson red, yellow, lilac respectively.

Uses of lithium
1) For the manufacture of alloys.
2) As a deoxidizer in the preparation of copper and nickel.
3) Lithium citrate and salicylate are used in the treatment of gout.
4) LiAlH4 is used as a reducing agent.
5) Its compounds are used in glass and pottery manufacture.

Uses of sodium
1) For the preparation of sodium peroxide, sodamide and sodium cyanide, tetraethyl lead etc.
2) Sodium amalgam is employed as a reducing agent.
3) As a deoxidizing agent in the preparation of light alloys and some rare earth metals from their oxides.
4) It acts as a catalyst in the polymerisation of isoprene (C5H3) into artificial rubber.
5) As a reagent in organic chemistry.

**Uses of magnesium**
1) As a purgative
2) In dyeing and tanning processes and in dressing cotton goods.
3) Platinised MgSO4 is used as a catalyst.

**Uses of Gypsum**
It is used
1. For preparing plasters
2. As a retardant for the setting of cement

A ray of light entering such a crystal may split up into two components each following a different path and travelling with a different velocity. This phenomenon is known as **double refraction** solids, in which the crystals are so small that can be recognized only under a powerful microscope, are said to be **microcrystalline**

The smallest structure of which the crystalline solid (or crystal) is built by its repetition in three dimensions is called as unit cell.

Boyle's law,
for given mass of a gas at constant temperature, the pressure (P) is inversely proportional to its volume (V).

**Charle's law**
Given mass of gas, at constant pressure, its volume (V) varies directly as its absolute temperature (T).

**Graham's Law of Diffusion**
When two gases are placed in contact, they mix spontaneously. This is due to the movement of molecule of one gas into the other gas. This process of mixing of gases by random motion of the molecules is called as **diffusion**.

When a gas escapes through a pin-hole into a region of low pressure or vacuum, the process is called **Effusion**

| Kossel-Lewis approach to Chemical Bonding |

In the periodic table, the highly electronegative halogens and the highly electropositive alkali metals are separated by the noble gases.
Therefore one or small number of electrons are easily gained and transferred to attain the stable noble gas configuration.
The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with the gain and loss of an electron by the respective atoms.
The negative and positive ions so formed attains stable noble gas electronic configurations. The noble gases (with the exception of helium which has two electrons in the outermost shell) have filled outer shell electronic configuration of eight electrons (octet of electrons) with a general representation nsnp6.

- The negative and positive ions are bonded and stabilised by force of electrostatic attraction.

**Some important features of lattice enthalpy are:**
- The greater the lattice enthalpy the more stable the ionic bond formed.
- The lattice enthalpy is greater for ions of higher charge and smaller radii.
- The lattice enthalpies affect the solubilities of ionic compounds.

**Fajan's rule**
Fajan points out that greater is the polarization of anion in a molecule, more is covalent character in it. This is **Fajan's rule**.

**Valence Shell Electron Pair Repulsion Theory (VSEPR) Theory**
Pairs of electrons in the valence shell of a central atom repel each other.

- These pairs of electrons tend to occupy positions in space that minimize repulsions and maximise the distance of separation between them.
- The valence shell is taken as a sphere with electron pairs localising on the spherical surface at maximum distance from one another.
iv) A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.

v) Where two or more resonance structures can depict a molecule the VSEPR model is applicable to any such structure.

**Hybridisation**
Dissimilar orbitals like s,p,d with one or many numbers, with nearly the same energy on the same atom may combine or mix completely to form an equal number of equivalent energy new orbitals with properties of their own. This is called as hybridisation of orbitals.

**Co-ordinate or Co-ordinate - Covalent or Dative bond.**
The bond thus formed between the donor and acceptor atoms is called as the **co-ordinate or co-ordinate - covalent or dative bond.**

According to Raoult's law, at constant temperature the vapour pressure of the solution \( p \) is directly proportional to the mol fraction of the solvent \( X_1 \) present in the solution. That is, \( p = kX_1 \) where \( k \) is the proportionality constant.

The lowering of the freezing point of the solution from that of the freezing point of the pure solvent is known as **depression in freezing point of the solution.**

**Cryoscopic constant (or) Molal Freezing Point Depression Constant.**
`\( K_f \)` is defined as the depression in freezing point produced when one mole of solute is dissolved in 1 kg solvent. It is also the depression in freezing point of one molal solution.

**Molal Boiling Point Elevation Constant** or **Ebulloscopic Constant.**
It is defined as the elevation of boiling point of one molal solution.

**Osmotic pressure**
It is the minimum external pressure which must be applied on solution side in order to prevent osmosis if separated by a solvent through a semi permeable membrane.

- A solution having lower or higher osmotic pressure than the other is said to be hypotonic or hypertonic respectively in respect to other solution.
- Two solutions of different substances having same osmotic pressure at same temperature are said to be isotonic to each other. They are known as isotonic solutions.

**System**
Thermodynamically a system is defined as any portion of matter under consideration which is separated from the rest of the universe by real or imaginary boundaries.

**Surroundings**
Everything in the universe that is not the part of system and can interact with it is called as surroundings.

**Boundary**
Anything (fixed or moving) which separates the system from its surroundings is called boundary.

**Types of systems**
In thermodynamics different types of systems are considered, which depends on the different kinds of interactions between the system and surroundings.

**Isolated system**
A system which can exchange neither energy nor matter with its surroundings is called an isolated system. For example, a sample in a sealed thermos flask with walls made of insulating materials represents an isolated system (Fig.12.1).

**Closed system**
A system which permits the exchange of energy but not mass, across the boundary with its surroundings is called a closed system.
For example: A liquid in equilibrium with its vapours in a sealed tube represents a closed system since the sealed container may be heated or cooled to add or remove energy from its contents while no matter (liquid or vapour) can be added or removed.

**Open system**
A system is said to be open if it can exchange both energy and matter with its surroundings.
For eg. a open beaker containing an aqueous salt solution represents open system. Here, matter and heat can be added or removed simultaneously or separately from the system to its surroundings. All living things (or systems) are open systems because they continuously exchange matter and energy with the surroundings.

**Homogeneous and Heterogeneous systems**
A system is said to be **homogeneous** if the physical states of all its matter are uniform. For eg. mixture of gases, completely miscible mixture of liquids etc.
A system is said to be **heterogeneous**, if its contents does not possess the same physical state. For eg: immiscible liquids, solid in contact with an immiscible liquid, solid in contact with a gas, etc.

The **initial state** of system refers to the starting state of the system before any kind of interaction with its surroundings.
The **final state** of system refers to the state after the interaction of system with its surroundings. A system can interact with its surroundings by means of exchange of matter or heat or energy or all.

A system which satisfies the conditions of thermal, mechanical and chemical equilibria and contains the macroscopic properties which are independent of time is said to be in **thermodynamic equilibrium**.

**Isothermal process** is defined as one in which the temperature of the system remains constant during the change from initial to final states. During the isothermal process, the system exchanges heat with its surroundings and the temperature of system remains constant.

**Adiabatic process** is defined as that one which does not exchange heat with its surroundings during the change from initial to final states of the system.

**Isobaric process** is that process in which the pressure of the system remains constant during its change from the initial to final state.

**Isochoric process** shows no change in volume of system during its change from initial to final state of the process.

**Cyclic process:** The process which brings back the system to its original or initial state after a series of changes is called as cyclic process.

**Spontaneous process** are those that occur on their own accord. For example heat flowing from a hotter end of a metal rod to a colder end. In these processes, the transformation of the system from initial, to final state is favourable in a particular direction only. Many of the spontaneous processes are natural processes and are also, irreversible processes.

**Non-spontaneous process** are those that does not occur on their own accord. For example, although carbon burns in air evolving heat to form carbon dioxide, on its own carbon does not catch fire and an initial heat supply is required. Since many of the non-spontaneous processes are slow processes, they also exist as equilibrium processes.

**Reversible process**. In a reversible process the series of changes carried out on the system during its transformation from initial to final state may be possibly reversed in an exact manner.

The **state functions** considered in a gaseous system like, P, V and T are called as state variables. A **state function** is a thermodynamic property of a system which has a specific value for each state of the system and does not depend on the path (or manner) in which a particular state is reached. Other than P,V,T there are other important thermodynamic properties existing as
state functions like internal energy (U), enthalpy (H), free energy (G) etc. (The properties of U, H and G are to be studied later).

A path function is a thermodynamic property of the system whose value depends on the path or manner by which the system goes from its initial to final states. It also depends on the previous history of the system.

For example, work (w) and heat (q) are some of the thermodynamic properties of the system that are path functions. Their values change when there is a change in manner in which the system goes from initial to final states.

**Zeroth law of thermodynamics**

`If two systems at different temperatures are separately in thermal equilibrium with a third one, then they tend to be in thermal equilibrium with themselves'.

**i) Gravitational work**

This work is said to be done when a body is raised to a certain height against the gravitational field. If a body of mass 'm' is raised through a height 'h' against acceleration due to gravity 'g', then the gravitational work carried out is `mgh`. In this expression, force is `mg` and the distance is `h`.

**ii) Electrical work**

This type of work is said to be done when a charged body moves from one potential region to another. The electrical work is Q .V. if V is the potential difference causing the quantity of electricity 'Q' during its movement.

**iii) Mechanical work**

This type of work is associated with changes in volume of a system when an external pressure is applied or lowered. This pressure-volume work is also referred to as the mechanical work.

**First law of thermodynamics**

"Energy may be converted from one form to another, but cannot be created or be destroyed".

"Energy of an isolated system must remain constant although it may be changed from one form to another".

(ii) "The change in the internal energy of a closed system is equal to the energy that passes through its boundary as heat or work".

(iii) "Heat and work are equivalent ways of changing a system's internal energy".

(iv) "Whenever other forms of energies are converted into heat or vice versa there is a fixed ratio between the quantities of energy and heat thus converted".

**Characteristics of H**

Enthalpy, H depends on three state functions U, P, V and hence it is also a state function. H is independent of the path by which it is reached. Enthalpy is also known by the term ‘heat content’

The enthalpy change of neutralisation is defined as the enthalpy change accompanied by the complete neutralisation of one gram-equivalent amount of a strong acid by a gram-equivalent amount of strong base under fully ionised state in dilute conditions.

Reactions which never proceed to completion in both forward and backward direction are called as **Equilibrium reactions**

A reaction which can go in the forward and backward direction simultaneously under the same conditions, is called a **reversible reaction**

The general definition of the equilibrium constant may thus be stated as: The product of the equilibrium concentrations of the products divided by the product of the equilibrium concentrations of the reactants, with each concentration term raised to a power equal to the coefficient of the substance in the balanced equation.

**Factors influencing reaction rates**

There are number of factors which influence the rate of the reaction.

These are:

(i) Nature of the reactants and products
(ii) Concentration of the reacting species
(iii) Temperature of the system
(iv) Presence of catalyst
(v) Surface area of reactants
(vi) Exposure to radiation

**Rate law**
According to concepts of chemical kinetics, the rate of the reaction is proportional to the product of the initial concentration of all the reactants with each reactant concentration raised to certain exponential powers.

**Second order reaction**
A reaction is said to be second order if its reaction rate is determined by the variation of two concentration terms or square of a single concentration term.

**Third order reactions**
A reaction is said to be third order if its rate is determined by the variation of three concentration terms.

**Catenation**
The tendency of atoms of an element to unite with each other forming a chain of covalent bond is known as catenation.

**Lassaigne's Test**
The organic compound is taken in an ignition tube. A pea-size sodium metal is added to it and heated to red hot. The hot tube is crushed to a powder under a few ml of water in a mortar. The solution is filtered and the filtrate is known as 'sodium extract' or 'lassaigne's filtrate'. The filtrate is used for the detection of the elements.