01. What is electron? What are the characteristics of electron and proton?

Answer:

Electron: Electron is the smallest particle of all sub atomic particles.

Characteristics:

1. Electron: It was discovered by Thomson in 1897. Its mass is 9.1×10^{-8} g which is equal to the $\frac{1}{1835}$ th of a hydrogen atom. It has a negative charge and it is -1.6×10^{-19} coulomb.
2. Proton: E. Goldstein (1886) discovered protons in the discharge tube containing hydrogen. The actual mass of proton is 1.672×10^{-24} g. Proton carries a charge $+1.60\times10^{-19}$ coulomb. Proton has mass 1 atomic mass unit (amu).

03. Write the postulates of Rutherford atomic model and its limitation?

Answer:

Postulates:

The atom model that Rutherford proposed in 1911 is very much similar to our solar system. For this reason it is called Rutherford's solar system atom model. The major propositions of the models are:

1. All atoms are very small round shaped particle which has two parts. One is nucleus and another is outer empty space of nucleus.
2. An atom consists of a small nucleus which contains the entire mass of the atom. The size of nucleus is very small compared to the size of atom.
3. The entire positive charge of the atom is located in the nucleus while electrons are distributed in vacant space around it.

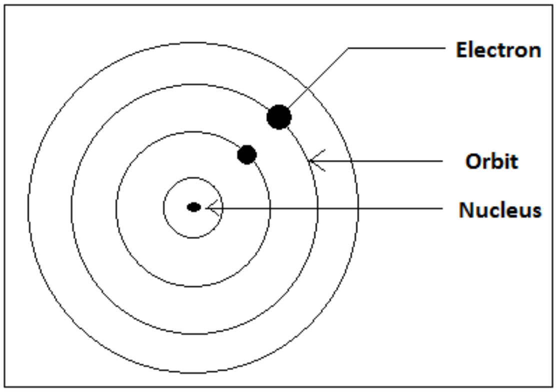


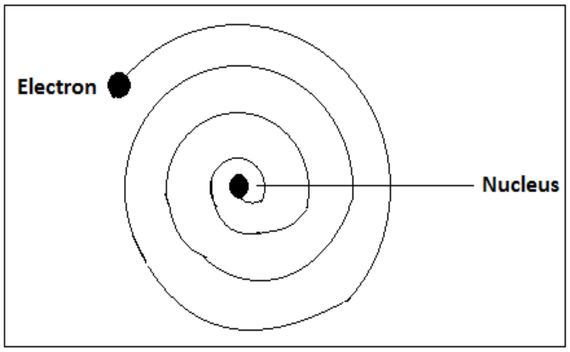
Figure 1: Electrons keep revolving in orbits around the nucleus.

4. The electrons are in constant motion around the nucleus like the planets which move around the sun.
5. The number of positive charge in the nucleus is equal to the number of negative charge possessed by electrons moving around the nucleus. For this every atom is electrically neutral.
6. Two equal and opposite force act on the moving electrons. They are the electrostatic force of attraction between the electron and positive nucleus and centrifugal force due to the motion of electrons acting between nucleus and electrons. These two forces are equal and opposite.

Limitations:

There are some difficulties in the model of Rutherford which are stated below:

1. Rutherford atom model is based on the solar system. But the planets in the solar system are electrically neutral and only the gravitational force act between them. But the electrons, which move around the positive nucleus are negatively charged and they repel each other.
2. According to Maxwell the charged electrons are supposed to emit energy continuously and in this way of losing energy they will move in a spiral way and fall to the nucleus. It happens that Rutherford's model becomes meaningless.
3. As this radiation is continuous, the spectrum of the atom should have continuous lines, which should look like a wide band. But these likes are discontinuous and very bright.



4. Rutherford did not give any idea about shape or size of the orbits-pattern in which the electrons move around the nucleus.
5. This model does not mention how electrons will move in an atom having large number of electrons.

05. Write down the characteristics of Alpha, Beta, Gamma particle and α-decay.

Answer:

Alpha particle:

1. The relative charge of α-paritcle is (+2).
2. The relative mass is 4.
3. Nature of a α-particle is bi-positive nucleus i.e. He^{2+}.
4. The penetrating power of a α-particle is low.

Beta particle:

1. The relative charge of β-particle is (-1).
2. The relative mass of β-particle is 0.
3. Nature of a β-particle is nonnegative electrons.
4. The penetrating power of a β-particle is 1000 times from α-particle.

Gamma particle:

1. The relative charge of γ-particle is 0.
2. The relative mass of γ-particle is 0.
3. Nature of a γ-particle is electromagnetic waves.
4. The penetrating power is 10000 times from α-particle.

α-decay:

1. α-ray is denoted by$^{4}_{2}He$.
2. Heavy particle.
3. Positive charged particle.
4. α-particles are double ionized helium atom i.e. He^{2+}.
5. Velocity low.

07. Write the postulates and limitation of Bohr's atomic model.

Answer:

Postulates:

In order to overcome the limitations of Rutherford's atom model Neil's Bohr in 1913 modified the Rutherford model. The Bohr atomic model is stable and correctly correlates the atomic structure and spectral phenomenon of atoms. The Bohr's atomic model is based on certain basic postulates as stated below:

1. **Postulate concerning energy level:** An electron rotates around the nucleus in circular orbits of definite energy. While rotating in an orbit an orbit an electron does not absorb any energy. These orbits are called energy levels and each energy level has a definite and foxed energy. These energy levels are denoted by n where n= 1,2,3,……….
2. **Postulate concerning angular momentum:** the permissible orbits are those for which the angular momentum of the electron is an integral multiple of $\frac{h}{2\pi}$.

   The angular momentum, mvr = n.$\frac{h}{2\pi}$, where n= 1,2,3,etc.

   h = Planck's constant, m= mass of an atom and r= distance of an electron from the nucleus.

   The quantity n is called the principal quantum number. It also represents the serial number of allowed orbits in order of increasing distance from the nucleus.
3. **Postulate concerning radiation of energy:** The atoms emit or absorb energy when the electron jumps from one orbit to another. If an electron jumps from higher energy level to lower energy level, then it radiates energy. On the other hand if an electron jumps from lover energy level to higher energy level, then it absorbs energy. The energy emitted is the difference between the energies of the two level such that, hv= E_2-E_1, where, v is the frequency of emitted radiation and h is Planck's constant.

Limitations:

1. Bohr's model can explain the spectra of H atom which has only one electron but it can't explain the spectral lines of atoms with many electrons.

2. According to Bohr's model when an electron jumps from one energy level to another, a single line is supposed to appear on the spectra. When a spectrograph is developed with high resolving power, there are two or more lines very close together observed. Bohr's atom model gives no explanation on this.

Bohr's theory fails to recognize the wave property of electron which has established by De-Broglie.

09. Why $^{19}_{8}O$ undergoes β emission reaction?

Answer: Oxygen is very well known and stable oxygen-18 isotope is by far the most occurring oxygen isotope. The oxugen-19 isotope is however not stable and it decays under emission of beta radiation which can be written as follows:

$$^{19}_{8}O \longrightarrow\ ^{19}_{9}F + {}^{0}_{-1}e$$

One of the neutrons in the oxugen-19 nucleus us transformed into a proton and an electron. The electron is emitted as beta radiation and because of the extra proton, the nucleus is now a fluorine nucleus with a total of 19 nucleons. For the oxugen-19, the electron is not a nucleon and its mass is extremely small relative the mass of protons and neutrons. The oxygen-19 isotope decays into a fluorine-19 isotope. Thus $^{19}_{8}O$ undergoes β emission reaction.

10. What is quantum number? Discuss the significant of four quantum numbers. Write the value of four quantum number for the last electron of Na.

Answer:

Quantum Number: The number which expresses the size, shapes and direction of the orbital from the nucleus and the spin of the electron of their own axes, are called quantum numbers.

There are four types of quantum number.

1. Principal quantum number (n)
2. Subsidiary quantum number (l)
3. Magnetic quantum number (m)
4. Spin quantum number (s)

Significance of four quantum numbers:

1. **Principal quantum number:** This expresses the orbit or principal energy level to which the electron belongs and represents the average distance of the electron from the nucleus. It is denoted by n. for the 1st orbit n=1, for the 2nd orbit n=2 etc.
2. **Subsidiary quantum number:** This expresses sub-levels and the shapes of the energy level. It is denoted by l. the value of l=0 to (n-1). When n=1 then l=0; so the 1st energy level has 1 sub shell.
3. **Magnetic quantum number:** This expresses the direction of the sub-shell of the orbital from the nucleus in three-dimensional spaces. This number is designated as 'm'. The value of m is $m=\pm l$, including 0.
4. **Spin quantum number:** The spin quantum number represents the direction of the electron's spin. This quantum number is designated as s. $s=+\frac{1}{2}$ or $s=-\frac{1}{2}$.

The value of four quantum numbers for the last electron of Na:

The electronic configuration of Na is,

$$Na(11) = 1s^2\ 2s^2\ 2p^6\ 3s^1$$

For the last electron of Na atom, the principal quantum number n=3

So, the subsidiary quantum number l= 0 to (n-1) that is l= 0,1,2

The magnetic quantum number $m= \pm l$, including 0.

i.e. m= -2,-1,0,+1,+2

Spin quantum number, s= $+\frac{1}{2}$ or $-\frac{1}{2}$

12. Prove that the distance of 1st level of Helium is half of the distance of 1st level for hydrogen atom.

Answer: Consider an electron of charge 'e' revolving around a nucleus of charge 'Ze' where Z is the atomic number and e is the charge of a proton.

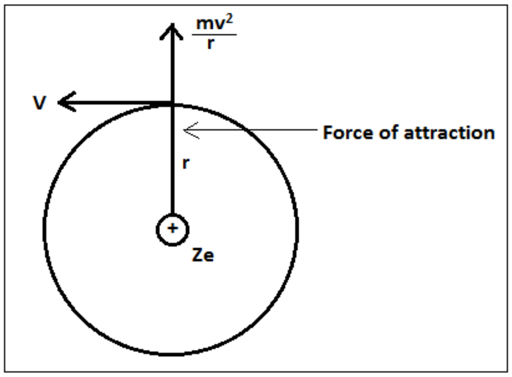
Let m be the mass of the electron, r be the radius of the orbit and v be the tangential velocity of the revolving electron.

The electrostatic force of attraction between nucleus and the electron,

$$F_e = \frac{Ze.e}{r^2}$$

The centrifugal force acting on the electron,

$$F_C = \frac{mv^2}{r}$$



Now, $F_e = F_C$

or, $\frac{Ze^2}{r^2} = \frac{mv^2}{r}$

or, $\frac{Ze^2}{r} = mv^2 \xrightarrow{\hspace{3cm}} (1)$

According to Bohr's 2nd postulate, the angular momentum,

$$mvr = \frac{nh}{2\pi}$$

or, $v = \frac{nh}{2\pi mr}$

Substituting the value of v in equation (1)

$$\frac{Ze^2}{r} = m\left(\frac{nh}{2\pi mr}\right)^2$$

or, $\frac{Ze^2}{r} = \frac{mn^2h^2}{4\pi^2m^2r^2}$

or, $\frac{Ze^2}{r} = \frac{n^2h^2}{4\pi^2mr^2}$

or, $Ze^2 = \frac{n^2h^2}{4\pi^2mr}$

$\therefore r = \frac{n^2h^2}{4\pi^2mZe^2} \longrightarrow (2)$

For Helium, n=1, Z=2

$\therefore r_{He} = \frac{1^2h^2}{4\pi^2m2e^2} = \frac{h^2}{2X4\pi^2me^2}$

For hydrogen, n=1, Z=1

$\therefore r_H = \frac{1^2h^2}{4\pi^2m1e^2} = \frac{h^2}{4\pi^2me^2}$

$\therefore r_{He} = ½ \times r_H$

(Proved)

15. Why the last electron of K occupies the 4s orbital rather than 3d orbital? Explain.

Answer: According to Aufbaw's law electron go to different orbital according to their increasing energy. Electron first go to the orbital of low energy and then systematically to the orbital of higher energy.

The orbital, which has lower value of (n+l) has the lower energy and higher value of (n+l) has higher energy. Here, n=principal quantum number and l=subsidiary quantum number. This entering of electron depends on the value of (n+l) and electrons will enter first where the value of (n+l) is lower.

For the K atom, the electron configuration of K is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$. As for the 4s orbital,
The value of , n=4 and the value of l=0

∴ The total value of (n+l)=4+0=4.

Again for the 3d orbital, n=3 and l=2

∴ The total value of (n+l)= 3+2=5

So, K(19)= $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^1$ (Wrong)

K(19)= $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^0\,4s^1$ (Right)
So, the last electron of K occupies the 4s orbital rather than 3d orbital.

16. Prove that the distance of energy level of an element increase with increasing the value of principal quantum number.

Answer: Consider an electron of charge 'e' revolving around a nucleus of charge 'Ze' where Z is the atomic number and e is the charge of a proton.

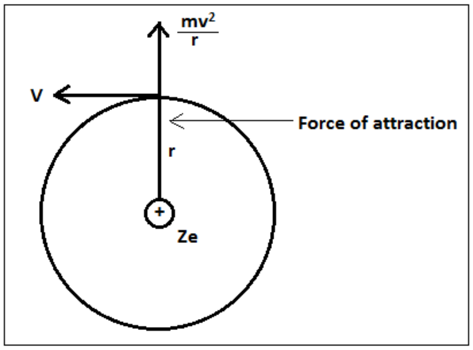
Let m be the mass of the electron, r be the radius of the orbit and v be the tangential velocity of the revolving electron.

The electrostatic force of attraction between nucleus and the electron,

$$F_e = \frac{Ze.e}{r^2}$$

The centrifugal force acting on the electron,

$$F_C = \frac{mv^2}{r}$$



Now, $F_e = F_C$

or, $$\frac{Ze^2}{r^2} = \frac{mv^2}{r}$$

or, $\frac{Ze^2}{r} = mv^2 \xrightarrow{\hspace{4cm}} (1)$

According to Bohr's 2nd postulate, the angular momentum,

$$mvr = \frac{nh}{2\pi}$$

or, $v = \frac{nh}{2\pi mr}$

Substituting the value of v in equation (1)

$$\frac{Ze^2}{r} = m(\frac{nh}{2\pi mr})^2$$

or, $\frac{Ze^2}{r} = \frac{mn^2h^2}{4\pi^2m^2r^2}$

or, $\frac{Ze^2}{r} = \frac{n^2h^2}{4\pi^2mr^2}$

or, $Ze^2 = \frac{n^2h^2}{4\pi^2mr}$

$\therefore r_n = \frac{n^2h^2}{4\pi^2mZe^2} \xrightarrow{\hspace{4cm}} (2)$

Where r_n= radius or distance of energy level and $\frac{h^2}{4\pi^2mZe^2}$ is constant=K, n=1,2,3……….etc.

$\therefore$ From equation (2),

$$r_n = K.n^2$$

or, $r_n \propto n^2$

(Proved)

17. Derive the energy expression for an electron moving in the nth orbit of hydrogen(H) atom.

Answer: Consider an electron of charge 'e' revolving around a nucleus of charge 'Ze' where Z is the atomic number and e is the charge of a proton.

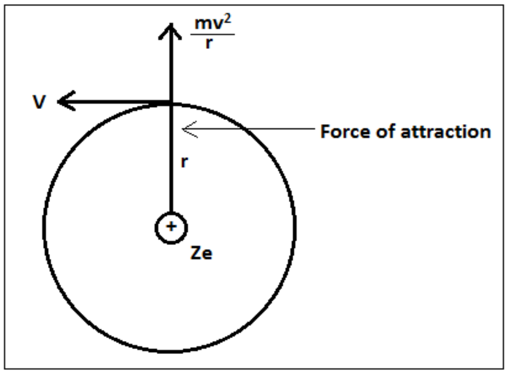
Let m be the mass of the electron, r be the radius of the orbit and v be the tangential velocity of the revolving electron.

The electrostatic force of attraction between nucleus and the electron,

$$F_e = \frac{Ze.e}{r^2}$$

The centrifugal force acting on the electron,

$$F_C = \frac{mv^2}{r}$$



Now, $F_e = F_C$

or, $$\frac{Ze^2}{r^2} = \frac{mv^2}{r}$$

For hydrogen, Z=1, therefore,

$$\frac{e^2}{r^2} = \frac{mv^2}{r}$$

or, $$\frac{e^2}{r} = mv^2 \longrightarrow (1)$$

According to Bohr's 2nd postulate, the angular momentum,

$$mvr = \frac{nh}{2\pi}$$

or, $$v = \frac{nh}{2\pi mr}$$

Substituting the value of v in equation (1)

$$\frac{e^2}{r} = m(\frac{nh}{2\pi mr})^2$$

or, $$\frac{e^2}{r} = \frac{mn^2h^2}{4\pi^2m^2r^2}$$

or, $\frac{e^2}{r} = \frac{n^2h^2}{4\pi^2mr^2}$

or, $e^2 = \frac{n^2h^2}{4\pi^2mr}$

$\therefore r = \frac{n^2h^2}{4\pi^2me^2}$; which is the expression for radius of orbit.

$E_n = K.E + P.E$

$= \frac{1}{2} mv^2 - \frac{e^2}{r}$

$= \frac{1}{2} \frac{e^2}{r} - \frac{e^2}{r}$ [from (1)]

$$\therefore En = -\frac{e^2}{2r} \longrightarrow (2)$$

We know, $r = \frac{n^2h^2}{4\pi^2me^2}$

Substituting the values of 'r' in equation (2)

$E = - e^2/ 2(\frac{n^2h^2}{4\pi^2me^2})$

$$= - \frac{2\pi^2me^4}{n^2h^2} \longrightarrow (3)$$

The energy of the electron in orbit n_1(lower) and n_2(higher) is

$E_{n1} = - \frac{2\pi^2me^4}{n_1{}^2h^2}$

$E_{n2} = - \frac{2\pi^2me^4}{n_2{}^2h^2}$

$\therefore$ The difference of energy between two level,

$$\Delta E = E_{n2}-E_{n1} = \frac{2\pi^2me^4}{h^2} [\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2}]$$

18. Derive the energy equation for spectrum line of an electron.

Answer: Now, suppose that an electron jumps from a higher energy level n_2 with energy E_2 to a lower energy level n_1 whose energy E_1. So that,

In S.I. unit,

$$\Delta E = E_2 - E_1$$

$$\text{or,} \quad \Delta E = \frac{me^4}{8h^2\varepsilon_\circ^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\text{or,} \quad h\nu = \frac{me^4}{8h^2\varepsilon_\circ^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\text{or,} \quad \nu = \frac{me^4}{8h^3\varepsilon_\circ^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Again, we know that, $1/\lambda = \bar{\nu} = \frac{\text{frequency}(\nu)}{\text{velocity of light (c)}}$

$$\text{or,} \quad \bar{\nu} = \nu/c$$

$$\text{or,} \quad \bar{\nu} = \frac{me^4}{8h^3\varepsilon_\circ^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\text{or,} \quad \bar{\nu} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Here, R_H is Rydberg's constant.

This is the energy equation for a spectral line.

Lymen series: $n_1=1$; $n_2= 2,3,4,\ldots\ldots\ldots\ldots\ldots\infty$

Balmer series: $n_1=2$; $n_2= 3,4,5,\ldots\ldots\ldots\ldots\ldots\infty$

Paschen series: $n_1=3$; $n_2= 4,5,6,\ldots\ldots\ldots\ldots\ldots\infty$

Brackett series: $n_1=4$; $n_2= 5,6,7,\ldots\ldots\ldots\ldots\ldots\infty$

Pfund series: $n_1=5$; $n_2= 6,7,8,\ldots\ldots\ldots\ldots\ldots\infty$

20. What is solution? Classify the solution?

Answer:

Solution: A solution is a homogeneous mixture of two or more substances whose composition can be changed within certain limit and the size of the particle of the components will be less than 10^{-7} cm.

Classification: Solution may be classified in various way-

1. **Liquid solution:** Sugar in water, alcohol in water, CO_2 in water etc.
2. **Solid solution:** Alloys of metals such as bronze, bronssze, steel etc.
3. **Gaseous solution:** Air liquid solution of divided into three classes-
   a) Solid in liquid: Glucose in water.
   b) Liquid in liquid: Methanol in water.
   c) Gas in liquid: CO_2 in water.

21. What is the relation between molarity and temperature?

Answer: The molarity of a solution is the number of moles of the solute present in one litre of the solution. In case of molarity it is a volumetric calculation with the rise of temperature, the volume increase while with the fall of temperature the volume decreases. So the molarity varies at different temperature. Now we can write the volume of molarity is proportional to the temperature.

23. What is the strength of 1M H_2SO_4?

Answer: We know, the molar mass of H_2SO_4 is 98. So, 1 mole H_2SO_4 = 98g H_2SO_4. If one litre of a solution contains 98g H_2SO_4 then it is a molar solution of H_2SO_4. It will be expressed as 1M H_2SO_4.

24. What is colligative property? What are the colligative properties?

Answer:

Colligative property: The properties which depend on the number of particles in solution and not in any way on the size or chemical nature of the particles are known as colligative properties.

Dilute solutions containing non-volatile solute exhibit the following properties-

- (i) Lowering of the vapour pressure
- (ii) Elevation of the boiling point
- (iii) Depression of the freezing point
- (iv) Osmotic pressure

26. State Raoult's law.

Answer: The relative lowering of the vapour pressure of a solvent of solution is equal to the mole fraction of the solute.

Let, the vapour pressure of the solvent p^o and vapour pressure of solution is p; the number of moles of solvent n_A and n_B is the number of moles of solute. According to Raoult's law-

The decrease of vapour pressure of solution= mole fraction of the solute.

But mole fraction of solute, $X_B = \frac{n_B}{n_B+n_A}$

or, $\frac{\text{lowering or decrease in V.P.of solution}}{\text{V.P. in solvent}} = \frac{n_B}{n_B+n_A} = X_B$

or, $\frac{p^\circ-p}{p^\circ} = \frac{n_B}{n_B+n_A} = X_B$

or, $1-\frac{p^\circ-p}{p^\circ} = 1-X_B$

or, $\frac{p^\circ - p^\circ + p}{p^\circ} = X_A$ $[\because X_A + X_B = 1]$

or, $\frac{p}{p^\circ} = X_A$

or, $p = p^o X_A$

since p^o is a constant at particular temperature, therefore $p \propto X_A$.

So, vapour pressure of a solution is directly proportional to the mole fraction of the solvent.

28. State Faraday's law.

Answer:

Faraday's 1st law of electrolysis: The amount of a substance (in gram) deposited at or dissolved from an electrode during electrolysis, is directly proportional to the quantity of electricity passed through the electrolyte.

If w gram is deposited or dissolved due to flow of Q coulomb of electricity, then according to Faraday's 1st law-

$w \propto Q$

or, $w = ZQ$

But we know that $Q = It$

$\therefore$ $w = Zit$

where, Z = electrochemical equivalent

I = amount of current in ampere

t = time in second

when, $I = 1$ amp, $t = 1$sec then $Q = 1 \times 1 = 1$ coulomb

$\therefore$ $w = Z$

Faraday's 2nd law of electrolysis: The second law states that, when the same amount of electricity is passed through solution of different electrolytes, the amount of different substances deposited from different electrolytes at the cathode are directly proportional to their chemical equivalents.

Chemical equivalent is defined as the gram of atom of the substance deposited by its valency.

That is, $E = \frac{\text{gram atom of an element}}{\text{valency of that element}}$

Now, if Z is the electrochemical equivalent of a substance deposited or dissolved by 1 coulomb of electricity, then

$$Z = \frac{E}{96500} = \frac{E}{F} \quad (F = 96500C)$$

From 1st law of electrolysis we know that,

$$W = Zit$$

or, $w = \frac{E}{F} It = \frac{EIt}{96500}$

or, $w \propto E$, since it is constant

or, $w = kE$

or, $\frac{w}{E} = k$

If w_1, w_2, w_3,………. are grams of substances dissolved of various substances having chemical equivalents E_1, E_2, E_3,……… respectively then form the 2nd law we get,

$$w_1 : w_2 : w_3 = E_1 : E_2 : E_3$$

or, $\frac{w_1}{w_2} : \frac{w_2}{w_3} = \frac{E_1}{E_2} : \frac{E_2}{E_3}$

or, $\frac{w_1}{w_2} = \frac{E_1}{E_2}$ or, $\frac{w_2}{w_3} = \frac{E_2}{E_3}$

or, $\frac{w_1}{E_1} = \frac{w_2}{E_2} = \text{-------------} = \frac{Wn}{En}$

That means the amount of substances deposited at the cathode divided by their chemical equivalent should be constant.

31. What is the relation between electrode potential and concentration of electrolytes?

Answer: At a definite temperature the potential of an electrode depends on the concentration of accompanying electrolyte solution. Let, in a electrochemical cell the following reversible reaction is occurred.

$$xA(s) + yB^{+}(aq) \rightleftharpoons xA+(aq) + yB(s)$$

By adjusting the catalysts of the reaction for electrochemical cell Nernest establish a equation and the equation is-

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln \frac{[A^{+}]^{x}}{[B^{+}]^{y}}$$

Here, E_{cell} = Cell potential

T = Absolute temperature

$[\ ]$ = Concentration

E°_{cell} = standard cell potential

F = Flowing electricity (Faraday)

n = Transformed number of moles of electron in a reaction

This is the relation between electrode potential and concentration of electrolytes.

32. What is chemical kinetics and reaction rate?

Answer:

Chemical kinetics: The branch of physical chemistry which deals with the rate of reaction and factors upon which rate of reaction depends is called chemical kinetics.

Rate of reaction: Decrease in concentration of the reactants or increase in concentration of the products per unit time i.e. the rate of change of concentration is called the rate of reaction.

The concentration of the reactant of t_2-t_1 = c_2-c_1.

∴ Rate of reaction = $\frac{c_2-c_1}{t_2-t_1}$= - $\frac{dc}{dt}$

where, c_1= concentration of reactant at time t_1

c_2= concentration of reactant decreases at t_2

- $\frac{dc}{dt}$= the decrease of the concentration of the reactant at unit time.

33. State rate law.

Answer: The rate of a reaction is directly proportional to the reactant concentrations, each concentration being raised to some power.

Thus for a substance A undergoing reaction

rate $\propto$ $[A]^n$

or, rate= K $[A]^n$

An expression which shows how the reaction rate is related to concentration is called the rate law.

36. Find the rate expression of a first order reaction.

Answer: Let us consider a first order reaction,

$$A \xrightarrow{\hspace{2cm}} \text{Product}$$

At initial state, a 0

After time t, (a-x) x

Let the initial concentration of A is ‘a’ mol/L. If ‘x’ mole product is formed after time t, then rest of concentration of the reactant A is (a-x) mol/L. Therefore at any time t, according to the law of mass action, the rate of reaction,

$$\frac{dx}{dt} = Kc^n$$

or, $\frac{dx}{dt} = Kc^1$ [K is a constant]

or, $\frac{dx}{dt} = K(a-x)^1$

or, $\frac{dx}{a-x} = Kdt \longrightarrow (1)$

By integrating equation (1)

$$\int\frac{dx}{a-x} = K\int dt$$

or, $-\ln(a-x) = kt + c \longrightarrow (2)$

At initial state t=0, x=0

∴ From equation (2), c=-ln a

∴ $-\ln(a-x) = kt - \ln a$

or, $kt = \ln a - \ln(a-x)$

or, $kt = \ln\frac{a}{a-x}$

∴ $k = \frac{1}{t}\ln\frac{a}{a-x}$

This is the rate equation of a first order reaction.

37. Find rate equation of a 2nd order reaction.

Answer: Let us consider a 2nd order reaction,

	2A $\longrightarrow$	Product
At initial state,	a	0
After time t,	(a-x)	x

Let, the initial concentration of A is 'a' mol/L. If 'x' mole product is formed after time t, then rest of concentration of the reactant A is (a-x) mol/L. Therefore at any time t, according to the law of mass action, the rate of reaction,

$$\frac{dx}{dt} = Kc^n$$

or, $\frac{dx}{dt} = kc^2$ [K is a constant]

or, $\frac{dx}{dt} = k(a-x)^2$

or, $\frac{dx}{(a-x)^2} = kdt \longrightarrow (1)$

By integrating equation (1)

$$\int\frac{dx}{(a-x)^2} = k\int dt$$

or, $\frac{1}{a-x} = kt + c \longrightarrow (2)$

At initial state t=0, then x=0

$\therefore c = \frac{1}{a}$

Now, putting the value of c to the equation (2) and we get,

or, $\frac{1}{a-x} = kt + \frac{1}{a}$

or, $$kt = \frac{a}{a-x} - \frac{1}{a}$$

or, $$kt = \frac{a-a+x}{a(a-x)}$$

or, $$kt = \frac{x}{a(a-x)}$$

$$\therefore k = \frac{1}{t}\,\frac{x}{a(a-x)}$$

This is the rate equation of 2nd order reaction.

38. What is half life? Find an equation for half life of 1st order reaction.

Answer: The rate equation of a first order reaction is,

$$k = \frac{1}{t} \ln \frac{a}{a-x}$$

or, $$t = \frac{1}{k} \ln \frac{a}{a-x}$$

For half life $t = t_{½}$ and $x = \frac{a}{2}$

Therefore, $$t_{½} = \frac{1}{k} \ln \frac{a}{a-(\frac{a}{2})}$$

$$= \frac{1}{k} \ln \frac{a}{\frac{a}{2}}$$

$$= \frac{1}{k} \ln 2$$

$$\therefore t_{½} = \frac{0.693}{k}$$

38. Find an expression for half life period of a second order reaction.

Answer: For a 2nd order reaction the rate equation is,

$$k = \frac{1}{t}\,\frac{x}{a(a-x)}$$

or, $$t = \frac{1}{k}\,\frac{x}{a(a-x)}$$

At half life, $t = t_{½}$ and $x = \frac{a}{2}$

$$\therefore t_{½} = \frac{1}{k}\,\frac{\frac{a}{2}}{a(a-\frac{a}{2})}$$

$$= \frac{1}{k}\,\frac{\frac{a}{2}}{a.\frac{a}{2}}$$

$$t_{½} = \frac{1}{ka}$$

39. What is reversible reaction and chemical equilibrium?

Answer:

Reversible reaction: The chemical reactions which take place in both directions under the same conditions are called reversible reactions.

Reversible reactions proceed slowly and step by step.

$$\begin{array}{lcl} NH_4Cl\,(s) & \longrightarrow & NH_3\,(g) + HCl\,(g) \\ NH_3\,(g) + HCl\,(g) & \longrightarrow & NH_4Cl\,(s) \\ \hline NH_4Cl(s) & \leftrightharpoons & NH_3(g) + HCl\,(g) \end{array}$$

which is reversible reaction.

Chemical equilibrium: Chemical equilibrium is an apparent state of rest at which the opposite reactions (forward or backward) are proceeding at the same rate.

41. What is the relation between K_p and K_c ?

Answer:

Let,

aA(g) + bB(g) ⇋ lL(g) + mM(g) be a general gaseous reversible reaction.

∴ Equilibrium constant, $K_c = \frac{[L]^l [M]^m}{[A]^a [B]^b} \longrightarrow (1)$

Here, [A], [B], [L], [M] are molar concentration of A, B, L and M respectively.

If the partial pressures of A, B, L and M are respectively P_A, P_B, P_L and P_M then

$$K_p = \frac{P_Ł^l P_M{}^m}{P_A{}^a P_B{}^b} \longrightarrow (2)$$

We know that for n moles of an ideal gas,

$$PV= nRT$$

or, $P= \frac{n}{V} RT$

or, $P= cRT \quad [\because c=\frac{n}{V}]$

If we substitute partial pressure P= cRT in equation (2) then we get,

$$K_p = \frac{(cRT)^l{}_Ł \ (cRT)^m{}_M}{(cRT)^a{}_A \ (cRT)^b{}_B}$$

$$= \frac{C_Ł{}^l . C_M{}^m}{C_A{}^a . C_B{}^b} \cdot \frac{(RT)^l (RT)^m}{(RT)^a (RT)^b}$$

$$= \frac{[L][M]}{[A][B]} \cdot (RT)^{\{(l+m)-(a+b)\}}$$

$$= K_c \cdot (RT)^{n_2-n_1}$$

∴ $K_p = K_c (RT)^{\Delta n}$

Where, $\Delta n = n_2 - n_1$

n_2 = l+m = Total mole number of products

n_1 = a+b = Total mole number of reactants

42. Derive La-Chattelier principle and effect of pressure, temperature and concentration on it?

Answer:

La-Chattelier's Principle: If a system in equilibrium is disturbed by the change of any of the factors like temperature, concentration or pressure, the equilibrium will shift so as to reduce the effect of that change. So the position of equilibrium depends upon three factors:

(i) Temperature
(ii) Pressure
(iii)Concentration of the component

1. **Effect of temperature on equilibrium:** According to the La-Chattelier's principle if the temperature of a reaction at equilibrium is increased, the equilibrium will shift in the direction in which added heat is absorbed up.
   a) For exothermic reaction: In case of exothermic reaction, increase of temperature will shift the reaction backward. Since in the backward reaction some heat will be absorbed, one such reaction which is of great commercial importance is the synthesis of ammonia from hydrogen and nitrogen.

   $$N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3\,(g);\ \Delta H° = -92\ kj$$

   In this case, the increase of temperature disfavors the yield of NH_3.

   b) For endothermic reaction: In case of endothermic reaction, the increase of temperature will shift the equilibrium to the forward direction, i.e. towards the directions of the products. Thus in a n endothermic reaction increase of temperature shift the equilibrium to the right.

$$N_2 + O_2 \leftrightharpoons 2NO; \Delta H = +180.75 \text{ kj}$$

If we apply heat, the production of NO will increase, while for the decrease in heat, the production of N_2 and O_2 will decrease.

2. **Effect of change of pressure:** According to La-Chattelier principle if the pressure on a system in equilibrium is changed, the system will tend to adjust itself in such a way that the effect of that change is diminished.
   - **a)** When there is no difference between numbers of molecules of reactants and products, pressure has no effect on the equilibrium.
     $H_2(g) + I_2(g)= 2HI(g)$
   - **b)** If in a reaction the number of molecules increases, then increase of pressure on the system in equilibrium will shift the equilibrium in the backward direction, i.e. toward the reactants.
     $PCl_5(g) = PCl_3(g) + Cl_2(g)$
   - **c)** If in a reaction the number of molecules decreases, then increase of pressure on the system in equilibrium will shift the equilibrium in the forward direction, i.e. toward the products.
     $N_2(g) + 3H_2(g) = 2NH_3(g)$
3. **Effect of change of concentration:** If a reaction is at equilibrium at a definite temperature and if the concentration of any component is changed, the equilibrium is shifted in such a way to diminish the effect of that change.

   Let us consider a reaction,

   $$PCl_5(g) \leftrightharpoons PCl_3(g) + Cl_2(g)$$

   $$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

   If PCl_5 is added, the denominator increases, so the numerator must increase to maintain K_C constant at fixed temperature. The equilibrium is therefore displaced towards right and concentration of PCl_3 and Cl_2 is increased and forward reaction is favored.

43. What is P^H and P^{OH}? What is P^H scale?

Answer: The hydrogen ion concentration is a measure of acidity of a solution. To express the wide range of hydrogen ion concentration in a most convenient way S.P.L by Sorensen in 1909 introduced P^H scale.

-log of H^+ concentration is called P^H of a solution.

$\therefore P^H = -\log [H^+]$

or, $P^H = -\log [H_3^+O]$

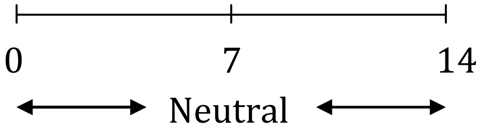
-log of OH^- concentration is called P^{OH} of a solution.

$\therefore P^{OH} = -\log [OH^-]$

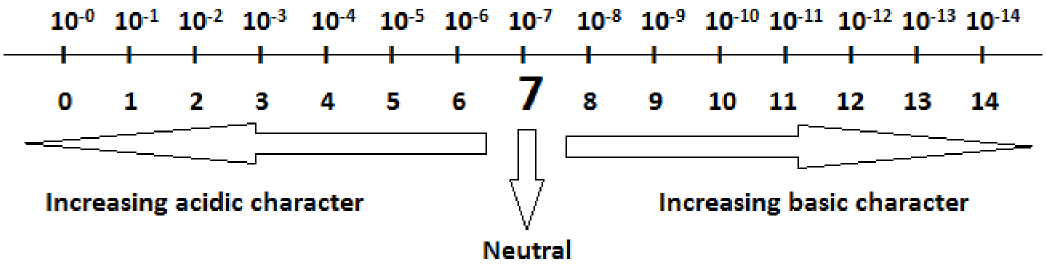
P^H Scale: If the value of P^H decreases gradually form 7 to zero then P^H increases and it reaches a maximum value of 14. Again if the P^H increases then P^{OH} decreases and it can be decreased up to zero when P^H is 14.

So the range of P^H is 0 to 14 and at the middle point neutral point, P^H=7

i.e. P^H value →



In a better way the scale may be shown as,



44. What is the relation between P^H and P^{OH}?

Answer: $H_2O \leftrightharpoons H^+ + OH^-$

$\therefore$ Equilibrium expression, $K = \frac{[H+][OH^-]}{[H_2O]}$

Or, $[H^+][OH^-]=K[H_2O]=K_W \xrightarrow{\qquad\qquad} (1)$

Where, K_W= water dissociation constant

Taking –log in both sides of equation (1)

$-\log K_W= -\log [H+]-\log [OH-]$

or, $-\log (1\times 10^{-14}) = P^H + P^{OH}$ [Since, $K_W = 1\times 10^{-14}$

or, $P^H + P^{OH} = 14$ [For any aqueous solution at 25^oC, P^H and P^{OH} add up 14]

45. What is buffer solution? How does buffer operate?

Answer:

Buffer solution: A solution of a weak acid and its salt or a weak base and its salt whose P^H value does not appreciably change by dilution or addition of small amount of acid or base from outside is called buffer solution.

The solution whose P^H remain unaltered even after addition of small amount of base or acid is called buffer solution.

Generally, a buffer solution may be prepared by two methods,

(i) Acidic buffer and **(ii)** Alkaline buffer.

Mechanism of the buffer action of acidic buffer:

Acidic buffer is a mixture of weak acid CH_3COOH and its salt CH_3COONa. At equilibrium state, the buffer has three ions which are: H^+, CH_3COO^-, Na^+ write wise from dissociations.

$CH_3COOH(aq) \leftrightharpoons H^+ + CH_3COO^-$

$CH_3COONa(aq) \leftrightharpoons Na^+ + CH_3COO^-$

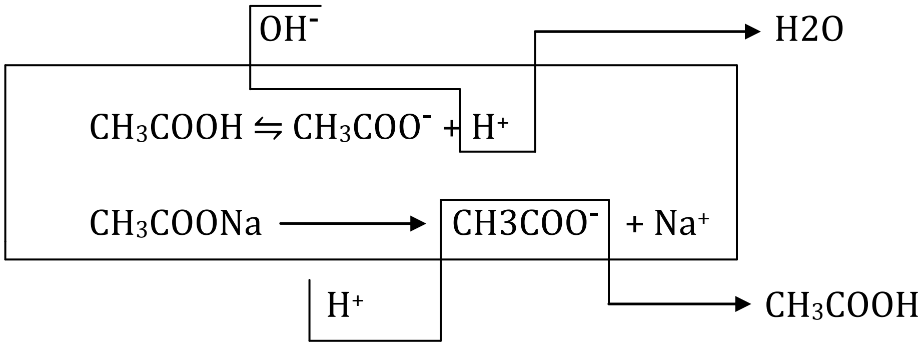
If a small amount of acid is added from outside the acetate ion will be neutralized into acetic acid:

$$CH_3COO^- + H^+ \longrightarrow CH_3COOH$$

As acetic acid is a weak acid and there is CH_3COO^- ion present in the buffer mixture, acetic acid will not ionize due to common ion (H_3COO^-) effect and the value of P^H will not change. On the other hand if a small amount of alkali is added, the OH^- ions of alkali will combine with H^+ to form water:

$$H^+ + OH^- \longrightarrow H_2O.$$

This water is neutral.



Mode of action of acidic buffer

So the value of P^H of the solution remains unchanged.

Mechanism of the buffer action of alkaline buffer:

An alkaline buffer is a mixture of NH_4OH and NH_4Cl. In buffer solution these two components dissociate as-

$$NH_4OH \leftrightharpoons NH_4^+ + OH^-$$

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

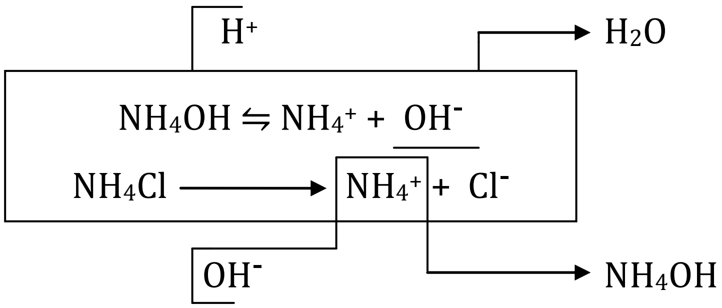
So in buffer solution of NH_4OH + NH_4Cl the following three ions are present: NH_4^+, Cl^-, OH^-.

Adding acid: In the buffer solution if small amount of acid (H^+) is added, it will react with OH^- to form water: $H^+ + OH^- = H_2O$. The neutralization of OH^- by added acid is compensated by dissociation of weak NH_4OH.

Adding base: Again if a small amount of alkali is added, the OH^- ions of alkali will combine with NH_4^+ ions to form NH_4OH.

$$NH_4^+ + OH^- \longrightarrow NH_4OH$$

As NH_4OH is a weak base, it remains un-dissociated. So, there will no change in the P^H of the mixture. The buffer action is shown in figure



46. Deduce Henderson equation to calculate the P^H of acidic buffer solution.

Answer: In acidic buffer solution the weak acid dissociates and an equilibrium is established:

$$CH_3COOH \leftrightharpoons CH_3COO^- + H^+$$

According to law of mass action,

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

or, $$[H^+] = \frac{K_a\,[CH_3COOH]}{[CH_3COO^-]} \longrightarrow (1)$$

where K_a is the ionization constant of the acid and the terms in the bracket stand for the concentration of various species involved.

Here, acetic acid is a weak acid, it will undergo dissociation to a very small extent. In the presence of sodium acetated which is completely dissociated as it is a salt, it can be assumed that acetic acid is not dissociated at all. So, concentration of unionized acetic acid can be taken equal to the initial concentration of the acid.

∴ From equation (1),

$$[H^+] = K_a \frac{[acid]}{[salt]}$$

Taking –log in both sides,

$$-\log [H+] = -\log K_a - \log \frac{[acid]}{[salt]}$$

or, $$P^H = p^{Ka} + \log \frac{[salt]}{[acid]}$$

This equation is known as Henderson equation.

46. Deduce Henderson equation to calculate the P^H of basic buffer solution.

Answer: A basic buffer is made by mixing a weak base, NH_4OH with a salt NH_4Cl of it which is made from a strong acid.

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$

The weak base dissociates as,

$$NH_4OH\ (aq) \leftrightharpoons NH_4^+\ (aq) + OH^-\ (aq)$$

∴ $$K_a = \frac{[NH_4^+][HO^-]}{[NH_4OH]}$$

or, $[OH^-] = K_b \frac{[NH_4OH]}{[NH_4^+]}$

The salt NH_4Cl completely ionizes in solution as

$$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

So, $[NH_4^+]$ may be taken as that $[NH_4Cl]$

$\therefore [OH^-] = K_b \frac{[NH_4OH]}{[NH_4Cl]}$

or, $[OH^-] = K_b \frac{[base]}{[salt]}$

Taking –log in both sides

$-\log [OH^-] = -\log K_b - \log \frac{[base]}{[salt]}$

or, $P^{OH} = p^{Kb} + \log \frac{[salt]}{[base]} \xrightarrow{\hspace{6em}} (1)$

We know, $K_w = [H^+][OH^-]$

or, $-\log {}^{Kw} = -\log [H^+] + (-\log [OH^-])$

$\therefore P^{Kw} = P^H + P^{OH}$

or, $P^{OH} = P^{Kw} - P^H$

From equation (1),

$P^{Kw} - P^H = P^{Kb} + \log \frac{[salt]}{[base]}$

or, $P^H = P^{Kw} - P^{Kb} - \log \frac{[salt]}{[base]}$

$\therefore P^H = P^{Kw} - P^{kb} + \log \frac{[base]}{[salt]}$

This is known as Henderson equation of a basic buffer solution.

47. Write down the Mendeleeff's periodic law, Modern periodic law and discuss the defects of Mendeleeff's periodic table.

Answer:

Mendeleeff's Perodic Law: In 1869, Mendeleeff, a Russian chemist, made the most significant contribution toward the classification of elements. He stated his famous periodic law- "The physical and chemical properties of elements are a periodic function of their atomic masses." This is known as Mendeleeff's Perodic Law.

Modern Periodic Law: In 1913, Mosley, a British physicist, discovered a new characteristic of the elements and gave it the name atomic number. The modern periodic law states- "The physical and chemical properties of the elements are a periodic function of their atomic numbers."

Defects of Mendeleeff's periodic table:

1. **In the arrangement of elements according to the atomic mass:** In Mendeleeff's periodic table, there are some defects in putting the elements according to the atomic masses. Such as argon(Ar) has more atomic mass (39.9) than potassium (39.1). but argon is placed before potassium in the periodic table. Such situation also arise for cobalt and nickel, tellurium and Iodine. These defects have made the periodic table weak.
2. **Similar elements separated and dissimilar elements placed in the same group:** Certain elements which posses similar properties are separated in the periodic table, for example Cu and Hg, Ag and Tl, while many dissimilar elements have been grouped together. For example, Cu, Ag and Au are grouped along with the alkali metals though there is little resemblance between them.

49. Write the merits and demerits of periodic table.

Answer: The merits and demerits of periodic table is given below-

1. The classification of the element is based on a more fundamental property that is number of proton.
2. In relates in position of an element to its electronic configuration. Thus each group contains elements with similar electronic configuration and has similar properties.
3. It explains the similarities and variation in the properties of the elements in terms of their electronic configuration.
4. The inert gas having completely filled electrons shell has been placed and the add of each group. Such a location of the inert gases represents in a logical complication of an each period.
5. In this form of period table the elements of two groups have been placed separately and thus dissimilar element do not fall together.
6. It provides a clear demarcation of different types of element like active, metal, non metal, metalloid, actinides, inert gases.
7. It is easier to remember, understand and reproduced.

Demerits:

1. The problem of the position of hydrogen still remains unsult.
2. Like the metallic periodic table it fails to accommodate the lanthanide, actinide.
3. The arrangement of the elements is unable to reflect the electronic configuration of many elements.

50. Classify the elements on the basis of their complete and incomplete electron shells.

Answer: Classification of the elements on the basis of their complete and incomplete electron shells are given below:

1. Nobel gases
2. Representative or normal element
3. Transition elements
4. Inner transition elements

Nobel Gases:

a) Outermost shell in completely filled
b) ns^2 np^6 ($1s^2$) He
c) They are stable and usually do not enter into chemical reactions.

Normal Elements:

a) Outermost shell in portly filled (n^{th} shell)
b) Inner shell (1^{st}, 2^{nd}, ………., $(n-1)^{th}$ shell are completely filled.
c) ns^1 ns^2 np^5 (s and p blocks elements) metal, nonmetal, metalloid.

Inner transition elements:

a) There outmost shells are incompletely filled. In general [(n^{th}, (n-1), $(n-2)^{th}$ shell] completely filled.

52. Explain that Ionization potential of element in a group decreasing top to bottom.

Answer: The ionization potential of element in a group decreases for the increase of atomic number in the periodic table. The fact is that, with the increase of atomic number in a group the number of electron shells increase and hence the atomic radius also increases. So the outermost electron is situated at more and more distance from the nucleus, hence the attraction of the nucleus on it decreases and hence the I.P also decreases.

Example: Li= 520 $kjmol^{-1}$; Na= 496 $kjmol^{-1}$; Rb= 403$kjmol^{-1}$; Cs= 376 $kjmol^{-1}$

53. Explain Ionization of elements increases across a period.

Answer: Across a period when the atomic number of elements increases, their atomic radius decreases. As a result, nuclear attraction on outmost electrons increases. This leads to progressive increase of Ionization potential.

Example: Properties across second period-

Li= 520 kjmol^{-1}; Be= 700 kjmol^{-1}; B= 800 kjmol^{-1}; C= 1100 kjmol^{-1}; N= 1400 kjmol^{-1}; O= 1320kjmol^{-1}; F= 1690kjmol^{-1}; Ne= 2100 kjmol^{-1}

55. Deduce the relation between heat of reaction at constant pressure and constant volume.

Answer: We know that heat of reaction at constant pressure is equal to the summation of internal energy and pressure volume work done,

$$Q_P = \Delta E + P\Delta V \longrightarrow (1)$$

Again we know that heat of reaction at constant pressure is equal t the change of enthalpy of the system.

$$Q_P = \Delta H \longrightarrow (2)$$

From equation (1) and (2)

$$\begin{aligned} \Delta H &= \Delta E + P\Delta V \\ &= \Delta E + P(V_2 - V_1) \\ &= \Delta E + PV_2 - PV_1 \\ &= \Delta E + n_2RT - n_1RT \qquad [PV=nRT] \\ &= \Delta E + (n_2 - n1)RT \\ &= \Delta E + \Delta nRT \\ \therefore \Delta H &= \Delta E + \Delta nRT \end{aligned}$$

This is the relation between heat of reaction at constant pressure and constant volume.

56. State and explain Hess's law.

Answer: In 1840 the Russian scientist G.H. Hess expressed an important law, which is known by his name Hess's law.

The law is-"If the initial reactants and final products remain fixed in a reaction, then the net change of enthalpy in the reaction will remain same, weather the reaction takes place in a single step or in several steps."

Suppose, a reactant A may be converted to a product D through two different routes.

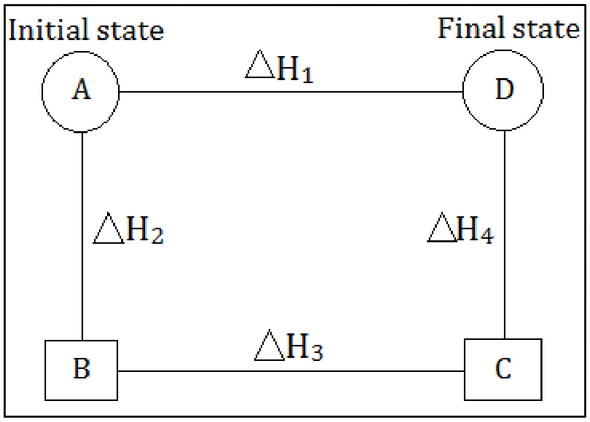


Figure: Explanation of Hess law with enthalpy diagram

(i) $A \xrightarrow{\triangle H_1} D$ (single step)

(ii) $A \xrightarrow{\triangle H_2} B \xrightarrow{\triangle H_3} C \xrightarrow{\triangle H_4} D$

So, according to Hess's law

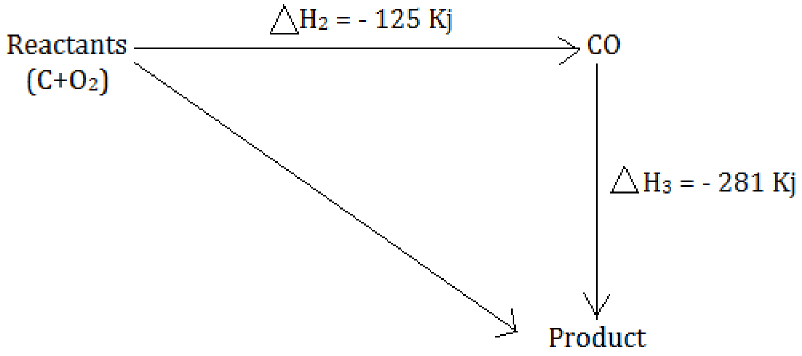
$\Delta H = \Delta H_1$ [1st route]

And, $\Delta H = \Delta H_2 + \Delta H_3 + \Delta H_4$ [2nd route]

$\therefore \Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$

Example: CO_2 may be prepared from carbon and oxygen in two ways:

1. Single step reaction:
   $C(s) + O_2(g) = CO_2(g)$ $\Delta H_1 = -406$ kj
2. Multi step reaction:



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$\triangle H_1$ = - 406 Kj

Adding the two steps we get,

$C(s) + O_2(g) = CO_2(g)$, $\Delta H_1 = \Delta H_1 + \Delta H_1 = -125-281 = -406$ kj

∴ $\Delta H_1 = \Delta H_2 + \Delta H_3$. Thus Hess's law is proved.

57. State and explain the law of Lavoisier and Laplace.

Answer: The law is called the first law of thermochemistry and it states that- "The quantity of heat required to decompose a compound into its elements is equal to the heat evolved when that compound is formed from its elements."

Simply it indicates that, the heat of decomposition of a compound us numerically equal to its heat of formation but they are of opposite sign i.e. $\Delta H_f^\circ = -\Delta H_{decom}$

Example: The heat of formation of H_2O form its elements hydrogen and oxygen is $\Delta H_f^\circ = -285.85$ kjmol^{-1} but the heat of decomposition of H_2O into its component elements H_2 and O_2 is $\Delta H_{decom} = +285.85$ kjmol^{-1}

$H_2(g) + O_2(g) = H_2O(l)$, $\Delta H = -285.85$ kjmol^{-1}

$H_2O(g) = H_2(g) + \frac{1}{2} O_2(g)$; $\Delta H = +285.85$ kjmol^{-1}

58. State the relation of Kirchhoff's equation/ Explain effect of temperature on the heat of enthalpy reaction?

Answer: The heat of reaction changes with change in temperature of a gas due to vibration in its specific heat. The equations representing the vibration of heat change of reaction with temperature are known as Kirchhoff's equation.

At constant volume, the heat of reaction, ΔE is given by the relation,

$$\Delta E = E_2 - E_1 \xrightarrow{\hspace{4cm}} (1)$$

Where, E_1 and E2 are the internal energies of the reactants and products.

Differentiating the equation (1) with respect to temperature at constant volume, we get,

$$[\frac{d\Delta E}{dT}]_v = (\frac{dE_2}{dT})_v - (\frac{dE_1}{dT})_v$$

But we know $(\frac{dE}{dT})_v = C_v$

∴ $$[\frac{d(\Delta E)}{dT}]_v = (C_v)_2 - (C_v)_1 = \Delta C_v$$

where, $(C_v)_2$ and $(C_v)_1$ are heat capacities of the products and reactants respectively.

Integrating the above equation between temperatures T_1 and T_2 we have,

$$\Delta E_2 - \Delta E_1 = \int_{T_1}^{T_2} \Delta C_v \, dt$$

or, $$\Delta E_2 - \Delta E_1 = \Delta C_v [T_2 - T_1]$$

where, ΔE_2 and ΔE_1 are heats of reaction at temperature T_2 and T_1 respectively.

Similarly, at constant pressure the heat of reaction ΔH is given by the reaction,

$$\Delta H = H_2 - H_1$$

where, H_2 is the heat content of the products and H1 being that of the reactants.

Differentiating with respect to temperature at constant pressure, we have

$$\left[\frac{d\Delta H}{dT}\right]_p = \left(\frac{dH_2}{dT}\right)_p - \left(\frac{dH_1}{dT}\right)_p$$

We know, $\left(\frac{dH}{dT}\right)_p = C_p$

$$\therefore \qquad \left[\frac{d(\Delta H)}{dT}\right]_p = (C_p)_2 - (C_p)_1 = \Delta C_p$$

where, $(C_p)_2$ and $(C_p)_1$ are the heat capacities of products and reactants respectively.

$$d(\Delta H) = \Delta C_p \times dT$$

59. What is chemical bond? Write down the classification and the causes of chemical bond.

Answer:

Chemical bond: The forces of attraction between the interacting atoms leading to the stabilization of a molecule are called chemical bonding. The bond id formed due to the tendency of having eight electrons in the outermost energy level of the atoms.

Classification of chemical bond:

(a) Bonding between the atoms of same elements or different elements: These bonds are four types-
1. Ionic bond
2. Co-valent bond
3. Co-ordinate bond
4. Metallic bond

(b) Bonding between the molecules of the some or different substances: These bonds are two types-
1. Hydrogen bond
2. Van der waal's interaction

Causes of chemical bond:

(i) Electronic theory if valency-attainment of noble gas configurations: When an element remains in atomic state then it is remain in unstable condition. But noble gases are extraordinarily stable and hardly from any compounds. The reason for the stability is their electronic configuration. In every case of inert gases (except He) there are eight electrons in the outermost orbit, as a result they are stable. **[The special stability of the electronic configuration of inert gases].**

On the other hand all other elements which are chemically reactive the outermost orbits are found to contain less than eight electrons. These atoms tend to complete their octets and thus attain a stable configuration by entering into chemical combination with other atoms and thus chemical bond occurred by losing, gaining and sharing electrons.[The eagerness of the atom to gain a state of lower potential energy.]

(ii) Modern concept in chemical bonding: In this concept, when two atoms approach each other then attraction and repulsion occurred between their electrons and nucleus. Then the potential energy of the system increases or decreases. If the potential energy decreases then a stable chemical bond is formed. But if the resultant effect of the new forces is the increase in potential energy then chemical bond cannot be formed.

61. Explain the melting point and boiling point of covalent bond is low.

Answer: The basic unit of covalent compounds is molecule. In a molecule the atoms are bound with strong covalent bond. On the other hand there is no bonding between the molecules. There is weak attractive force called vander waal's force among the molecules. For this reason when even a small amount of thermal energy is supplied to the molecules, their vibrational and traditional energy are sufficient to overcome the intermolecular force. That way the molting point and boiling point of covalent bond is low. For example the melting point of methane is 182.5^{o}C and the boiling point -164^{o}C.

62. Explain a co-ordinate bond is combination of ionic and covalent bond/co-ordinate is semi polar.

Answer: The formation of a co-ordinate bond between two atoms A and B may be regarded to occur in the following two steps-

1st step: In this stage the donor atom 'A' transfer one electron of its lone pair to the acceptor atom 'B'. This results in that atom 'A' develops unit positive charge and atom 'B' develops a unit negative charge. This charge is known as formal charge. This step is similar to the formation of ionic bond.

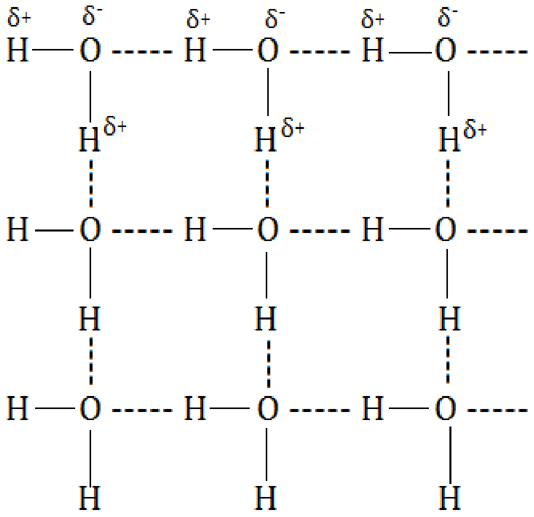
2nd step: In this step the two electrons are each with A^+ and B^- are shared by both the ions. This step is similar to the formation of a covalent bond.

$$A:^{+} \quad + \quad {}^{\cdot}B^{-} \longrightarrow A{:}B \longrightarrow A \longrightarrow B$$

Thus we see that the co-ordinate bond is a combination of ionic and covalent bond and equivalent to a combination of a polar and a non polar. So that co-ordinate bond is semi polar.

63. Explain the boiling point if H_2O is greater than HF.

Answer: The structure of H_2O and HF is given below-



$H_2O \Rightarrow$

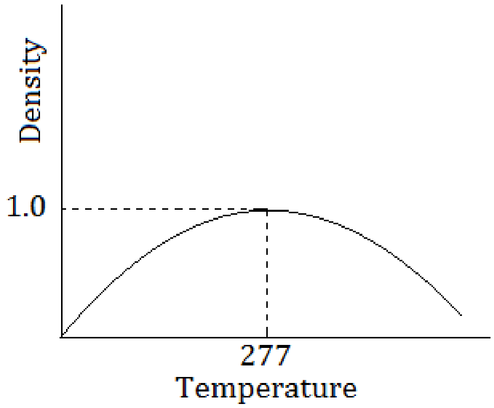
$$HF \Rightarrow \overset{\delta+}{H}—\overset{\delta^-}{F}\text{ ----- }\overset{\delta+}{H}—\overset{\delta^-}{F}\text{ ----- }\overset{\delta+}{H}—\overset{\delta^-}{F}\text{ ----- }\overset{\delta+}{H}—\overset{\delta^-}{F}\text{-----}$$

We can see that the atomic structure of H_2O is big in size. H_2O is created by hydrogen bond and there the oxygen is partially negatively charged and hydrogen is positively charged. The oxygen and hydrogen atom bonded together by hydrogen bond and there is a dipole-dipole attraction force between them. As the molecule is big in size, so the boiling point is high. For boiling water we have to break all hydrogen bond.

Again in the molecule H and F are fractionally positive and negatively charged. The atomic structure is like as a straight line. For breaking the bond low temperature is needed. We can say the boiling point of H_2O is greater than HF.

64. Explain the density of water is maximum at 4°C.

Answer: On melting ice, the hydrogen bonds break and water molecules occupy the valent spaces. This results in decrease on volume and increase in density ($d=\frac{m}{v}$). Hence density of water keeps on increasing when it is heated. This continues up to 4°C. Above this temperature water molecules start moving away from one another due to increase in kinetic energy. So volume increases and density decreases.



65. Electrical conductivity of most metal decreases with increasing temperature.

Answer: When temperature increases the ions began to vibrate and their motion hinders the free movement of the mobile electron. Thus the vibrating metal ions create resistance to the flow of electrons forward the positive pole. So electrical conductivity of most metals decreases with increasing temperature.

66. The reactivity of σ bond is less than π bond, explain it.

Answer: In sigma bonding the orbital are laid in same line; but in π bonding, the orbitals are laid in parallel. We know when the orbitals overlap in same phase then the sigma bond is formed. But the π bond is formed by the sidewise or parallel overlapping. So, the sigma (σ) is stronger than the Pi(π) bond. That's why the sigma (σ) bond cannot easily disintegrate to participate in a reaction but the π bond can participate in a reaction because it can easily disintegrate. So, because of this particular fact, the reactivity of the sigma bond is less than the Pi (π) bond.

67. What is hybridization? Write down the characteristics of hybridization.

Answer:

Hybridization: Hybridization is a process of mixing up of two or more atomic orbitals to form new orbital all of which are equivalent in symmetry and shape.

Characteristics of hybridization:

1. The number of hybridized orbitals is equal to the number of orbitals being hybridized.
2. The hybrid orbitals are identical in shape and have equivalent energy.
3. The hybrid orbitals are more effective in forming stable bond than the pure ones.
4. The type of hybridization indicates the geometry of the molecules.
5. The hybrid orbits can hold maximum of two electrons.

68. Discuss the shape of $BeCl_2$.

Answer: The central atom Be in $BeCl_2$ molecule is surrounded by two bonded electron pairs. To minimize the repulsion, these electron pairs tend to keep themselves far away from each other i.e. 180^o apart. Thus the two bond pairs of electrons are at the maximum possible distance. This is the arrangement with lowest energy and maximum stability.

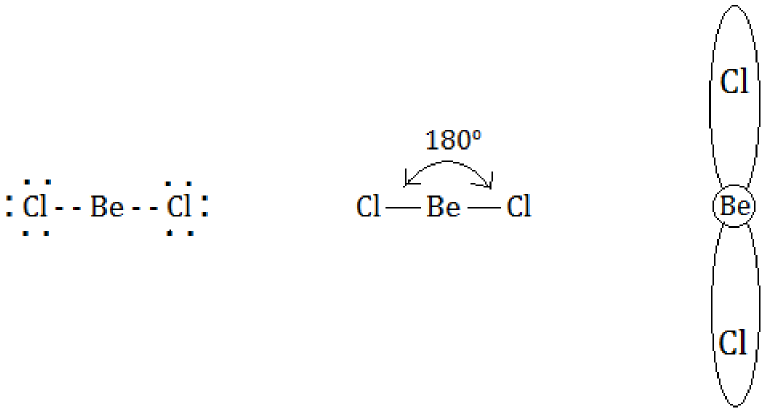


Fig. : $BeCl_2$ molecule, Linear

69. Explain the shape of BCl_3/BF_3 molecule.

Answer: The central Boron atom in BF_3 molecule is surrounded by three bonded electron pairs. To minimize the inter-electron pair repulsions, the bound orbitals are directed towards the three corners of a trigonal planar. Thus the shape of BF_3 molecule is trigonal planar and the F–B–F bond abgle is 120^{o}.

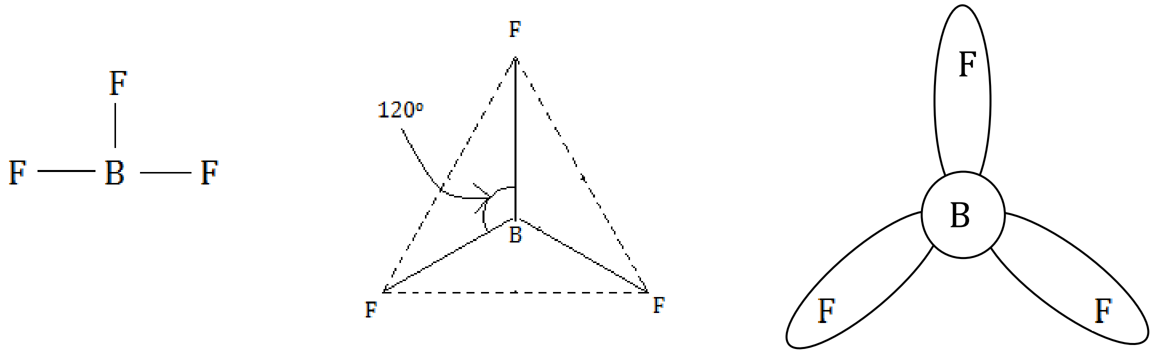


Fig. : BF_3 molecule

➢ **Question: Write the characteristics of a first order reaction.**

Answer: The important characteristics of first order reaction are-

1. A first order reaction never goes to completion or completes.
2. The time needed for the completion of a definite portion of a reaction does not depend on initial concentration of the reactant.
3. The rate constant of first order reaction does not depend on the unit of concentration.
4. Half time of first order reaction is constant.

➢ **Question: Define Ionic bond. Write the limitations and general properties of ionic bond.**

Answer:

Ionic bond: The ionic bond is a bond which is formed by the transfer of one or more electrons form one atom or radical to another.

Limitations:

1. Ionic bond is possible only in between metal and non metal atoms.
2. Among all the non metals only group VII(A) elements and oxygen of group VI(A) and in some cases sulpher form ionic bond.
3. Octet rule disobeying of transition and inner transition elements.

The general properties of ionic bond:

(i) All ionic compounds remain in crystalline form in solid state.

(ii) Ionic compounds form isomorphic crystal.

(iii) The ionic compounds have high melting and boiling points. They are non volatile.

(iv) Ionic compounds are generally soluble in polar solvent and non soluble in bob polar solvents.

(v) In solid state ionic compounds do not conduct electricity but in liquid state they conduct electricity.

(vi) The reactions between ionic compounds are very fast.

(vii) In chemical reaction they keep their individuality intact.

- **Question: Explain why Fe^{3+} ion is stable than Fe^{2+} ion.**

Answer: Let us see the electron configuration of Fe^{2+} and Fe^{3+},

$$Fe^{2+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3d^6\ 4s^2\ 3d^4$$

$$Fe^{3+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 2p^5\ 4s^2\ 3d^3$$

We know ‘d’ orbital’s highest capacity of hold is 10 electrons. At fulfill stage d orbital is stable. Again half full orbital is more stable than nearly half full orbital. We could see that in Fe^{3+} d orbital is half full. So this is more stable condition than Fe^{2+}. Spectrographic data and magnetic properties of elements justify the above statement.

- **Question: Explain why F is the most electro-negative element?**

Answer: Electro-negativity increases in a period and decreases in a group. So in a periodic table when we go from left to right electro-negativity increases and when top to bottom electro-negativity decreases. From periodic table we could see that F is the most right in period and top in a group. So F is the most electronegative element. F's electro-negativity is 4.

- **Question: Explain why Ice is lighter than water?**

Answer: The structure of water is tetrahedral in nature. Each oxygen atom is linked to two H-atoms by covalent bonds and other two JH-atoms by hydrogen bonding. In its solid state (as Ice) this tetrahedral structure is packed and a number of vacant spaces created. Hence in this structure the volume increases for a given mass of liquid water resulting in lesser density. For this reason ice floats on water.

- **Question: Explain why metals are good conductors of electricity?**

Answer: According to electron sea model the mobile electrons are free to move through the vacant space between metal ions. When electric voltage is applied at a metal wire, it causes electrons to be displaced in a given direction. Thus metal conducts electricity. The best conductors are those metals which attracts their outer electrons the least (low ionization energy) and thus allow then the greatest freedom of movement.

- **Question: Explain Electro-negativity of Halogens decreases on order F>Cl>Br>I.**

Answer:

1. In a periodic table in a group atoms size is increasing from top to bottom. We know increasing size of atoms results decreasing electro-negativity.
2. In a going down group the ionization energy and electron affinity on which electro-negativity is related decrease. So with this two quantities electro-negativity decrease.

For the above two reasons Halogens decrease in order F>Cl>Br>I.

- **Question: Explain electron sea theory of metallic bond.**

Answer: According to this theory the outermost orbital's electrons of a metal atom are loosely held. So this electrons can leave easily and the atom form positive ion. These electrons make a electron sea and the positive ions floats in this sea of electron. The positive ions remain fixed, but the valance electron can move freely from one end to another. The electron density of the valance electrons is uniformly distributed through the metal crystal. Thus the electrostatic force of attraction between the positive charged particles and mobile electrons help the atoms together to form a metal lattice.