UNIT -1

SAME BASIC CONCEPTS

Law of conservation of mass: 'Mass can neither be created nor destroyed'. In all physical and chemical changes, the total mass of reactants is equal to that of products.

Law of constant composition: A chemical compound is always found to be made of same elements combined together in the same fixed ratio by mass"

Law of multiple proportion: Two elements combined together to form two or more chemical compounds then the masses of the elements which that with a fixed mass of another bear a simple ratio to one anothere.

Law of reciprocal proportion: The ratio of the masses of two elements A and B which combine with a fixed mass of third elements C is either the same or simple multiple ratio of the masses of A and B that directly combine with each other.

Gaylussac's law: At the same temperature and pressure, when gases react together or are produced, they always do so by volume in a simple ratio.

Avogadro's Hypothesis: Equal volumes of all gases under the similar conditions of temperature and pressure contain equal number of molecules.

Atomic mass: It is the average relative mass of an atom as compared with an atom of C-12 isotope.

Molecular mass: It is the average relative mass of its molecule as compared with an atom of C-12 isotope.

Gram atomic mass or molar mass of an element is mass of 1 mol of atoms or atomic mass expressed in grams. For example, atomic mass of Ag = 108 u , therefore, molar mass of Ag is 108 grams per mol. Molar mass of an element is also called one gram atom.

Gram molecular mass or the molar mass of molecular substances : is the mass of 1 mol of molecules or molecular mass expressed is grams. For example , molecular mass of CO_2 in 44 u, therefore , molar mass of CO_2 is 44 grams /mol .

Molar mass of ionic substance is the mass of 1 mol of formula units of ionic substance.

Molar mass and standard molar volume of gaseous substances :

1 mole of any gas occupies a volume of 22.4 L at STP i.e. , at 298 K and 1 atm. If standard pressure is taken as 1 bar, then, the standard molar volume is taken as 22.7L

Equiralent mass of:

(1) an acid = molar mass of acid / No.of replaceable H atoms in acid molecule

(2) a base = molar mass of base/ No. of OH groups replaceable in base molecule

(3) a salt = molar mass of salt / total charge on cationic or anionic part

(4) an ion = formula mass of the ion / charge on the ion

(5) an oxidising and reducing agent = molar mass of oxidizing agent / No. of electrons gained / lost by one molecular or ionic species.

Quantitative information from balanced equations: (Chemical Stoichiometry) Consider the

following equation:

$2\ Cu\ FeS_2 + 5\ O_2 \rightarrow 2\ Cu + 2FeO + 4SO_2$

The coefficients in balanced equation can be interpreted both as relative number of molecules (or formula units) involved in the reaction and as the relative number of moles.

Calculation of mass of Cu that can be obtained by 1 g of Cu Fe S_2: The stoichiometrically equivalent quantities of the reaction are related as follows;

$2mol\ Cu\ Fe\ S_2 \equiv 5mol\ O_2 \equiv 2mol\ Cu \equiv 2\ mol\ Fe\ 0 \equiv 4\ mol\ SO_2$

$$\text{Moles of Cu Fe } S_2 = 1g \text{ Cu Fe } S_2 \times \frac{1 \text{ mol Cu Fe } S_2}{183g \text{ Cu Fe } S_2} = 5.46\times 10^{-3} \text{ mol Cu Fe } S_2$$

$$\text{Grams Cu} = 5.46\times10^{-3}\text{mol Cu FeS}_2\times\frac{2\text{mol cu}}{2\text{ mol cuFeS}_2}\times\frac{63.5\text{g cu}}{1\text{ mol cu}}$$

$= 5.46\text{x}10^{-3} \text{ x } 63.\ 52\ Cu$

$= 0.347g\ Cu$

This method is called factor label method (or dimensional analysis)

Limiting reagent: It determines, or limits the amount of the product formed because it is completely consumed in the reaction.

Example: Determine the limiting reagent if 50.0 kg N_2 and 10.0 kg H_2 are mixed to produce NH_3 (g). Find also the amount of NH_3 formed.

Solution: $N_2 + 3H_2 \rightarrow 2NH_3$

Stoichiometrically equivalent amount of the reagent is given by

$$= \frac{\text{Moles of the reagent}}{\text{stoichiometric coefficient of the reagent in balanced chemical equation}}$$

Stoichemetrically equivalent amount of N_2 $= \frac{50x10^3/28}{1} = 1785.7$ mol

Stoichmetrically equivalent amount of H_2 $= \frac{10x10^3/2}{3} = 1666.67$ mol

Since H_2 is present in lesser stoichiometric amount, therefore it is limiting reagent and moles of NH_3 produced will be

= stoichiometric equivalent amount of H_2 x stoichrometric coefficient of NH_3

Table for Emprical formula & molecular formula

Element	Moles of each element	Relative number of moles of each element	Smallest whole number molar ratio

NOTE: The ratio 1.33 : 1.50 $=1:\frac{4}{3}:\frac{3}{2}=6:8:9$

Law of Equivalence :

In a chemical reaction the reactants combine in a 1: 1 ratio of equivalents.

Number of equivalents of solute = normality of solution x volume of solution in litres

Similarly milliequivalents of solute (meq) = Nx V_{ml}

Normality equation for a reaction

$N_1V_1 = N_2 V_2$

The molarity equation for the same reaction will be

$\frac{M_1V_1}{a_1} = \frac{M_2V_2}{a_2}$ Where a_1 and a_2 are the stoicheimetric coefficients of the reactants " 1" and "2" respectively.

Relationship between normally and molarity is given by ;

Normality (N) = nx molarity (M)

Where n= number of mol of replaceable H atoms from 1 mole acid

= number of mol of replaceable OH groups per mol of a base

= number of mol of elections gained / lost per mol of oxidizing or reducing agent.

In case of molar concentration of solutes:

No. of mol of solute = Molarity x volume of solution in litres, i.e. MV_L

Similarly, mmol of solute = MV_{mL}

Example: 45.7 ml of 0.500 M H_2SO_4 is required to react completely with 20.0 ml sample of NaOH of Calculate the molar concentration of solution?

Solution:

$H_2SO4 + 2\ Na\ OH \rightarrow 2H_2O + Na_2\ SO_4$

Moles of $H_2\ SO_4$ = 45.7 mL Solution $X \frac{1L\ Solution}{1000mL\ Solution} X \frac{0.500\ Mol\ H_2SO_4}{1L\ solution}$

= $2.28X\ 10^{-2}$ mol H_2SO_4

Moles of NaoH = $2.28X10^{-2}$ mol $H_2\ SO_4$ X $\frac{2\ mol\ NaOH}{1\ mol\ H_2\ SO_4} = 4.56x10^{-2} mol\ NaOH$

Moles of NaOH = $\frac{4.56x10^{-2}\ mol\ NaOH}{20.0\ mL\ Solution} X \frac{1000mL}{1L\ Solution}$ solution

= 2.28 M

ALTERNATIVELY, We Can Use following relation :

$$\frac{mol\ of\ H_2\ SO_4}{1} = \frac{mol\ of\ NaOH}{2}$$

$$\frac{M_{H_2SO_4}\ V_{H_2SO4}}{1} = \frac{M_{NaOH} \cdot V_{NaOH}}{2}$$

For a General reaetion : $aA + bB \rightarrow cC + dD$

$\frac{M_A V_A}{a} = \frac{M_B V_B}{b}$ Where a & b are the Stoichiometric coeffieionts of A and B respectively.

Example: Burning a small quantity of a welding gas containg carton and hydrogen, gives 3.38 g CO_2 and 0.690 g H_2O. Calculate empirical formula of the hydrocarbon :

Solution:

Mol of C = 3. 38 g CO_2 x $\frac{1mol\ CO_2}{44\ g\ CO_2} X \frac{1mol\ C}{1mol\ CO_2}$

$= \frac{3.38}{44} mol\ C = 0.0768\ mol\ C$

Mol of H = $0.690\ g\ H_2O\ X \frac{1mol\ H_2O}{18gH_2O} X \frac{2mol\ H}{1mol\ H_2O}$

$= \frac{0.690x2}{18} mol\ H = 0.0767$ mol H.

mol C : mol H = 0.0768 : 0.0767 = 1 : 1

Therefore, empirical formula of hydrocarbon = CH

Example: Calculate the volume of 0.1 M NaOH solution required to neartralise the solution produced by dissolving 1.1 g of P_4O_6 in water

Solution: $P_4O_6 + 6\,H_2O \rightarrow 4\,H_3PO_3$

$2\,NaOH + H_3PO_3 \rightarrow Na_2HPO_3 + 2H_20$

mol of P_4O_6 = 1.1g P_4O_6 $X \frac{1\text{mol } P_4O_6}{220\text{g } P_4O_6} = 0.5X10^{-2}\text{mol } P_4O_6$

mol of NaoH = $0.5X10^{-2}$ mol P_4O_6 $X \frac{4\text{mol } H_3PO_3}{1\text{mol } P_4O_6} X \frac{2\text{mol NaOH}}{1\text{mol } H_3PO_3}$

= 4×10^{-2} mol NaOH

∵ Volume of NaOH solution in litres = $4x10^{-2}$ mol NaoH $X \frac{\text{IL NaoH Solution}}{0.1 \text{ mol NaOH}}$

= 4×10^{-1} L = 0.4 L

UNIT-1

BASIC CONCEPT IN CHEMISTRY

(MOCK TEST)

(1) If 10^{21} molecules CO_2 are removed from 200mg of its mass. The number of moles of CO_2 that left are:

(a) 2.88×10^{-3} (b) 28.8×10^{-3} (c) 0.288×10^{-3} (d) 1.66×10^{-2}

(2) The number of oxygen atoms in 4.4g of CO_2 will be

(a) 1.2×10^{23} (b) 6.0×10^{22} (c) 6.0×102^{23} (d) 12×10^{23}

(3) The number of electrons in one mole of hydrogen moleules is

(a) 6.02×10^{23} (b) 12.046×10^{23} (c) 3.01×10^{23} (d) Only one elacton

(4) An aqueous solution of 6.3 g of oxalic acid dilrydrate is made upto 250 ml. The volume of 0.1ml NaOh required to neutralize 10 ml of the solution will be

(a) 40ml (b) 20ml (c) 10mL (d) 4mL

(5) 10.0 g of $CaCO_3$ on strong heating gives CO_2 The mass of quick lime obtained will be

(a) 5.0 g (b) 5.6 g (c) 4.4 g (d) 4.0 g

(6) The mass of one molecule of water is:

(a) 3×10^{-26} kg (b) 3×10^{-25}kg (c) 1.5×10^{-26} kg (d) 2.5×10^{-26} kg

(7) The amount of Zn required to produce 224 ml of H_2 at STP by the reaction: $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$ will be

(a) 0.65 g (b) 6.5 g (c) 65 g (d) 0.065 g

(8) Haemogeobin contains 0.33% of iron by weight . The molecular mass of haemoglobin is approx 0.67200 u .The number of iron atoms present in 1 mol of haemoglobin: (At Wt. of Fe = 56 u)

(a) 6 mol (b) 1 mol (c) 4 mol (d) 2mol

(9) In the reaction ; $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$, when 1 mol of NH_3 and 1 mol of O_2 are made to react completely. On completion,

(a) 1.0 mol of H_2O is produced

(b) 1.0 mol of NO is produced

(c) all oxygen is consumed

(d) all ammonia is consumed

(10) A compound has haemoglobin like structure. It has one Fe atom. It contain 4.6% of Fe. The approximate molecular mass is.

(a) 100g mol^{-1}

(b) 1200g mol^{-1}

(c) 1400g mol^{-1}

(d) 1600g mol^{-1}

(11) The decomposition of certain mass of $CaCO_3$ gave 11.2 dm^3 of CO_2 at STP.

The mass of KOH required to neutralize the gas is

(a) 56g (b) 28g (c) 45g (d) 20g

UNIT-2

STRUCTURE OF ATOM

Atom is the smallest indivisible particle of the matter. atom is made of electron, proton and neutrons.

Sir J. J. Thomson (1869)	ELECTORN	PROTON	NEUTORN
DISCOVERY	Goldstein (1886)	Chadwick (1932)	
Nature of charge	Negative	Positive	Neutral
Amount of charge	1.6×10^{-19} Coloumb	1.6×10^{-19} Coloumb	–
Mass	1.60211×10^{-31}kg	1.672614×10^{-27}kg	1.67492×10^{-27}kg

Nucleus was discovered by Rutherford in 1911 .When alpha rays were allowed to hit a thin gold foil, most of the alpha rays passed through without undergoing any deflation (showing large empty space in the atom.) some were deflection through a small angle (showing presence of positive charge) and a few deflected back showing that charged body occupy small space and heavy called nucleus (contain proton + neutron).

Atomic Number (z) Number of proton present in the nucleus (Mosley 1913)

<u>Mass Number (A):-</u> Sum of the number of protons and neutrons present in the nucleus (called nucleons)

wavelength, frequency and wave-velocity are related to each other by

$C = \upsilon$ ë Where C = velocity of light = 3.0×10^{-8} m/s

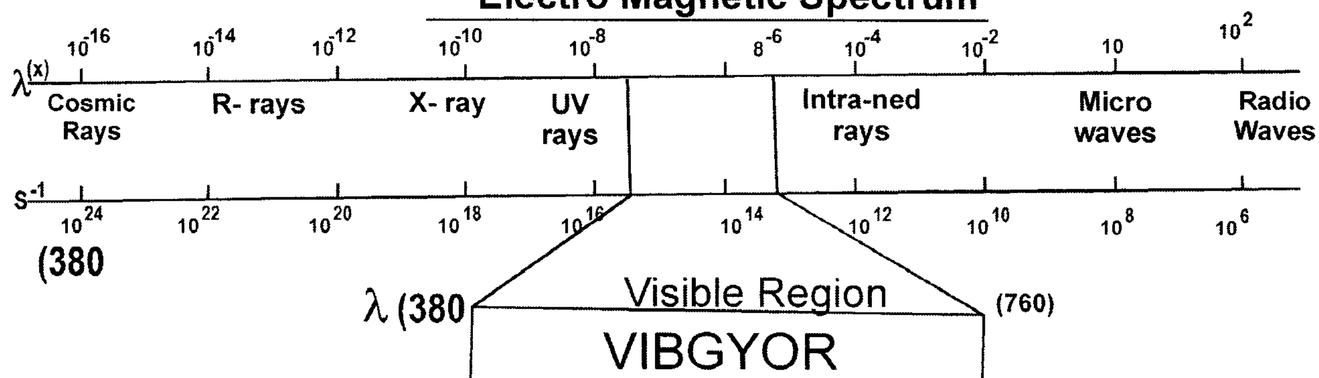
y = Frequency

ë = Wavelength

<u>Wave number</u> $(\bar{\nu})$ is the reciprocal of wavelength $\left(\bar{\upsilon} = \frac{1}{\lambda}\right)$

ELECTROMAGNETIC SPECTRUM

Electro Magnetic Spectrum



According to Plank's quantum theory, the energy is emitted or absorbed not continuously but discontinuously in the form of packets called quanta. A quantum of light is called photons, The energy of a quantum bhoters is E= hí, where h = plank constant, í = frequency of radiation.

The line spectrum of hydrogen consist of Lyman's Series(Lyman series in UV region) Balmer series (visible region) and Paschen. Brakett and Pfund series (IR Region)

The wave number of lines can be calculated by the following relation :

$$\bar{\upsilon} = R\left(\frac{1}{n^2} - \frac{1}{n_2^2}\right)$$

R = Rydberg's constant = 109677 cm^{-1}

For, Lymns series : n_1 =1, n_2 = 2,3,4, ...

Balmer series : n_1 = 2, n_2= 3,4,5,......

Paschen series : n_1 = 3 and n_2 = 4, 5, 6, ...

Brackett series : n_1 = 4 and n_2 = 5, 6, 7, ...

Pfund series : n_1 = 5 and n_2 = 6, 7, 8, ...

The energy of electron in hydrogen atom is given by

$$En = -\frac{2\pi^2 mZ^2e^4}{n^2h^2}$$

M = mass of electron, e = charge of electron, z = atomic number of element

For hyrdrogen atom, energy of electron in nth orbit, is,

$En = \frac{-1.312\times10^6 Z^2}{n^2}$ j mol^{-1} or $= \frac{-2.178\times10^{-18} Z^2}{n^2}$ Joule $atom^{-1}$, Z = atomic mumber of H or hydrogen like ions

The lowest energy state of an electron in atom is called ground state (n=1), when an electron absorb energy, it jumps to higher energy level called excited state, (first excited state n=2 for H).

The energy absorbed or emitted during electronic transition is given by the difference of the energies of two levels i.e. $E_2 - E_1 = -2.18\times10^{-18}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ J/atom such that $n_2 > n_1$

The radius of the nth orbit is given by $r_n = \frac{(0.529A^\circ)n^2}{z}$

Limitations of Bohr's model. (i) Bohr's model of atom could explain the line spectra of H-atom and H- like particle but failed to explain the spectra of multi-electron atoms. (ii) It also could not explain the splitting of lines when the source is placed in a magnetic field (called Zeeman effect) and when placed in an electric field (called **Stark effect**). (iii) This model is also not concordant with de Broglie concept of dual nature of matter of matter and Heisenberg's uncertainty principle.

Photoelectric effect. When radiation with certain minimum frequency (v_0), called threshold frequency, strike the surface of a metal, electrons (called photoectrons) are ejected from the surface. With this frequency, the kinetic energy of the photoectrons ejected is zero. However If the incident radiation having frequency $v > v_0$, the difference of energy ($hv - hv_0$) is converted into kinetic energy of the photoelectrons i.e. $\frac{1}{2}$ m $\vartheta^2 = hv_0$. The minimum energy hv_0 required for emission of photoelectrons is called **threshold energy** or **work function.** No photoelectric effect is shown if incident frequency is less than v_0 even if intensity of a radiation is increased. However number of photoelectrons ejected is proportional to the intensity of incident radiation.

The phenomenon of photoelectric effect and black body radiation can be explained if light is considered to be made up of particles, called photons (i.e. it is corpuscular in nature, as suggested by Newton). On the other hand, phenomenon of interference and diffraction can be explained only if light is supposed to have wave nature. Hence light has dual natrue. This idea was put forward by Einstein. The idea of dual nature of matter was put forward by de broglie in 1924.

According to de **Broglie concept**, all material particles (microscopic as well as macroscopic) possess wave character as well as particle charactor. The wave associated with a material particle is called de Broglie wave or matter wave.

The relationship between the wavelenth (l) of the wave and the mass (m) of the material particle moving with a velocity v is called de **Brolie equation.** It is given by

$$\lambda = \frac{h}{m\upsilon} = \frac{h}{p}$$

where *h* is Planck's constant and *p* is momentum of the particle.

The wave nature of electron has been confirmed by **Davisson and Germer's experiment** and by G..P. Thomson's experiment whereas the particle nature is confirmed by **scintillation method** as well as by the photoelectic effect.

Heisenberg's uncertainty principle states that "It is impossible to measure simultaneously the position and momentum of a microscopic particle with absolute accuracy. If one of them is measurd with greater accuracy, the other becomes less accurate. The product of their uncertainties as always equal

to or grater accuracy, the other than $\frac{h}{4\pi}$" Mathematically

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

where Δx = uncertainty in position,

Δp = uncertainty in momentum

Note that (i) uncertainty principle applies to position and momentum along the same axis. Thus, if Δx is along X-axis, then Δp should also be along X-axis. (ii) Uncertainty principle is not on account of any limitation of the measuring instrument.

de Broglie concept as well as uncertainty principle have no significance in every day life because they have significance only for microscopic particles but we come across macroscopic bodies in every day life.

Quantum numbers

The four quantum numbers provide the following informations :

1. Principal quantum number (n)

n =1, 2, 3, 4, ... α

It identifies shell, determiners size and energy of orbitals and number of orbitals in the n^{th} shell which is equal n^2

2. Azimuthal quantum number (l) For a given value of n it can have n values ranging from o to n-1. It identifies subshell, determines the shape of orbitals, energy of orbitals in multi electron atoms along with principal quantum number and orbital angular momentum, i.e., $\sqrt{\ell(\ell+1)}\ \frac{h}{2\pi}$ the number of orbitals in a subshell = $2\ell+1$

Subshell nolation	= s	p	d,	f,	g
value of 'l'	= o,	1,	2,	3,	4
Number of orbitals	= 1,	3,	5,	7,	9

Magnetic orbital quantum number (m_l): For a given value of 'l', ml has a total of $(2\ell+1)$ values ranging from $-\ell$ to $+\ell$ including 'o'. It determines the orientation of orbital.

Magnetic spin quantum number (m_s) : It can take the values of +1/2 or -1/2 and determiners the orientation of spin

Pauli's Exclusion Principle:- " No two electrons in an atom can have the same set of four quantam numbers". Two electrons can have same values for n, l and m_l provided their spins are opposite (m_s is different).

Hund's Rule:- "the electron start pairing only when all the degenerate orbitals are singly occupied." e.g., N : $1s^2$, $2s^2$, $2px^1$, $2py^1$, $2pz^1$

Aufbau Principle:- "Orbitals are filled up in the increasing order of their energy"

1. Orbitals are filled up in the increasing order of their(n + l) values.

2. If two orbitals have same ($n+l$) values then the one which has lower n value , will be filled up first.

Exception to aufbau Principle:- Extra stability is associated with the exactly half filled and fully filled orbitals. Thus the p^3, p^6, d^5, d^{10}, f^7, f^{14} etc. have stability i.e., lower energy and therfore, more stable.

Energy of orbitals :- The energy of orbitals in hydrogen atom increases as following :

1s < 2s = 2p < 3s = 3p = 3d < 4s = 4b = 4f < ....

But in a multi electron atom, the energy orbitals depends on both principal quantum number and azimuthal quantum number and vary as follows :

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s........

UNIT-2

ATOMIC STRUCTURE

(MOCK TEST)

(1) Principle quantum number of an atom is related to, the

(a) size of the atomic orbital (b) spin angular momentum

(c) orbital angular momentum (d) orientation of orbital in space

(2) The radius atomic nucleus is of the order of

(a) 10^{-12} m (b) 10^{-8}m

(c) 10^{-15}m (d) 10^{-10}m

(3) Magnetic Quantum number specifies

(a) the size of atomic orbital (b) shape of atomic orbital

(c) Orientation of atomic orbital (d) nuclear stability

(4) The ground state electronic configuration of chromium atom is

(a) $[Ar]3d^3 4s^2 5s^1$ (b) $[Ar]3d^4 4s^2$

(c) $[Ar]\ 3d^6 4s^0$ (d) $[Ar]\ 3d^5\ 4s^1$

(5) In a given atom, no two electrons can have the same set of four quantum numbers. This is called:

(a) Hund's Rule (b) Aufbau Rule

(c) Uncertainty Principle (d) Pauli's exclusion principle

(6) Neutron was discovered by:

(a) Rutherford (b) Langmuir

(c) Chadwick (d) Austin

(7) Maximum number of electrons in any orbit is :-

(a) n^2 (b) $2n^2$

(c) $1/2n^2$ (d) $3n^2$

(8) It is impossible to know simultaneously the postion and momentum of a moving particle with absolute exactness at any instant this is known as:

(a) Aufbau Principle (b) Hund's Rule

(c) Heisenberg's Principle (d) Pauli's Exclusion Principle.

(9) The value of Planks' constant is :

(a) 6.6256×10^{-27} erg sec (b) 66.256×10^{-27} erg sec.

(c) 6.02×10^{-15} erg sec (d) 3.01×10^{-23} erg sec.

(10) The quantum numbers for the designation of 3d orbital are:

(a) n=3 m_l=-3 (b) n=3 ℓ=3

(c) n=4 ℓ=1 (d) n=3 ℓ2

(11) Which of the following ions has the maximum magnetic moment?

(a) Mn^{2+} (b) Fe^{2+}

(c) Ti^{2+} (d) Cr^{2+}

(12) If the Nitrogen atom had electronic configuration $1s^7$, it would have energy lower than that of the normal ground state configuration $1s^2\ 2s^2\ 2p^3$, because the electrons would be closer to the nucleus. Yet $1s^2$ is not observed because it violates

(a) Heisenberg's uncertainty principle (b) Hund's rule

(c) Pauli exclusion principle (d) Bohr postulate of stationary orbits.

(13) For how many orbitals, the quantum numbers n = 3, l = 2, m_l = +2 are possible?

(a) 1 (b) 2

(c) 3 (d) 4

(14) The de broglie wavelenth of a tennis ball of mass 60g moving with a velocity of 10 metres per second is approximately

(a) 10^{-31} m (b) 10^{-16} m

(c) 10^{-25} m (d) 10^{-33} m

(15) In Bohr series of lines of hydrogen spectrum, the third line from the red end corresponds to which one of the following inter-orbit jumps of the electron for Bohr orbits in an atom of hydrogen?

(a) $5 \rightarrow 2$ (b) $4 \rightarrow 1$

(c) $2 \rightarrow 5$ (d) $3 \rightarrow 2$

(16) The value of Planck's constant is 6.63×10^{-34} J s. The velocity of light is 3.0×10^{8} ms $^{-1}$. Which value is closest to the wavelenght in nanometers of a quantum of light with frequency of 8×10^{15} s^{-1}?

(a) 2×10^{-25} (b) 5×10^{-18}

(c) 4×10^{1} (d) 3×10^{7}

(17) The frequency of the radiation emitted when the electron falls from $n = 4$ to $n = 1$ in a hydrogen atom will be (Given ionization enery of H = 2. 15 x 10 $^{-18}$ J atom^{-1} and $h = 6.625 \times 10^{-34}$ J s)

(a) 1.54×10^{15}s^{-1} (b) 1.03×10^{15}Js^{-1}

(c) 3.08×10^{15}s^{-1} (d) 2.0×10^{15}Js^{-1}

(18) Consider the gruond state of Cr atom (Z = 24). The number of electrons with the azimuthal quantum numbers $l = 1$ and 2 are respectively

(a) 12 and 4 (b) 12 and 5

(c) 16 and 4 (c) 16 and 5

(19) The one electron species having ionization energy of 54.4 eV is

(a) H (b) He^{+}

(c) B^{4+} (d) Li^{2+}

(20) The wavelenght of the electron emitted, when in a hydrogen atom, electron falls from infinity to staionary state 1, would be (Rydberg constant = 1.097×10^{7} m^{-1})

(a) 91 nm (b) 192 nm

(c) 406 nm (d) 9.1×10^{-8} nm

(21) The energy of the second Bohr orbit of the hydrogen atom is -328kJ mol^{-1}; hence the energy of fourth Bohr orbit would be

(a) -1312 kJ mol^{-1} (b) -82 kJ mol^{-1}

(c) - 41 kJ mol^{-1} (d) -164 kJ mol^{-1}

(22) In a multi-electron atom, which of the following orbitals described by the three quantum numbers will have the same energy in the absence of magnetic and electric fields?

(1) n = 1, $l = 0$, $m_l = 0$ (2) n = 2, $l = 0$, $m_l = 0$

(3) n = 2, $l = 0$, $m_l = 1$ (4) n = 3, $l = 2$, $m_l = 1$

(5) n = 3, $l = 2$, $m_l = 0$

(a) (1) and (2) (b) (2) and (3)

(c) (3) and (4) (d) (4) and (5)

(23) A metal surface is exposed to solar radiations

(a) The emitted electrons havc energy less than a maximum value of energy depending upon the frequency of the incident radiation.

(b) The emitted electrons have energy less than the maximum value of energy depending upon intensity of incident radiations.

(c) The emitted electrons have zero energy.

(d) The emitted electrons have energy equal to energy of photons of incident light.

(24) Which of the following transitions will have minimum wavelength?

(a) $n_4 \rightarrow n_1$ (b) $n_2 \rightarrow n_1$

(c) $n_4 \rightarrow n_2$ (d) $n_3 \rightarrow n_1$

(25) According to Bohr's theory, the angular momentum of an electron in 5th orbit is

(a) 10 h/p (b) 2.5 h/p

(c) 25 h/p (d) 1.0 h/p

(26) Uncertainty in the position of an electron (mass) = 9.1×10^{-31} kg) moving with a velocity 300 ms^{-1}, accurate upto 0.001%, will be

(a) 1.92×10^{-2} m (b) 3.84×10^{-2}m

(c) 19.2×10^{-2} m (c) $5. 76 \times 10^{-2}$m

(h=6.63×10^{-34}Js)

(27) Given : The mass of electron is 9.11×10^{-31} kg, Planck constant is 6.626×10^{-34} J s, the uncertainty involved in the measurement of velocity within a distance of 0.1A is

(a) 5.79×10^{8} ms^{-1} (b) 5.79×10^{5} ms^{-1}

(c) 5.79×10^{6} ms^{-1} (d) 5.79×10^{7} ms^{-1}

(28) The orientation of an atomic orbital is governed by

(a) Magnet quantum number (b) Principal quantum number

(c) Azimuthal quantum number (d) Spin quantum number

(29) Which pair is of isoelectronic species?

(a) CN^- , NO^+ (B) CN^- , O_2^+

(C) NO^+ , O_2+ (D) none of these

UNIT-3
STATES OF MATTER

Amount of gas is expressed as the number of moles

$$\text{No. of moles} = \frac{\text{Given mass of gas in grams}}{\text{Molecular mass}}$$

Expression of volume: volume is expressed in litres

$1\ L = 10^3\ cm^3 = 1\ dm^3$, and $1\ mL = 1\ cm^3$

Expression of pressure : Pressure is expressed in

$1 atm = 760\ mmHg = 760\ torr = 101325\ pascal = 10^2\ kPa$.

$1\ bar = 0.986923\ atm = 10^6\ dynes\ cm^{-2} = 10^5\ Nm^{-2}$

Expression of temperature: Temperature t°c measured on celcius scale is obtained on kelvin scale (TK) as give below :

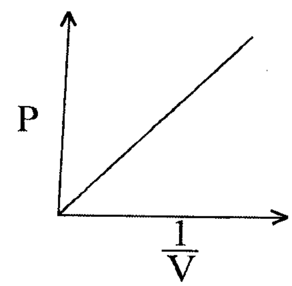
$T = 273.15 + t$ and $0°c = 273.15K \approx 273K$

Boyle's law: Temperature remaining constant, the volume of given mass of a gas is inversely proportional to its presume.

$V \alpha \frac{1}{P}$ (constant mass and pressure)

$PV = K$

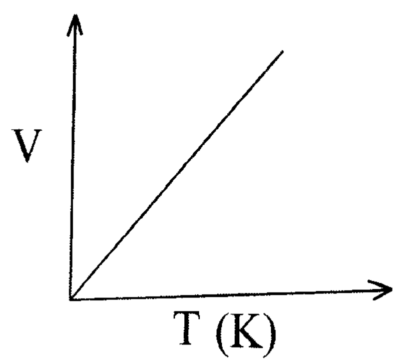
$P_1 V_1 = P_2 V_2$



Charles law: Pressure remaining constant, the volume of given mass of a gas is directly proportional to the absolute temperature.

$V \alpha T$ (constant mass and pressure)

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$



Pressure–temperature law: Volume remaining constant, the pressure of a given mass of a gas is directly proportional to its absolute temperature.

$P \alpha T$ (constant mass and volume)

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Ideal gas equation; $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$\frac{PV}{T} = R$ (gas constant); $n = \frac{M}{m} = \frac{\text{given mass}}{\text{molar mass}}$

n = no. of moles of the gas

units of R, $R = \frac{PV}{NT} = \frac{1\text{atm x } 22.4\text{L}}{1\text{x } 273} = 0.082\text{L atm k}^{-1}\text{mol}^{-1}$

$R = 8.314\ JK^{-1}\ mol^{-1}$

$R = 8.\ 314x\ 10^7$ ergs degree^{-1} mol^{-1}= 2 Cal degree^{-1} mol^{-1}

Dalton's law of partial pressure. "If two or more gases which do not react chemically are enclosed in a vessel, then the total pressure exerted by the gaseous mixture is equal to the sum of all the partial pressures that each gas would exert when present alone in the same vessel at the same temperature."

Mathematically $P = p_1 + p_2 + p_3 + \ldots\ldots\ldots\ldots$

Aqueous tension. The pressure exerted by the water vapour at a particular temperature is called aqueous tension at that temperature. It depends only on temperatue.

Calculation of pressure of a dry gas from that of the moist gas. When a gas is collected over water at t°C, it is moist. According to Dalton's law of partial pressures,

$P_{\text{moist gas}} = P_{\text{dry gas}}$ + aq. tension (at t°C)

or $P_{\text{dry gas}} = P_{\text{moist gas}}$ – aqueous tension (at t°C)

Graham's law of diffusion: *"Under the similar conditions of temperature and pressure, rate of diffusion of different gases are inversely proportional to the square root of their densities".* Mathematically

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \qquad (\because \text{ Mass Mass} = 2 \times \text{V.D.})$$

Rate of diffusion $= \frac{\text{Volume of gas diffused}}{\text{Taken taken}}$ i.e. $r = \frac{V_1 / t_1}{V_2 / t_2} = \sqrt{\frac{d_2}{d_1}}$

For the volumes diffused in the same time ($t_1 = t_2$),

$$\frac{V_1}{V_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

For the diffusion of same volume of two gases ($V_1 = V_2$),

$$\frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

Difference between diffusion and effusion. Diffusion refers to the spreading of a gas throughout the space or into a second gas or substance whereas effusion refers the escape of a gas through an orifice (a tiny hole.)

According to the kinetic theory of gases average translation kinetic energy of a gas molecule is directly proportional to the absolute temperature of gas and average kinetic energy per mole of the gas is equal = $\frac{3}{2}RT$

$$\text{Avarage kinetic energy of 1 mol of gas} = \frac{3}{2}RT$$

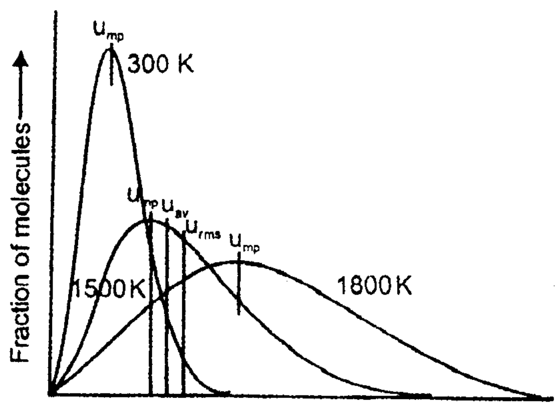
$$\text{Average kinetic energy of a molecule} = \frac{3}{2}\frac{R}{N_A}T$$

$$= \frac{3}{2}kT$$

N_A = Avogadro number

k = Bolzmann constant

Distribution of speeds of the molecules of gas at a particular temperature:



Distribution of molecular speeds for carbon dioxide at different temperature

U_{mp} = Most probable speed

U_{av} = Average speed

U_{rms} = Root Mean Square Speed

Relationship beetween u_{mp}, u_{av} and u_{rms}

$$u_{mp} : u_{av} : u_{rms} = \left(\frac{2RT}{M}\right)^{1/2} : \left(\frac{2.55RT}{M}\right)^{1/2} : \left(\frac{3RT}{M}\right)^{1/2}$$

$$= 1 : 1.128 : 1.224$$

Compressibility factor : The extent of deviation of a real gas from an ideal behaviour is expressed in terms of compressibility factor, Z, defined as $= \frac{PV}{nRT}$

For ideal gas, Z = 1 at all temperatures and pressures. For real gases, greater is the departure in the value of Z from 1, greater is the derivation from ideal behaviour. When Z < 1, the gas is said to show *negative* deviation.This implies that gas is more compressible than expected from ideal behaviour when z > 1, the gas is said to show positive deviation and the gas is less compressible than expected from ideal behaviour.

At ordinary temperatures, H_2 and He show positive deviations only. However at low temperatures, even these gases show negative deviation i.e. $Z < 1$. For example, in case of these gases, if $T << 273$ K, $Z < 1$.

Boyle temperature. The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is called Boyle temperature or Boyle point.

Causes of deviation from ideal behaviour. The following two assumptions of the kinetic theory of gases are faulty:

(i) The volume occupied by the gas molecules is negligible as compared to the total volume of the gas.

(ii) The forces of attraction or repulsion between the gas molecules are negligible.

The above assumptions are correct only if the temperature is high or pressure is low.

Van der Waal's equation :

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \text{ for 1 mol of the gas}$$

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \text{ for n moles of the gas}$$

a and b are constants called van der Waal's constants.

Significance and units of van der Waal's constants : 'a' gives the idea of the magnitude of attractive forces among the gas molecules. As correlation in pressure is $p = \frac{an^2}{V^2}$, therefore $a = (p \times V^2)/n^2$ = atm L^2 mol^{-2}, As correlation in volume $\upsilon = nb$, therefore 'b' has the unit of L mol^{-1}. The near constancy in the value of 'b' *shows that the gas molecules are incompressible*.

Solid State

$$d = \frac{Z \times M}{a^3 \times N_A}$$

d = Density (g/cm^3)

Z = number of atoms per unit all

a = Edge length in cm

M = Molar mass in g / mol

N_A = Avogadro constant in per mol

value of z for

simple cubic lattice =1

bcc lattice = 2

ccp or fcc lattice = 4

Radius Ratio: It is the ratio of radius of cation to the radius of anion.

$$\text{radius ratio} = \frac{r^+}{r^-}$$

S. No	Radius Ratio	C. N.	Type of void or hole	Example
1	0.1547 - 0.225	3	Trigonal planar	B_2O_3
2	0.225 - 0.414	4	Tetrahedral	ZnS
3	0.414 - 0.732	6	Octahedral	NaCl
5	0.732 - 1.000	8	Cubic	CsCl

Relationship between Atomic Radius and edgelength.

Simple Cubic	BCC	FCC
$r=\frac{a}{2}$	$r=\frac{\sqrt{3}\,a}{4}$	$r=\frac{\sqrt{2}\,a}{4}$

In ccp or hcp packing two types of voids namely (i) tetrahedral (ii) octahedral are generated.

No.of octahendral voids present in a lattice = Number of close packed particles

No.of tetrahedral voids present in a lattice = 2 × number of close packed particles

In ionic solids, the larger ions (usually anions) from close packed structure and the smaller ions (usually cations) occupy voids. If the cation is small enough then tetrahedral voids are occupied, if bigger, then octahedral voids. Not all octrahedral or teterahedral voids are occupied. The fraction of octahedral or tetrahedral voids that are occupied, depends upon the chemical formula of the compound.

Imperfections in crystals :

Schottky defects : Cations and equal number of anions are missing from the lattice site, of a crystal of the type $A^+ B^-$ e.g., there are10^6 schottky pairs per cm^3 at room temperature of NaCl . Schottky defect lowers the density of crystal.

Frenkel defects : Cation is missing from the lattice site but trapped within interstitial position, e.g., Ag Br.

F-centre : Anions are missing from lattice sites and these anionic sites are occupied by unpaired electrons. Anionic sites occupied by unpaired electrons are called F-centres and are responsible for colour imparted to crystals.

Metal deficiency defect: Some metal oxides contain less amount of metal as compared to the stoichiometric proportion. In iron oxide of composition $Fe_{0.95}.O$, some Fe^{2+} are replaced by definite number of Fe^{3+} resulting in the metal deficiency.

UNIT-3

STATES OF MATTER

(MOCK TEST)

(1) The number of atoms contained in a FCC unit cell of monoatomic substance is

(a) 1 (b) 2 (c) 4 (d) 6

(2) In a solid lattice, the cation has left a lattic site and is located in an interstitial position. The lattice defect is konwn as.

(a) Interstitial defect (b) Vacancy defect

(c) Frenkel defect (d) Schottky defect

(3) An octahedral void is surrounded by how many spheres

(a) 6 (b) 4 (c) 8 (d) 12

(4) In NaCl crystal number of Cl^- around each Na^+ will be

(a) 3 (b) 4 (c) 6 (d) 8

(5) For an ionic crystal of general formula AB and coordination number 6. The radius ratio will be

(a) greater than 0.732 (b) between 0.414 to 0.732

(c) between 0.225 to 0.414 (d) between 0.1547 to 0.225

(6) If pentavalent impurity is mixed in a crystal lattice of germanium,the semiconductor will be

(a) p-type (b) n-type (c) pnp (d) npn

(7) A metallic crystal containing a sequence of layer's AB AB AB .... Any packing of spheres leaves out voids in the lattice. What percent of volume of thus lattice is empty space.

(a) 74% (b) 26% (c) 52% (d) 68%

(8) When electrons are trapped into anion vacancies the defect is known as.

(a) schottky defect (b) frenkel defect

(c) Non-stoichiometric defect (d) F – centre

(9) If 300 mL of a gas at 27°C is cooled to 7°C at constant pressure, its final volume will be;

(a) 135 mL (b) 540 mL (c) 350 mL (d) 280 mL

(10) The number of atoms in HCP unit cell is

(a) 12 (b) 4 (c) 6 (d) 17

(11) The empty space in CCP unit cell is

(a) 74% (b) 32% (c) 47.6% (d) 26%

(12) The packing efficiecy of HCP unit is

(a) 26% (b) 74% (c) 32% (d) 47.6%

(13) The coordination number of metal crystallizing in hexagonal close packed structure is

(a) 4 (b) 6 (c) 12 (d) 8

(14) A substance consisting of two elements, 'P' and 'Q', has atoms of 'P' occupying each corner of the cube and atoms of 'Q' occupying the body centre. The composition of the substance is

(a) PQ_3 (b) P_4Q_3 (c) PQ

(d) composition cannot be specifed

(15) A compound is formed by two elements 'X' and Y. Atoms of element Y (as anions) make ccp arrangement and those of element X (as cations) occupy 50% of tetrahedral and octahedral voids . The formula of compound is

(a) X_3Y_2 (b) X_3Y_3 (c) X_2Y_3 (d) XY_2

(16) Atoms of elements B form hcp lattice and those of element A coupy $\frac{2}{3}$ rd of tetrahedral voids . The formula of the compound formed is

(a) A_3B_4 (b) AB_2 (c) A_4B_3 (d) A_2B

(17) On the basis of their magnetic properties, substances can be classified into various categories like paramagnetic, diamagnetice, fersomagnetic, antiferromagnetic and ferromagnetic. Schematic alignment of magnetic moments in above- mentioned solids are;

(a) $\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$ (b) $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$ (c) $\uparrow\uparrow\downarrow\uparrow\uparrow\downarrow$

These reprsentions respectively are of :

(a) Ferromagnetic, ferrimagnetic, and antiferromgnetic

(b) Ferrimagnetic; ferromagnetic; and antiferromagnetic

(c) Ferromagnetic; antiferromagnetic , and ferrimagnetic

(d) Ferrimagnetic, antiferromagnetic, and ferromagnetic

(18) Which one of the following substances produce impurity defects when added to molten NaCl?

(a) KCl (b) AgCl (c) $SrCl_2$ (d) AgBr

(19) Germanium crystal doped with equal number of phosphorus and antimony atoms is

(a) an intrinsic semiconductor (b) P- type semiconductor

(c) an n-type semiconductor (d) a superconductor

(20) If 'a' stands for the edge length of cubic systems sc , bcc and fcc, then ratio of radii of the spheres in these systems will be respectively,

(a) $1a:\sqrt{3}a:\sqrt{2}a$ (b) $\frac{1}{2}a:\frac{\sqrt{3}}{4}a:\frac{1}{2\sqrt{2}}a$

(c) $\frac{1}{2}a:\sqrt{3}a:\frac{1}{\sqrt{2}}a$ (d) $\frac{1}{2}a:\frac{\sqrt{3}}{2}a:\frac{\sqrt{2}}{2}a$

(21) Which of the following statements is not correct ?

(a) The number of Bravais lattices in which a crystal can be categorised is 14

(b) The fraction of total volume occupied by the atoms in a primitive cell is 0.524

(c) Molecular solids are generally volatile

(d) Number of carbon atoms in an unit cell of diamond is '4'

UNIT-4

CHEMICAL BONDING AND MOLECULAR STRUCTURE

Atoms do form chemical bonds since their formation lead to the decrease in the energy of the system. Types of chemical bonds are;

(a) Covalent bonds involving the sharing of electrons

(b) Ionic bonds formed by the transference of electron from the metallic atom having low $\Delta_i H$ to the more electronegative and non-metallic atom having more – ve $\Delta_{eg} H$ resulting in the formation of a crystal having high lattice enthalpy $(\Delta_L H)$

(c) Hydrogen bonds and van der waals forces; please refer to NCERT text book for class XI page 133 to 134:

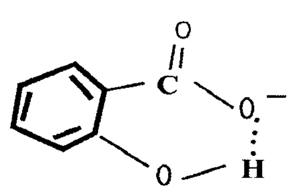
The strength of hydrogen bond depends on the electronegativity difference between H atom and the highly electronegative atoms like F, O and N.

The strength of hydrogen bond decreases in the order

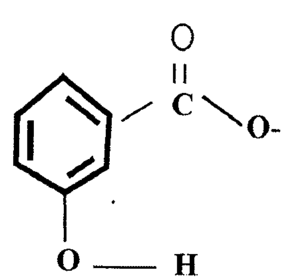
F – H ..... F > O – H. ..... O > N – H ..... N.

Effects of hydrogen bonding : Intermolecular hydrogen bonding increases m.p. ,b.p., solubility viscosity and surface tension while intramolecular hydrogen bonding has reverse effects.

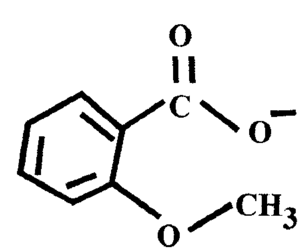
For example, 0- hydroxy benzoic acid is stronger than 0- methoxy benzoic acid or m-hydroxy benzoic acid because O – hydroxybenzoate ion is stabilized by intramolecular hydrogen bonding (chelation)



(Chelation occurs)



and



(No chelation Occurs)

Factors affecting bond length:

(1) bond length increases with the increase in the size of bonded atoms.

(2) **Multiplicity of bonds:** It decreases with the increase in the multiplicity of bonds, for example, bond length decreases in the order C–C> C=C> C≡C

(3) **Type of hybridistion:** As an s-orbital in smaller in size, greater the s - character, the shorter (smaller) is the size of hybrid orbital and, therefore ,shorter is the bond length .For example,

sp^3 C-H > sp^2 C-H> sp C– H

Bond energy or bond dissociation enthalpy: Smaller the bond length the stronger will be the bond formed and larger will be bond dissociation enthalpy

Dipole moment : The dipole moment help to predict whether the molecule is polar or non-polar. A molecule may contain polar bonds but its dipole moment may be zero if it has symmetrical structure ,that is , if it has no lone pair (s) of electrons in the valence shell of the central atom and all the terminal atoms are identical. For example, dipole moment (u) = 0 in case of CCl_4 but u $\neq$ 0 in case $CHCl_3$. Dipole moment of NH_3 is more than that of NF_3 although N-F bond is more polar than N-H bond (Refer to class XI NCERT textbook Part II, page 107)

Just as all covalent bonds have some partial ionic character,the ionic bond also have partial covalent character. The partial covalent character of ionic bonds can be discussed with the help of Fajan rules. (please refer the Fajan's rule in NCERT textbook page 108 class XI)

Geometrical shapes can be predicated with the help of Valence shell-Electron pair –Repulsion (VSEPR) theory. (please refer the pages 108 to 113 of NCERT text book, class XI). The geometry of molecules or ions depends upon the no. of electron pairs around the central atom in its Lewis structure. While counting the electron pairs, lone pair (s) as well as bond pair (s), the multiple bond is treated as if it is a single bond or single electron pair. The repulsive interaction between electron pairs decrease in the order lp-lp>lp-bp.> bp-bp

Presence of lone pair (s) on the central atom of a species results in deviation from idealized shapes and changes in bond angles.

Type of Molecule	bp	lp	Total Number of electron pairs around the central atom	Geometry
CH_4	4	0	4	Tetrahedral, H–C–H angle 1095°
NH_3	3	1	4	Pyramidal, H–N–H angle 107°
H_2O	2	2	4	Bent, H–O–H angle 104.5°

For Valence – bond theory: Hybridisation (Please refer the NCERT text book class XI, pages 116 – 121)

Type of Molceule	Total No. of electron pairs around the central atom	Shape of Moleceule lions	Hybridisation type	Example
AB_2	2	Linear	sp	BeF_2
AB_3	3	Trigonal blaner	sp^2	BF_3, $AlCl_3$ NO_3, CO_3

AB_2E	3	Bent	sp^3	SO_2, O_3
AB_4	4	Tetrahedral	sp^3	CH_4, NH_4
AB_3E	4	Trigonal pyrmaidal	sp^3	NH_3, PX_3 X=F, CL, B, I
AB_2E_2	4	Bent	sp^3	H_2O, OF_2, NH_2^-
AB_5	5	Tirgonal bipyramidal	sp^3d	PF_5, PCl_5
AB_4E	5	See Saw / Irregular Tetrahedral	sp^3d	SF_4
AB_3E_2	5	Bent T-shaped	sp^3d	ClF_3
AB_2E_3	5	Linear	sp^3d	XeF_2, ICl_2^-, I_3^-
AB_6	6	Octahedral	sp^3d^2	SF_6, PF_6
AB_5E	6	Square pyramidal	sp^3d^2	BrF_5, $XeOF_4$, ClF_5
AB_4E_2	6	Square planar	sp^3d^2	XeF_4, ICl_4^-
AB_7	7	Pentagonal Bipyramidal	sp^3d^3	IF_7

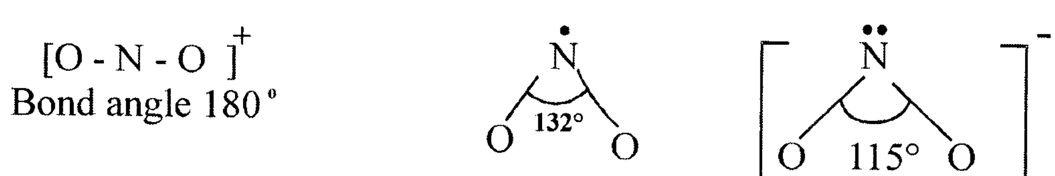
Hybridization scheme in complex ions (coordination entities) can be discussed with the help of valence bond theory and crystal field theory.

Shape of co-ordination entity	Hybridisation type	Example
Linear	sp	$[Ag(NH_3)_2]$
Tetrahedral	sp^3	$[Ni(CO)_4]$, $[NiCl_4]^{2-}$
Square planar	dsp^2	$[Ni(CN)_4]^{2-}$, $[PtCl_4]^{2-}$
Trigonal bipyramidal	dsp^3	$[Fe(CO)_5]$
Octahedral	sp^3d^3 d^2sp^3	$[CrF_6]^{3-}$, $[CoF_6]^{3-}$ $[FeF_6]^{3-}$ $[Fe(CN)_6]^{3-}$, $[Co(C_2O_4)_3]^3$

Molecular orbital theory (M. O. theory) : Valence bond theory failed to explain the paramagnetic nature of O_2 molecule but molecular orbital theory explained the paramagnetic native of O_2 molecule. (please refer NCERT text book class XI part I. Pages 122 to 126) The molecular configuration of C_2 moleculer shows that both the bonds joining the two carbon atoms are π- bonds. In most cases, a π- bond is not formed alone and is formed alongwith the σ – bond.

Effect of unshared elections present on the central atom of molecule/ ion on the bond angle

NO_2^+ NO_2 NO_2^-



Effect of electronegativity of central atom: The bond angle of the species having the same terminal atoms decreases with the decrease in the eledronegativity or increase in the size of central atom

H_2O	H_2S	H_2Se	H_2Te
104.5°	92.5°	91.°	90.5°

Effect of electronegativity (or size) of the terminal atoms on bond angle: The bond angle increases with decrease in the electronegatity (or with the increase in size) of the terminal

Atoms:	PF_3	PCl_3	PBr_3	PI_3
	97°	100°	101.5°	102°

Note: If a molecule / ion does not have unshared electrons on the central atom and if it possesses symmetrical structure having identical terminal atoms, the bond angle in the molecule / ion will be independent of the electronegativity or size of central or terminal atoms.

UNIT 4

CHEMICAL BONDING AND MOLECULAR STRUCTURE

MOCK TEST

(1) How many σ and π bonds are present in C_2 species ?

(2) Which of the following species has minimum bond angle?

NO_2, NO_2^+ and NO_2^-

(3) Which of the two has smaller dipole moment and why?

(a) CH_3F and CH_3 Cl

(b) NH_3 and NF_3

(4) 2- methoxy benzoic acid is less acidic than 2- hydroxy benzoic acid. Explain why?

(5) Predict the geometry and hybridization scheme in SF_4 molecule.

(6) Dipole moment of 1,4 – dimethoxybezone is not zero whereas that of 1,4 dichlorbenzone is zero. Explain why?

(7) The compound in which C uses sp^3 hybrid orbitats for bond formation is

(a) HCOOH (b) NH_2 CO NH_2 (c) $(CH_3)_3$ COH (d) CH_3 CHO

(8) Which of the following has zero dipole moment?

(a) ClF (b) PCl_5 (c) SF_4 (d) $CFCl_3$

(9) Among the following species identify the isostructural pairs NF_3, NO_3^-, BF_3, H_3O^+, HN_3

(a) [NF_3, NO_3^-] and [BF_3, H_3O^+] (b) [NF_3, HN_3] and [NO_3^-, BF_3]

(c) [NF_3, H_3O^+] and [NO_3^-, BF_3] (d) [NF_3, H_3O^+] and [HN_3, BF_3]

(10) Which of the following species has lowest ionization enthalpy?

(a) O (b) O_2 (c) O_2^+ (d) O_2^-

(11) The common features among the species CN^- , CO and NO^+ are

(a) b.o. three and isoelectronic (b) b.o. three and weak field ligand

(c) b.o. two and π acceptors (d) isoelectronic and weak field ligands

(12) The correct order of bond angles (smallest first) in H_2S, NH_3, BF_3 and Si H_4

(a) $H_2S < SiH_4 < NH_3 < BF_3$ (b) $NH_3 < H_2S < SiH_4 < BF_3$

(c) $H_2S < NH_3 < SiH_4 < BF_3$ (d) $H_2S < NH_3 < BF_3 < SiH_4$

(13) The state of hybridization of boron and oxygen atoms boric acid (H_3 BO_3) are respectively .

(a) sp^2 and sp^2 (b) sp^2 and sp^3

(c) sp^3 and sp^3 (d) sp^3 and sp^3

(14) The number and type of bonds between two carbon atoms in calcium carbide are

(a) One σ, one π (b) one σ, two π

(c) 2σ, one π (d) 2σ, one π

(15) The decreasing values of bond angles from NH_3 to (107°) to SbH_3 91.3°) down group 15 of periodic table is due to;

(a) decreasing lp- bp repulsion (b) decreasing electronegativity

(c) increasing bp- bp repulsion (d) increasing p-orbital character in sp hybrid orbitals

(16) Which of the following contains maximum number of lone pairs on the central atom?

(a) ClO_3^- (b) Xe F_4 (c) SF_4 (d) I^-_3

UNIT 5

THERMODYNAMICS

A system is a part of universe in which observations are made. The remaining universe which can interact with the system constitutes the surroundings . A boundry,real or imaginary separate the system from the surroundings.

[For the definitions of types of system, state functions (extensive and intensive,) , please refer the NCERT text book part 1, page 155 and 156 .] NOTE : the value of extensive property of the system for 1 mol of the substance also becomes intensive property. A process that occurs infimitermally slowly such that system always remains in equilibrium with its surroundings, is called reversible process.

Internal energy change (ΔU): Heat absorbed or released by the system at constant volume i.e. $\Delta U = q_v$

Enthalpy change (DH): Heat absorbed or released by the system at constant pressure $\Delta H = q_p$; $\Delta H < 0$ (Exothermic process), $\Delta H > 0$ (Endothermic process)

First law of thermodynamics: $\Delta U = q + w$. For a given change in state, q and w vary depending how the change is carried out . However, $q + w = \Delta U$ will depend upon the initial and final state of the system. Hence ΔU is also a state function.

Mechanical work or pressure – volume work is given by $W = - P_{ex} (\Delta V) = - P_{ex} (V_f - V_i)$ where P_{ex} is external pressure acting on the system.

If external pressure is not constant but changes during the process such that it is always infinitesimally greater that the pressure of gas (p_{in}). In an expansion process, the external pressure is always less than pressure of gas (p_{in} or simply 'p'). The work done in a reversible process is given by

$$W_{rev} = -\int_{V_i}^{V_f} p_{in}\, dv = -\int_{V_i}^{V_f} p dv = -2.303\, nRT \log \frac{V_f}{V_i} \quad \text{where} \quad V_i = \text{Initial volume; } V_f = \text{Final volume}$$

$$= -2.303\, nRT \log \frac{P_i}{P_f} \quad \text{where} \quad P_i = \text{Initial volume; } P_f = \text{Final volume}$$

In free expansion of an ideal gas in vacuum, no work is done by the gas because no force is opposing expansion ($p_{ex} = 0$) in a reversible or irreversible process. If the gas neither lose nor gain heat from the surroundings, then q = 0 and therefore, there will be no change in the internal energy of the system. ($\Delta U=0$)

For isothermal irreversible change : $\Delta U=0$

$$\therefore q = -w = -[-p_{ex}(V_f - V_i)]$$

For isothermal reversible change : $\Delta U=0$

$$q = -w = 2.303\ nRT \log\frac{V_f}{V_i}$$

Relationship between ΔU and ΔH for the reactions involving gaseous reactions acid gaseous products occurring at constant T and P

$\Delta H = \Delta U + \Delta n_g RT$ where Δn_g : No. of moles of gaseous products minus no. of mol of gaseous reactants.

Standard enthalpy of reaction $(\Delta r H^{\theta})$ is the enthalpy change for the reaction when the reactants and products are in their standard states. The standard state of a substance at a specified temperature (not necessary 298 K) is its pure and most stable form at 1 bar pressure.

Second law of thermodynamics: For a spontaneous change in a system, the total entropy change ΔS_{total} is positive, i.e., $\Delta S_{sys} + \Delta S_{surr.} > 0$

When a system is in equilibrium, the entropy is maximum. Hence ΔS_{total} = O (at equilibrium).

Third law of thermodynamics : The entropy of a perfectly crystalline substance approaches zero as the absolute zero of temperature is approached.(walther Nernst)

Gibbs energy change $(\Delta_r G)$ and spontaneity :

$\Delta_r G < 0$	spontaneous process
$\Delta_r G > 0$	non-spontaneous process
$\Delta_r G = 0$	(At equilibrium)

The reaction is called exoergonic if $\Delta G < 0$ and endoergonic if $\Delta G > 0$. The sign of $\Delta G = \Delta H - T\Delta S$ also depends upon temperature. The temperature at which equilibrium is attained, is given by $T = \frac{\Delta H}{\Delta S}$

Important formulas used in thermodynamic calculations

$$\Delta_r S = \frac{q_{rev}}{T}$$

$$\Delta_{fus} S = \frac{\Delta_{fus} H}{T}, \text{ and } \Delta_{vap} S = \frac{\Delta_{vap} H}{T}$$

$$\Delta_r S^{\varnothing} = \Sigma \upsilon_p \Delta S^{\varnothing}(\text{products}) - \Sigma\ \upsilon_r \Delta S^{\varnothing}(\text{reactants})$$

$$\Delta_r H^{\varnothing} = \Sigma \upsilon_p\ \Delta_r H^{\varnothing}(\text{products}) - \Sigma \upsilon_r\ \Delta r H^{\varnothing}(\text{Reactants})$$

$\Delta_r G^{\varnothing} = \sum \upsilon_p \Delta_r G^{\varnothing}(\text{products}) - \sum \upsilon_r \; \Delta_f G^{\varnothing}(\text{Reactants})$

Gibbs energy and useful work: $T\Delta S$ is the energy of the system which is not available to do useful work. ΔH is the enthalphy change of the reaction. Therefore, $\Delta H - T\Delta S$ is the energy which is available to do useful work. The decrease in the Gibbs energy is equal to the maximum possible useful work that can be derived from a process. $-\Delta_r G = W_{useful.}$

In case of galvanic cells, useful work done by the cell is given by: $\Delta_r G^{\varnothing} = -\, n\, Ecell^{\varnothing}\, F$ and in standard states $\Delta_r G^{\varnothing} = -\, n\, Ecell^{\varnothing}\, F$

Hess's law of constant heat summation is based on the law of conservation of energy. if a reaction is the sum of two or more constituent reactions, then enthalpy of overall reaction is the sum of enthalpy changes of the constituent reactions.

$$\Delta_r H^{\varnothing} = \Delta H_a^{\varnothing} + \Delta H_b^{\varnothing} + \Delta H_c^{\varnothing} + \ldots\ldots\ldots\ldots$$

(For definition of $\Delta_c H^{\varnothing}, \Delta_a H^{\varnothing}$, mean bond dissociation enthalpy $\left(\Delta H^{\varnothing}{}_{A\text{-}B}\right)$, lattice enthalpy. $\left(\Delta_L\ H^{\varnothing}\right)$, $\Delta_{fus} H^{\varnothing}$, $\Delta_{vap} H^{\varnothing}$, $\Delta_{sub} H^{\varnothing}$ please refer NCERT text book Part I, Page 171 to 173.

Gibbs energy and equilibrium : A reversible reaction occur in either direction simultaneously so that a dynamic equilibrium in set up. This means that forward and reverse reaction should proceed with the decrease in Gibbs energy which is possible if the free energy of the system in minimum at equilibrium i.e. $\Delta_r G = O$.

$O = \Delta_r G^{\varnothing} + 2.303\ RT \log K$

and $\Delta_r G^{\varnothing} = \Delta_r H^{\varnothing} - T\, \Delta_r S^{\varnothing}$

UNIT 5

THEMODYAMICS

(MOCK TEST)

(1) For the reaction 2 Cl (g) $\rightarrow$ Cl_2 (g), the signs of ΔH and ΔS respectively are

(a) +, - (b) + , + (c) - , - (d) - ,+

(2) Identify the correct statement regarding entropy

(a) at absolute zero of temperature entropy of perfectly crystalline substance is (+) ve

(b) at absolute zero of temperature, entropy of all crystalline substances are zero.

(c) at absolute zero of temperature, entropy of a perfectly crystalline substances is taken to be zero.

(d) at o°C entropy, of a perfectly crystalline substance is taken to be zero.

(3) The factor of ΔG values is important in metallurgy . The values for following reaction at 800°C are given as:

$S_2(g) + 2\ O_2 \rightarrow 2SO_2(g); \Delta G = -544\ kJ\ mol^{-1}$

$2\ Zn\ (s) + S_2(g) \rightarrow 2\ ZnS\ (s)\ ; \Delta G = -293\ k\ J\ mol^{-1}$

$2\ Zn\ (s) + O_2(g) \rightarrow 2\ ZnO\ (s)\ ; \Delta G = -480\ k\ J\ mol^{-1}$

The ΔG for the reaction:

$(2)\ ZnS\ (s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2\ (g)$

(a) $-731\ k\ J\ mol^{-1}$ (b) $-733\ k\ J\ mol^{-1}$

(c) $-229\ k\ J\ mol^{-1}$ (d) $-357\ k\ J\ mol^{-1}$

(4) For an isothermal expansion of 1 mol of an ideal gas from $1dm^3$ to $4dm^3$ at 27°C, the value of ΔU is

(a) 57 cal (b) 0 (c) 8.314 Cal (d) 83.14 Cal

(5) The standard Gibbs energy change $\Delta_r G^{\varnothing}$ is related equilibrium constant Kp as

(a) $K_p = -RT \ln \Delta_r G^{\varnothing}$

(b) $K_p = \frac{1}{RT} \frac{1}{e^{RT}}$

(c) $K_p = -\frac{\Delta_r G^{\varnothing}}{RT}$

(d) $K_p = e^{\frac{\Delta G^{\varnothing}}{R}}$

(6) One mole of a gas is heated at constant volume,the temperature is raised from 298K to 308K. Heat supplied is 500J . Then which statement is correct ?

(a) q = w = 500J , $\Delta U = 0$

(b) q = $\Delta U = 500J$, $\Delta V = 0$

(c) q = w = 500J , $\Delta V = 0$

(d) ΔU = 0 , q =w = -500J

(7) For which one of the following equation is $\Delta_r H^{\varnothing}$ is equal to $\Delta_f H^{\varnothing}$ for the product

(a) $N_2\ (g) + O_3\ (g) \rightarrow N_2O_3\ (g)$

(b) $CH_4\ (g) + 2\ Cl_2\ (g) \rightarrow CH_2\ Cl_2 + 2H\,Cl\ (g)$

(c) $Xe\ (g) + 2F_2\ (g) \rightarrow XeF_4\ (g)$

(d) $2\ CO\ (g) + O_2\ (g) \rightarrow 2\ CO_2\ (g)$

(8) The enthalpy of vaporization of a liquid in 30 KJ mol^{-1} and entropy of vaporisation is 75 JK^{-1} .The boiling point of the liquid is

(a) 250K

(b) 400K

(c) 450K

(d) 600K

Hint $T = \frac{\Delta_{vap} H}{\Delta_{vap} S}$

(9) An ideal gas expands in volume from 1×10^{-3} m^3 to 1×10^{-2} m^3 at 300K against a constant pressure of 1×10^5 N m^{-2}. The work done

(a) - 900 J

(b) - 900 KJ

(c) 270 KJ

(d) 9600 KJ

(10) $(\Delta H - \Delta U)$ for the formation of CO from its elements at 298 k is :

(a) + 16.8 KJ mol^{-1}

(b) + 244.8 KJ mol^{-1}

(c) -1238.78 KJ mol^{-1}

(d) 1238.78 KJ mol^{-1}

(11) The enthalpy of reaction : CaO (s) + CO_2(g) ® $CaCO_3$(s), $\Delta_r H$ = -178.3 kJ mol is not an enthalpy of formation of Ca CO_3. Explain why ?

(12) Predict in which the following entropy increases / decreases

(a) H_2 (g) $\rightarrow$ 2H (g)

(b) Normal egg $\rightarrow$ hard–boiled egg

(13) For an isolated system, ΔU = o, what wil be the sign of Δs?

(14) For the reaction : 2Cl (g) $\rightarrow$ Cl_2 (g) what are signs of ΔH and ΔS?

(15) Two moles of CO and one mole of O_2 are taken in 1L container. They completely react to form two moles of CO_2 . The gases deviate from ideal behaviour appreciably and pressure in the vessel changes from 70 to 40 atm.Find the absolute value of DU at 500 K (1 L atm = 0.1 KJ) Ans 557 KJ

[Hint : $\Delta H = \Delta U + \Delta(PV) = \Delta U + V\Delta P$]

(16) Given that $C + O_2 \rightarrow CO_2$; $\Delta_r H$ = x KJ/ mol

2 $CO + O_2 \rightarrow 2CO_2$; $\Delta_r H$ = -y KJ/mol

Calculate $\Delta_f H^{\varnothing}(CO)$.

UNIT-6
SOLUTION
Expression of Concentration

MOLARITY (M) is the number of moles of solute dissolved per litre of solution. Its unit is mol/L.

$$M = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litres}}$$

For liquids where concentration is expressed in percentage and density

$$M = \frac{\text{Percentage} \times \text{density} \times 10}{\text{Molar mass of solute}}$$

MOLALITY (m) is the number of moles of solute dissolved per kg of solvent. Its unit is mol/kg

$$m = \frac{\text{Number of moles of solute}}{\text{Mass of solvent}}$$

NORMALITY (N) is the number of gram equivalents of solute dissolved per litre of solution. Its unit is equivalents per litre.

$$N = \frac{\text{Number of g-equivalents}}{\text{Volume of solution in litres}}$$

Mole fraction: It is the ratio of number of moles of one component to the total no.of moles of solution.

$$X = \frac{\text{Number of moles of a component}}{\text{Number of moles of solution}}$$

For binary solution $X_A + X_B = 1$

ppm (parts per million): mass of solute dissolved per million parts of the system.

$$ppm = \frac{\text{Number of parts by mass or volume of a component}}{\text{Total parts by mass or volume of the solution}}$$

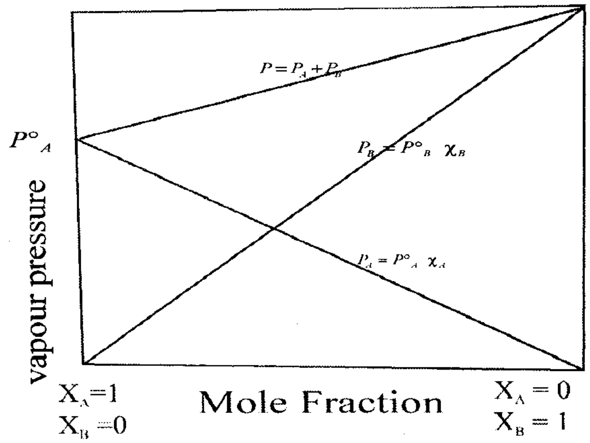
VAPOUR PRESSURE

Pressure exerted by vapour phase over liquid surface in equilibrium with each other at a given temperature is known as vapour pressure of that liquid.

Vapour pressure of liquid decreases when a non-volatile solute is added to it as molecules of the solvent are attracted by the particles of solute resulting in decrease in escaping tendencies of solvent.

Raoult's Law: For solution of volatile liquids, the partial vapour pressure of each component in solution is directly proportional to its mole fraction.

$$P_A \propto X_A$$
$$P_A = P_A^0 \times_A$$
$$P_B = P_B^0 X_B$$
$$P_{Total} = P_A^0 X_A + P_B^0 X_B$$
$$P_{Total} = P_A^0 (1 - X_B) + P_B^0 X_B$$
$$P_{Total} = P_A^0 + (P_B^0 - P_A^0) X_B$$



Raoult's Law for non-volatile solute:- Relative lowering of vapour pressure of a solution is equal to the mole fraction of solute when solvent alone is volatile and the solute in non-volatile and non- electrolyte [when solution is dilute, i.e., $n_A + n_B \approx n_A$]

$$\frac{P_A^0 - P_{sol^n}}{P_A^0} = X_B = \frac{W_B.M_B}{M_B.W_A}$$

IDEAL SOLUTIONS

The solution, where unlike interations (A-B) are identical to like interactions (A-A) and (B-B) type, are known as ideal solutions.

Characteristics-1. Vapour pressure of such solutions is the same as given by Raoult's law.

(2) $\Delta H_{mix} = 0$

(3) $\Delta V_{mix} = 0$

Chorobenzene and bromobenzene, benzene and toluene, n-hexane and n-heptane form nearly ideal solutions.

NON IDEAL SOLUTIONS

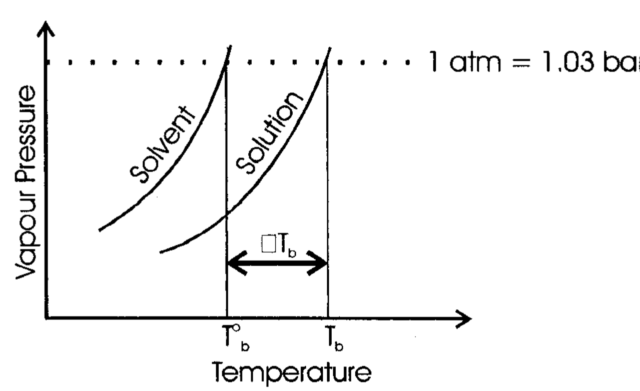
Elevation of Boiling point:-

Boiling point of a liquid in the temperature at which its vapour pressure becomes equal to that of 1 atm or 1.013 bar. The elevation of b.p. is related to the molality (m) of the solution as below :

$$\Delta T_b = K_b m = K_b \frac{W_B \times 1000}{M_B \times W_A}$$

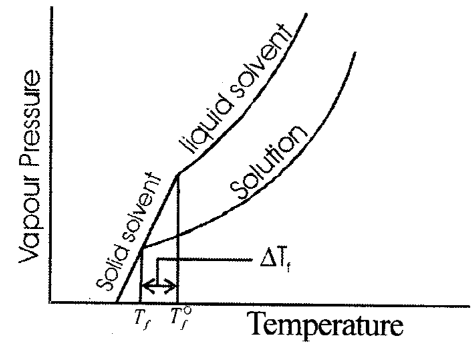
$$\Delta T_b = T_b - T_b^{\circ} = \text{Elevation of boiling point}$$

K_b = Molal boiling point elevation constant



Depression of freezing point:- Freezing point of liquid is the temperature at which liquid and solid phases coexist and have the same vapour pressure. Freezing point of the liquid solvent in depressed when a non-volatile solute is added to it.

$$\Delta T_f = K_f m = K_f \frac{W_B \times 1000}{M_B \times W_A}$$



$\Delta T_f = T^o{}_f - T_f$ = Depression of freezing point

K_f = Molal freezing point depression constant.

Non-ideal solution showing + ve and – ve deviations from Raoult's law:

Showing positive deviation	Showing negative deviation
Acetone + Carbon disulphide	Chloroform + Benzene
Acetone + Ethyl alcohol	Chloroform + Acetone
Acetone + Benzene	Chloroform + Diethyl ether
Methyl alcohol + Water	
Ethyl alcohol + water	Acetone + Aniline
Carbon tetrachloride + Chloroform	HCl + Water
Carbon tetrachloride + Benzene	HNO_3 + Water
Carbon tetrachloride + Toluene	Acetic and + pyridine, phenol & aniline

Characterists of solution showing -ve deviation from Raoult's law:

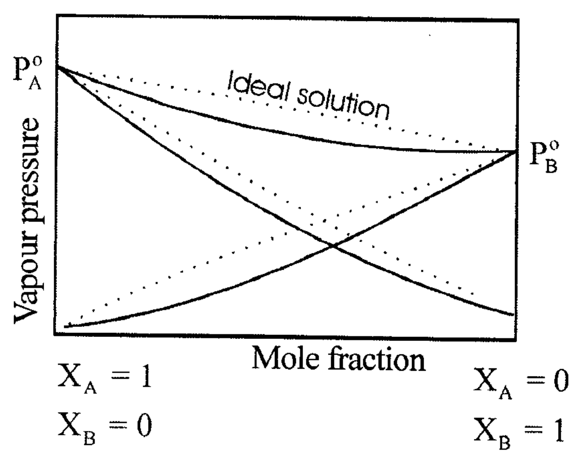
(a) $\Delta H_{mix} < 0$ (b) $\Delta V_{mix} < 0$

(c) Vapour pressure of solution is less than what is given by Raoult's law.

$P_{sol^n} < P_B^o \chi_A + p_B^o \chi_B$

$p_A < P_A^o \chi_A$

$p_B < P_B^o \chi_A$



Characteristics of solution showing + ve deviation

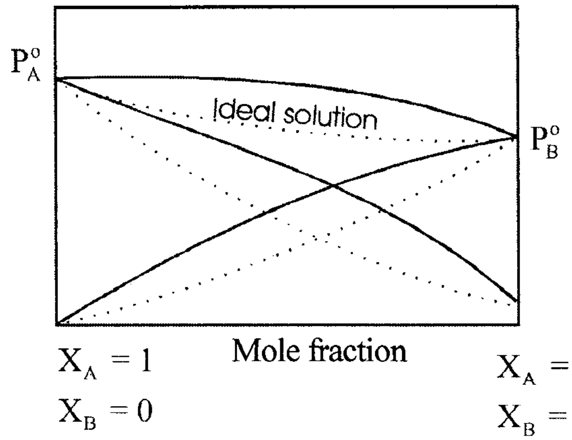
(a) $\Delta H_{mix} > 0$ (b) $\Delta V_{mix} > 0$

(c) Vapour pressure of soluton is more than what is given by raoult's law.

$P_{sol^n} > P_A^o \chi_A + p_B^o \chi_B$

$p_A > P_A^o \chi_A$

$p_B > P_B^o \chi_B$



Note: Curved lines show non-ideal behaviour and dotted line, ideal behaviour.

AZEOTROPES

(i) Azeotropic mixtures with minimum point i.e. whose boiling point is less than either of the two pure components. This is formed by that composition of non-ideal solution showing positive deviation for which the vapour pressure is maximum. (95% ethanol + 5% H_2O)

(ii) Azeotropic mixtures wtih maximum boiling point i.e. whose boiling is more than either of the two pure components. This is formed by that composition of a non-ideal solution showing negative for which the vapour pressure is minimum. (68% HNO_3 + 32% H_2O), (20% HCl + 80% H_2O).

COLLIGATIVE PROPERTIES

The properties of a solution which depends on number of moles of solute but are independent of its nature are known as colligative properties. These are

1. Relative lowering of vapour pressure.
2. Elevation of Boiling point.
3. Depression of Freezing point.
4. Osmotic pressure.

Osmotic pressure:- pressure applied on solution to stop osmosis is known as osmotic pressure

$$\pi \propto \frac{n_B T}{V} \text{ or } \pi = \frac{n_B RT}{V}$$

Osmotic pressure of a solution is directly proportional to the number of moles of solute dissolved per litre of solution at a given temperature.

Solutions having equal molar concentration and equal osmotic pressure called at a given temperature are called isotonic solutions, e.g., A 0.91% solution of NaCl is isotanic with human RBC. A solution of NaCl with concentration > 0.90% is hypotonic and RBC will swells up and even burst in solution. A NaCl solution with concentration < 0.91% is called hypertonic, RBC will shrink in such solution.

Abnormal molecular mass. When the molecular mass of a substance as determined by using colligative properties, does not come out to be same as expected theoretically, it is said to show abnormal molecular mass.

Abnormal molecular mass is obtained when the substance in the solution undergoes dissociation (e.g. NaCl in water) or **association** (e.g. organic acids in benzene). Dissociation results in the increases in the number of particles and hence increase in the value of colligative property and decrease in the molecular mass. Association results in the reverse.

Van't Hoff factor (i) is given by

$$v = \frac{\text{Experimental value of the colligative property}}{\text{Calculated value of the colligative property}}$$

$$\text{As molecular mass } \alpha \frac{1}{\text{Colligative property}},$$

$$\text{hence } i = \frac{\text{Calculated molecular mass}}{\text{Observed molecular mass}} = \frac{M_{\text{normal}}}{M_{\text{observed}}}$$

Modified formulas for substacne undergoing dissociation or association in the solution are

(i) $\Delta T_b = i\ K_b\ m$

(ii) $\Delta T_f = i\ K_f\ m$

(iii) $\pi = i \frac{n}{V} RT$

(iv) $\frac{P_A^0 - p_{sol^n}}{P_A^o} = i\chi_B$

If one molecule of a substance A dissociated to from n molecules or ions and α is the degree of dissociation, then starting wtih one mole of A,

	A	$\rightarrow$	n P
Initial mol :	1		o
At eqn.	$1 - \alpha$		$n\ \alpha$

Total no. of moles at equilibrium = $1 - \alpha + n\ \alpha$

$$i = \frac{1 - \alpha + n\alpha}{1} \quad \text{or} \quad \alpha = \frac{i - 1}{n - 1}$$

If n molecules of a substance A associate to from A_n and α is the degree of association then starting with one mole of A

	A	$\rightarrow$	A_n
Initial mol :	1		o
Ateqm.	$1-\alpha$		$\frac{n}{\alpha}$

Total no. of moles at equilibrium = $1 - \alpha + \frac{\alpha}{n}$

$$i = \frac{1 - \alpha + \frac{\alpha}{n}}{1} \quad \text{or} \quad \alpha = (1 - i)\,\frac{n}{n - 1}$$

(MOCK TEST) UNIT - 6

1. An azeotropic mixture of two liquids has boiling point higher than either of them when it.
   (a) Shows positive deviation from Raoult's law
   (b) Show no deviation from Raoult's law
   (c) Show negative deviation from Raoult's law
   (d) is saturated

2. Consider 0.02 M aqueous solutions of
   1. NaCl 2. $BaCl_2$ and 3. urea
   The relative lowering of vapour pressures in these solutions will be such that
   (a) 2 < 1 < 3 (b) 2 > 3 >1 (c) 1 > 2 > 3 (d) 3 < 1 < 2

3. Phenol associates in benzene as
   $C_6H_5OH \rightleftarrows \frac{1}{2}(C_6H_5OH)_2$ If 'x' is the degree of association of phenol then the total number of moles of particles present at equilibrium is
   (a) 1 -x (b) 1+x (c) $1+\frac{x}{2}$ (d) $1-\frac{x}{2}$

Pick out the incorrect statement :

4. On mixing two pure liquids to form an ideal solution , there is
   (a) no change in volume
   (b) no change in Gibbs energy
   (c) no evolution or absorption of heat
   (d) entropy change

(5) The dissolution of NH_4Cl in water is endothermic even though dissolves in water spontaneously. Which one of the following statement best explains this behaviour
   (a) The bonds in solid are weak
   (b) The entropy driving force causes dissolution
   (c) Endothermic processes are energetically favourable.
   (d) The dissolving process is unrelated to energy.

(6) Which of following O.1.M aqueous solutions will have the lowest freezing point
   (a) K_2SO_4 (b) NaCl (c) NH_2CONH_2 (d) $C_6H_{12}O_6$

(7) 0.2 molal acid HX is 20% ionized in solution (K_b = 0.52 K/m) The boiling point of solution is (standard boiling of water is 373K)
   (a) 373.12K (b) 373.10K (c) 373.24K (d) 373.30K

(8) At 80°C, the vapour pressure of pure liquid 'A' is 520 mm Hg and that of pure liquid 'B' is 1000 mmHg. If the solution of 'A' and 'B' boils at 80°C and 1 atm pressure, the amount liquid of 'A' in the mixture is (1 atm = 760 mm Hg)

(a) 48 percent mol (b) 50 percent mol

(c) 52 percent mol (d) 34 percent mol

(9) A solution 'X' is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9 then more water is added to the solution 'X' such that the mole fraction of water in solution becomes 0.9 the boiling point of this solution is

(a) 380.4 K (b) 376.2 K (c) 375.5 K (d) 354.7 K

(10) During depression of freezing point in a solution, the following are in equilibrium

(a) Liquid solution, solid solvent (b) Liquid solvent, solid solute

(c) Liquid solute, solid solute (d) Liquid solute, solid solvent

(11) 2g of $C_6 H_5$ COOH dissolved in 25g benzene shows a depression in freezing pint equal to 1.62K. (K_f = 4.9 k kg mol^{-1}) The value of van't hoff factor is:

(a) 0.5 (b) 1 (c) 2 (d) 1.5

(12) Pick out the incorrect statement:

(a) The vapour pressure of solution containing non volatile and non dissociative solute in less than that of pure solvent.

(b) Reverse osmosis occurs if a pressure smaller than the osmotic pressure of solution is applied on solution side.

(c) Only solvent molecules solidify at the freezing point

(d) Molar mass of NaCl determined by any of the colligative properties is found to be less than that of normal (expected) value.

(13) Which one of the following colligative properties can provide molar mass of proteins with greatest precision?

(a) Relative lowering of vapour pressure

(b) Osmotic pressure

(c) Elevation of boiling point

(d) Depression of freezing point

(14) Which of 0.05 m aq. solutions of following compounds exhibit the largest depression of freezing point?

(a) NaCl (b) K_2SO_4 (c) C_6H_{12} (d) $Al_2(SO_4)_3$

(15) Which of the following is not true for an ideal solution?

(a) Raoult's law is obeyed in the entire concentration range of a binary solution.

(b) $\Delta H_{mix} = 0$ (c) $\Delta V_{mix} = 0$ (d) $\Delta S_{mix} = 0$

UNIT - 7

EQUILIBRIUM

A state of equilibrium is attained when two opposing process (forward and reverse) occur simultaneously at the same rate . The criterion for equilibrium for the reaction; aA + bB $\rightleftarrows$ cC + dD is $\Delta_r G = 0$. This is possible only if at equilibrium, Gibbs energy of system is minimum, i.e., $\Delta_r G$ is zero. $\Delta_r G^{\varnothing}$ can never be zero because it is calculated from the $\Delta_f G^{\varnothing}$ of the reactants and products. The $\Delta_r G^{\varnothing}$ is related to equilibrium constant K_c or Kp as follows: $O = \Delta_r G^{\varnothing} - 2.303\ RT \log K$

and $\Delta_r G^{\varnothing} = \Delta_r H^{\varnothing} - T\Delta_r S^{\varnothing} = -2.303\ RT \log K$

Law of equilibrium: There is no net change in the composition of the equilibrium mixture at a given temperature. At constant temperature, the product of concentrations of reaction products raised to respective stoichiometric coefficients in balanced chemical equation divided by product of concentration of reactants raised to their individual stoichiometric coefficients has a constant value:

$$Kc = \frac{[C]^C\ [D]^d}{[A]^a\ [B]^b} \text{ and } kp = \frac{p_C^c\ p_D^d}{p_A^a\ p_B^b}$$

Where $K_p = K_c\ (RT)^{\Delta ng}$

Δng = [sum of stoichiometric coefficients of gaseous products–sum of stoichiometric coefficients of gaseous reactants]

Priedicting the direction of reaction: Reaction quotient is ratio of product of concentrations of products to prducts of concentrations of reactants raised to powers equal to their respective stoiehiometric coefficients. Concentrations of reactants and products are different from equilibrium concentrations

If $Q_C > K_C$, the reaction proceeds in the reverse direction and it $Q_C < K_C$ the reaction will proceed in the forward direction if $Q_C = K_C$, no net reaction occurs.

Magnitude of equilibirum constant depends upon the way in which a reaction is written.

Chemical equation	Equilibrium constant
a A + bB $\rightleftarrows$ cC + dD	K
cC + dD $\rightleftarrows$ aA + bB	$K_1 = \frac{1}{K}$
N aA + n bB $\rightleftarrows$ n c C + n d D	$K_2 = K^n$

$$\frac{a}{n}A\frac{b}{n}B \rightleftarrows \frac{c}{m}C + \frac{d}{n}D \qquad K_3 = K^{1/n}$$

When individual balanced equations are combined, multiply their equilibrium constants to obtain the equilibrium constant for the net reaction. For example,

$$N_2 + O_2 \rightleftarrows 2NO ; K_1$$

$$N_2O \rightleftarrows N_2 + \frac{1}{2}O_2 \;; K_2$$

$$N_2 + \frac{1}{2}O_2 \rightleftarrows 2NO, K = K_1 \times K_2$$

Hetrogeneous equilibria do not include the concentration term for pure solids and pure liquids in equilibrium constant expressions. A very large value of K_c or K_p signifies that forward reaction goes to completion or very nealy so. A very small value of K_c of K_p signifies that forward reaction does not occur to any significant extent. If the numerical value of K_c or K_p in neither too large (i.e. very large) nor very small, the reaction is most likely to reach a state of equilibrium.

Le Chatelier's principle When a system of equilibrium is subjected to a change in temperature, pressure or concentration of a reacting species, the system changes in a way that partially contracts the change while reaching a new state of equilibrium.

Arrhenius acids and Bases: Acids dissociates in water to given H^+ ion and bases to give OH^- ions.

Bronsted Acids and bases:-

Bronsted Acids : Proton donor ; Bronsted Bases : Proton acceptor

Each conjugate acid has are extra proton and each conjugate base has one proton less

Species	Conjugate acid	Conjugate Base
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{2-}
NH_3	NH_4^+	NH_2^-

Lewis acids and bases:-

Lewis acids : Electron pair acceptor ; Lewis bases : Electron pair donor

The pH Scale:-

Activity of hydrogen in $(a_H+) = [H^+]/\text{mol L}^{-1}$

$$PH = -\log a_H + = -\log \{[H^+]/\text{mol L}^{-1}\}$$

$$POH = -\log \{[OH^-]/\text{mol L}^{-1}\}$$

and pH + pOH = 14

$\because$ $[H^+][OH^-] = 1.0\times10^{-14}$

Ionisation constant of water and its ionic product.

$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$

or simply $H_2O \rightleftarrows H^+ + OH^-$

$$k_a = \frac{[H^+][OH^-]}{[H_2O]}$$

$k_a[H_2O] = K_w = [H^+][OH^-]$

$k_w = [H^+] = [OH^-] = 10^{-14}$ at 298K

Ionisation constants of Acid and bases (Acid - Base Equilibrium)

	$HX \rightleftarrows$	H^+	$+X^-$
Initial Concen /M	C	0	0
Change in Concen/M	$-C\alpha$	$+C\alpha$	$+C\alpha$
Equilib Concn/M	$C(1-\alpha)$	$C\alpha$	$C\alpha$

Where α = degree of ionisation

$$k_a = \frac{[H+][X^{-1}]}{[Hx]} = \frac{C\alpha.C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

Similarly for base MOH $\rightleftarrows$ $M^+ + OH^-$

$$K_b = \frac{C\alpha^2}{1-\alpha}$$

Product of ionisation constants of an acid (k_a) and its cerjugate base (k_b) is equal to ionic product of water i.e., $K_a \times k_b = k_w$

Ionisation of di and polybasic acids and di and polyacidic bases:

For example for diabasic acid (H_2X)

$H_2 \rightleftarrows H^+ + HX^-$

$$Ka_1 = \frac{[H^+][HX^-]}{[H_2X]}$$

and $HX^- \rightleftarrows H^+ + X^{2-}$

$$Ka_2 = \frac{[H^+][X^{2-}]}{[HX^-]}$$

Higher order ionisation constants are smaller than lower order ionisation constants. Poly protic acid solution contain a mixture of acids like H_2X, HX^- and X^{2-} in case, of diprotic acids like H_2S. H_2CO_3 and oxalic acid.

Common in effect : The depression of ionisation of weak electrolyte by the presence of common ion from a strong electrolyte is called common ion effect.

Hydrolysis of salts and pH of their solutions:-

- Salts of strong acids and strong bases (e.g., NaCl) do not hydrolyse. The solution pH = 7
- Sall of weak acids and strong bases (e.g, CH_3 COO Na) hydrolyse : pH > 7 (The anion acts as base)
- Salt of strong acids and weak bases (e.g, NH_4Cl) hydrolyuse : PH < 7 (The cation acts as an acid)
- Salt of weak acids and weak based (e.g., CH_3 $COONH_4$) hydrolyse (The cation acts as an acid and anion as a base but whether the solution is acidic or basic depends upon the relative values of K_a and K_b for these ions.
- The pH of solution of salts of weak acids and strong bases i.e. given by

$$X^- + H_2O \rightleftarrows HX \quad + \quad OH^-$$

(Weak acid) (Strong base)

- The pH of solution of salts of strong acid and weak base is given by :

  MOH is weak base and H^+, strong acid.

$$M^+ + H_2O \rightleftarrows MOH + H^+$$

$$PH = 7 - \frac{1}{2}(Pk_b + \log c)$$

- The pH of solution of salts of weak and and weak base is given by

$$M^+ + X^- + H_2O \rightarrow M\,OH + HX$$

$$PH = 7 + \frac{1}{2}(pk_a - pk_b)$$

Buffer solutions:- The solutions, which resist the change in pH on dilution or addition of small amounts of acid or base, are called buffer solutions.

Acid buffer:- Solution of weak base and its salt with strong acid e.g., NH_4 OH + NH_4Cl

Basic buffer:- Solution of weak acid and its salt with strong base, e.g., CH_3COOH + NaOH

Buffer Capacity:- It is the change in pH with the number of waves of acid or base added.

$$\text{Buffer capacity} = \frac{d\,pH}{d\,n_{\text{acid a base}}}$$

Henderson- Hasselbalch. Equation for a buffer solution of weak acid and its salts:

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \qquad pH = Pk_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

pH of a buffer solution of weak base and its salt is given by

$$P_{OH} = pK_b + \log \frac{[BH^+]}{[B]} = pK_b + \log \frac{[\text{conjugate acid}]}{[\text{Base}]}$$

$$\text{Or} \qquad 14\text{-pH} = pk_b + \log \frac{[\text{conjugate acid}]}{[\text{base}]}$$

Solubility product constant (K_{sp}) :- The equilibrium constant that represent the equilibrium between undissolved salt (solute) and its ions in a saturated solution is called solubility product constant (Ksp). In the absence of equilibrium i.e, if the concentration of one or more species is not the equilibrium concentration, the product of concentration of ions raised to powers equal to respective stoichiometric coefficients appearing in balanced chemical equation is called Q_{sp}.

$$CaF_2\,(s) \rightleftarrows Ca^{2+}_{(aq)} + 2F^-(aq)$$

$$K_{sp} = [Ca^{2+}]\,[F^-]^2$$

If the concentration of any one of the ions is increased, it will combine with the ion of opposite charge and some of the salt will be precipitated till once again $K_{sp} = Q_{sp}$ and if the concentration of any one of thier ions decreased more salt will dissolve to increase the concentration of both the ions till once again $K_{sp} = Q_{sp}$

UNIT-7

EQUILIBRIUM

(MOCK TEST)

(1) $K_p|K_c$ for the reaction : $CO(g) + \frac{1}{2} O_2(g) \rightleftarrows CO_2(g)$ is

(a) 1 (b) RT (c) $\frac{1}{\sqrt{RT}}$ (d) $R(T)^{1/2}$

(2) If K_1 and K_2 are respective equilibrium constants for the two reactions:

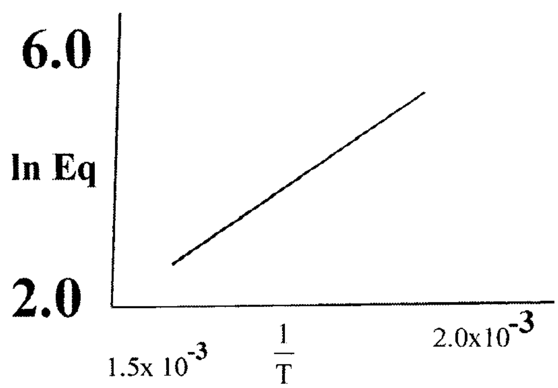
$XeF_6(g) + H_2O(g) \rightleftarrows XeOF_4(g) + 2HF(g)$

$XeF_6(9) + XeF_6 \rightleftarrows XeOF_4(g) + XeO_3F_2(g)$

then equilibrium constant for the reaction: $XeO_4(g) + 2HF \rightleftarrows XeO_3F_2(g) + H_2O(g)$ will be

(a) K_1/K^2_2 (b) $K_1 K_2$ (c) K_1/K_2 (d) K_2/K_1

(3) The plot of log keq V/s inverse of temperature for a reaction in shown below.



The reaction must be

(a) exothermic

(b) endothermic

(c) One with negligible enthalphy change

(d) highly spontaneous at ordinary temperature

(4) For the reaction: $CH_4(g) + 2O_2(g) \rightleftarrows CO_2(g) + 2H_2O(g)$ $\Delta_rH = -170.8$ KJ

Which of the following statements in not true?

(a) Addition of $CH_4(g)$ or $O_2(g)$ at equilibrium will cause a shift to the right.

(b) The reaction is exothermic

(c) At equilibrium, the concentrations of CO_2 (g) and H_2O (g) are not equal.

(d) The equilibrium constant for the reaction is given by

$$K_p = \frac{[CO_2]}{[CH_4]\,[O_2]^2}$$

(5) The equilibrium constant of a reaction is 300. If the volume of the reaction flask is tripled, the equilibrium constant will be.................at the same temperature.

(a) 300 (b) 600 (c) 900 (d) 100

(6) The pH of 10^{-8}M HCl in water in

(a) 9 (b) between 6 and 7

(c) between 7 and 8 (d) - 8

(7) Which is the weaket base?

(a) $C_2H_5O^-$ (b) ClO_4^- (c) NO_3^- (d) $CH_3\,COO^-$

(8) pH of water is 7. when a substance 'Y' is dissolved in water its pH becomes13. The substance is a salt of

(a) Weak acid and weak base (b) strong acid and strong base

(c) strong acid and weak base (d) weak acid and strong base

(9) 40 mL of 0.1M NH_3 is mixed with 20 mL of 0.1M HCl. What is pH of the mixture (Pk_b of NH_3 is 4.74)

(a) 4.74 (b) 2.26 (c) 9.26 (d) 5.0

(10) Solubility product of salt AB is 1×10^{-8} if the conc. Of A^+ ion is 10^{-3} M, The salt will start precipitating when the concentration of B^- is kept

(a) between 10^{-8} M to 10^{-7} M (b) between 10^{-7} to 10^{-6} M.

(c) greater than 10^{-5} M (d) smaller than 10^{-8} M.

(11) K_p for the reaction: $N_2 + 3H_2 \rightleftarrows 2NH_3$ is 49 at a certain temperature. Calculate the value of Kp at the same temperature for the reaction:

$$NH_3\ (g) \rightleftarrows \frac{1}{2} N_2\ (g) + \frac{3}{2} H_2\ (g)$$

(12) 9.2 g N_2O_4 (g) is taken in a closed 1L vessel and heated till the following equilibrium is reached $N_2O_4 \rightleftarrows 2NO_2$. At equilibrium 50% N_2O_4 is dissociated. What is the value of equilibrium constant?

(Ans. 0.2)

(13) Describe the effect of addition of Noble gas to the equilibrium mixture; $2SO_2 + O_2 \rightleftarrows 2SO_3$ at

(i) constant volume

(ii) constant pressure at a given temperature.

(14) Calculate the pH of the mixture containing 10 ml of 0.1 M H_2SO_4 and 10 ml of 0.1 M KOH .

(15) Calculate the pH of a solution which is 0.53 M CH_3 COO Na and 0.270 M CH_3 COOH. (K_a for CH_3 COOH = 1.8×10^{-5})

(16) Three drops of 0.20 M KI are added to 100ml of 0.01 M Pb $(NO_3)_2$. Will precipitate of Pb I_2 form? (Assume 1 drop = 0.05 mL) K_{sp} for Pb I_2 = 7.1×10^{-9} (No precipitate)