CONTENTS

1. Some Basic Concepts of Chemistry

Theory---------- 1-9
Ncert---------- 10-15
Question Alike----------16-23
Objective questions & Exampler----------24-28
JEE & NEET Previous Year----------29-32

2. Classification of Elements Periodicity in Properties

Theory---------- 81-92
Ncert----------93-100
Question Alike----------101-106
Objective questions & Exampler---------- 107-111
JEE & NEET Previous Year----------112-114

3. Chemical Bonding And Molecular Structure

Theory---------- 115-129
Ncert---------- 130-138
Question Alike----------139-142
Objective questions & Exampler----------143-148
JEE & NEET Previous Year---------- 149-154

4. Thermodynamics

Theory---------- 187-195
Ncert---------- 196-198
Question Alike----------199-201
Objective questions & Exampler----------202-206
JEE & NEET Previous Year---------- 207-212

5. Equilibrium

Theory---------- 213-229
Ncert---------- 230-246
Question Alike----------247-256
Objective questions & Exampler----------257-261
JEE & NEET Previous Year---------- 262-267

1

SOME BASIC CONCEPT OF CHEMISTRY

Chemistry is the science of molecules and their transformations. It is the science not so much of the one hendred elements but of the infinite variety of molecules that may be built from them. Chemistry is defined as the systematic investigation of the properties structure and behaviour of matter and the reaction of material substances is called chemistry.

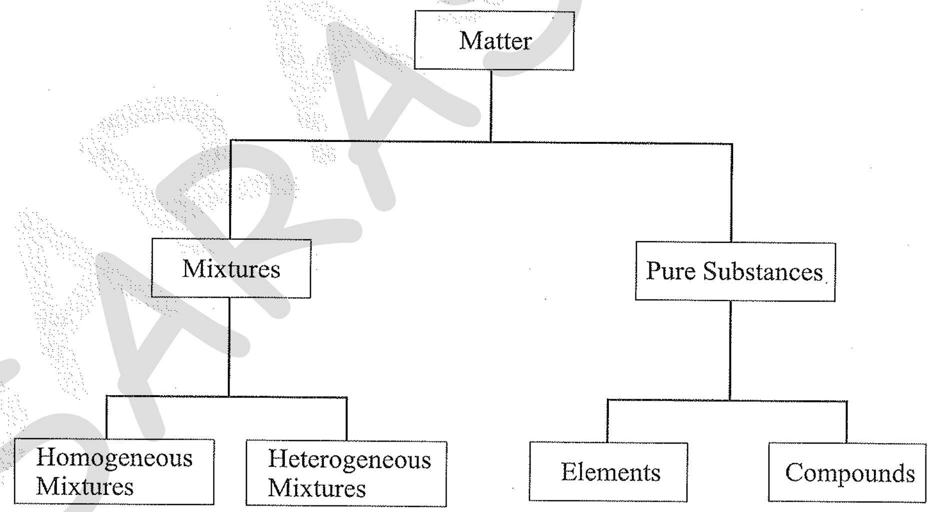
IMPORTANCE OF CHEMISTRY

Life savings drugs like cis platin and taxol have been found to be very effective for cancer therapy and AZT (Aziodothymidine) is used for AIDS victims. These compounds are obtained from animals and plants or by synthetic methods.

Matter

Matter is defined as anything that occupies space, possesses mass and the presence of which can be felt by anyone or more of our five senses.

Classification of Matter



PROPERTIES OF MATTER

Every substance has unique. Properties. These properties can be classified into two categoris.

Physical Properties

It can be measured or observed without changing the identity or the composition of the substance. Such as colour, odour, melting point, boiling point, density.

Chemical Properties

Require a chemical change to occur and ability to produce a change in the composition of matter.
Eg: Combustibility, Reactivity with acid of base.

LAWS OF CHEMICAL COMBINATION

One of the most important aspect of the subject of chemistry is the study of chemical reactions.
These chemical reactions take place according to certain laws, called the 'laws of chemical combination'.
These are :

1. Law of Conversation of Mass
2. Law of Constant Composition
3. Law of Multiple Proportions
4. Law of Reciprocal Proportions
5. Law of Combining Volumes (Gay Lussac's Law of Gaseous Volumes).

NOTE -The first four laws deal with the mass relationship whereas the fifth law deals with the volumes of the reacting gases.

Law of conservation of mass

1. This law was studied by the great French chemist Antoine Lavoisier in 1789 but verified by Landolt
2. This law may be stated as follows :
   It states that matter can neither be created nor destroyed.
   OR
   In all physical and chemical changes, the total mass of the reactants is equal to that of the products.
3. This law is also called the Law of indestructibility of matter.

Law of constant composition or definite proportions

1. This law was discovered by a French chemist J.L. Proust in 1799 but verified by Stas and Richads
2. It states that –
   A chemical compound is always found to be made up of the same elements combined together in the same fixed proportion by mass.

Law of multiple proportions

1. This law which was first studied by Dalton in 1804 and verified by Berzilius
2. It states that:
   When two elements combine to combine to form two or more chemical compounds, then the masses of one of the elements which combine with a fixed mass of the other, bear a simple ratio to one another.

Law of reciprocal proportions

1. This law was put forward by Richter in 1792 and verified by Stas
2. It states as follows :
   The ratio of the masses of two elements A and B which combine separately with a fixed mass of the third element C is either the same or some simple multiple of the ratio of the masses in which A and B combine directly with each other.
3. Law of reciprocal proportions is also called law of equivalent proportion

GAY LUSSAC'S LAW OF GASEOUS VOLUMES

When gases react together, they always do so in volumes which bear a simple ratio to one another and to the volumes of the gaseous products, if temperature and pressure remains constant.
Eg : It has been experimentally observed that one volume of hydrogen reacts with one volume of chlorine to form two volumes of hydrogen chloride gas.

$$H_2 + Cl_2 \rightarrow 2HCl$$

The ratio by volume of various reactants and products is
1 : 1 : 2 which is a simple whole number ratio.

AVOGADRO'S HYPOTHESIS

1. Berzelius to put forward his hypothesis called Berzelius Hypothesis.
2. It may be stated as –
   Equal volumes of all gases under similar conditions of temperature and pressure contain equal number of atoms.
3. Avogadro, an Italian scientist put forward the hypothesis known as Avogadro's hypothesis. This states that
   Equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules

DALTON'S ATOMIC THEORY

Although the origin of idea that matter is composed of small indivisible particles called '*a – tomio*' (meaning — *indivisible*), dates back to the time of Democritus, a Greek
Philosopher (460 — 370 BC), it again started emerging as a result of several experimental studies which led to the Laws mentioned above.
In 1808, Dalton published **'A New System of Chemical Philosophy'** in which he proposed the following :

1. Matter consists of indivisible atoms.
2. All the atoms of a given element have identical properties including identical mass. Atoms of different elements differ in mass.
3. Compounds are formed when atoms of different elements combine in a fixed ratio.
4. Chemical reactions involve reorganization of atoms. These are neither created nor destroyed in a chemical reaction.

Dalton's theory could explain the laws of chemical combination.
NOTE- Dalton's atomic theory was able to explain the law of conservation of mass, law of constant composition and law of multiple proportion very successfully. However, it failedto explain the results of many experiments, for example, it was known that substances like glass or ebonite when rubbed with silk or fur generate electricity.

ATOMIC AND MOLECULAR MASSES AND MOLE CONCEPT

Atomic Masses

1. The atomic mass of an element is the number of times an atom of that element is heavier than an atom of carbon taken as 12.
2. These masses on the atomic mass scale are expressed in terms of atomic mass units (abbreviated as amu).
3. *One atomic mass unit (amu) is equal to* $\frac{1}{12}$*th of the mass of an atom of carbon-12 isotope.*
4. The atomic masses of the element have been determined accurately during the recent years using an instrument called "**mass spectrometer**

Average atomic mass

Average atomic mass is the sum of the products of fractional abundances of the isotopes and their corresponding mass numbers .

Molecular Mass

The molecular mass of a substance is the average relative mass of its molecules as compared with an atom of carbon-12 isotope taken as 12.

Strength

The strength of a solution is defined as the amount of the solute in grams present per litre of the solution (i.e., g/L or $g\,L^{-1}$).

$$\text{Strength} = \frac{\textit{Mass of the solute in g}}{\textit{Volume of solution in litres}}$$

Mass percentage

Mass percentage (w/w): The mass % of a component in a given solution is the mass of the component per 100 g of the solution. e.g. Let A be the solute and B be the solvent

Mass % of a component

$$= \frac{\textit{Mass of the component in the solution}}{\textit{Total mass of the solution}} \times 100 = \text{Mass \% of A} = \frac{W_A}{W_A + W_B} \times 100$$

NOTE-5% By weight $\left(\frac{w}{W}\right)$ = 5 g of solute dissolve in 100 g of solution

Volume percentage

Volume percentage (v/v): The volume % of a component is defined as the vol. of the component per 100 part of a solution.

$$\text{Volume \% of a component} = \frac{\textit{Volume of the component}}{\textit{Total volume of solution}} \times 100$$

e.g. Let A be the solute and B be the solvent

$$\text{Volume \%} = \frac{V_A}{V_A + V_B} \times 100$$

NOTE-5% by volume $\left(\frac{v}{V}\right)$ = 5 ml of solute dissolve in 100 ml of solution

Mass by volume percentage

Mass by volume percentage (w/v): The mass by volume % of a component is defined as the mass of the component per 100 part of a solution.

5% $\left(\frac{w}{V}\right)$ = 5 g of solute dissolve in 100 ml of solution

Molarity

1. The molarity of a solution is defined as the number of moles of the solute present per litre of the solution.

$$\text{Molarity} = \frac{\textit{Moles of the solute}}{\textit{Volume of the solution in kg}}$$

2. It is represented by the symbol, M.

3.

$$\text{Moles} = \frac{\textit{Mass of the solute}}{\textit{Molar mass of the solute}}$$

4.It is compulsory that the volume should be in litres, if in case it is in ml then convert it into litres by $\frac{V\,ml}{1000}$.
Unit of molarity = moles/litre or M.

5. Molarity is temperature dependent because volume changes with temperature.

6. Dilution formula or **Molarity equation.** If a solution having molarity M_1 and volume V_1 is diluted to volume V_2 so that the new molarity is M_2, then as the total number of moles in the solutions remains the same, we have

$$\boxed{M_1 \times V_1 = M_2 \times V_2}$$

7. Mixture formula

$$M_f V_f = M_1 V_1 + M_2 V_2 + M_3 V_3 + ...$$

$$V_f = V_1 + V_2 + V_3 + ...$$

8. **Relationship between Molarity and Mass percentage** If p is the mass percentage and d is the density of the solution the *molarity/normality* are given by :

$$Molarity = \frac{p \times d \times 10}{Mol.mass\,(solute)},$$

Normality

1. **Normality (N)** The normality of a solution is defined as the number of gram equivalents of the solute present/litre of the solution. It is represented by the symbol, N.

$$\boxed{\begin{aligned}\text{Normality} &= \frac{Gram\,equivalent\,of\,the\,solute}{Volume\,of\,the\,solution\,in\,litres}\\ &= \frac{\text{wt in gm / equivalent wt.}}{\text{Vol.of solution }(L)}\end{aligned}}$$

2. Normality is temperature dependent. This is because volume depends on temperature.
3. Unit of normality = gm equivalent/lit or N
4. $\boxed{N_1 \times V_1 = N_2 \times V_2}$

   This equation is called normality equation.
5. $N_f V_f = N_1 V_1 + N_2 V_2 + ...$
6. **Relationship between Normality and Mass percentage**

$$Normality = \frac{p \times d \times 10}{Eq.mass\,(solute)}$$

7. Equivalent wt.

   The equivalent masses of acids, bases and salts are calculated as follows :

$$\text{Eq. mass of an acid} = \frac{Mol.mass\,of\,the\,acid}{Basicity}$$

$$\text{Eq. mass of a base} = \frac{Mol.mass\,of\,the\,base}{Acidity}$$

$$\text{Eq. mass of a salt} = \frac{Mol.mass\,of\,the\,salt}{Total\ positive\ valency\ of\ metal\ atoms}$$

Basicity is the number of displaceable H^+ ions present in one molecule of the acid (e.g., 1 for HCl, 2 for H_2SO_4, for H_3PO_4 etc.)

Acidity is the number of displaceable OH^- ions present in one molecule of the base (e.g., 1 for $NaOH$, 2 for $Ca(OH)_2$ etc.).

Relationship between Molarity and Normality

Normality = Molarity × Acidity (for base)

Normality = Molarity × Basicity (for acid)

Formality

Formality: Formality is the number of formula weights present in one litre of the solution.

$$\textbf{Formality} = \frac{\text{gm in wt./Formula wt.}}{\text{Vol.of sol}^{\text{n}}\text{ [L]}}$$

Molality

1. **Molality** (*m*)The molality of a solution is defined as the number of moles of the solute dissolved in 1 kg (1000 g) of the solvent.
   It is represented by the symbol, m.

$$\boxed{\text{Molality} = \frac{\text{Moles of the solute}}{\text{Mass of the solvent in kg}}}$$

$$Molarity(m) = \frac{Moles\ of\ solute}{Mass\ of\ solvent\ in\ kg}$$

2. It is denoted by 'm'.
3. Unit = moles/kg or m
4. Molality is temperature independent.
5. Wt. of solution = wt. of solvent + wt. of solute.
6. If solvent wt. is in gm then, $\frac{wg}{1000} = Wkg$.

$$\underset{\text{Solute}}{x_1} + \underset{\text{Solvent}}{x_2} \longrightarrow \text{Solution}$$

Mole Fraction

1. The mole fraction of any component in the solution is equal to the number of moles of that component divided by the total number of moles of all the components.
2. It is represented by the letter χ (chi).
3. For a solution containing n_2 moles of the solute dissolved in n_1 moles of the solvent,
   Mole fraction of solute in the solution $(x_2) = \frac{n_2}{n_1 + n_2}$
   Mole fraction of solvent in the solution $(x_1) = \frac{n_1}{n_1 + n_2}$
4. Mole fraction of solute + mole fraction of solvent = 1
   $\chi_{solute} + \chi_{solvent} = 1$
5. Mole fraction is independent of temperature

Relationship between Molarity and Molality

$$m = \frac{1000 \times M}{(1000 \times d) - (M \times GMM_{solute})}$$

where GM_{solute} is molecular wt. of solute

RELATION OF mole fraction AND molality

$$\chi_{solute} = \frac{m}{m + \frac{1000}{Molar\ mass\ of\ solvent}}$$

Parts per million

1. When a solute is present in **trace** quantities, it is convenient to express concentration in **parts per million (ppm)**.
2. It is the part of a component per million part of the solution
3. Parts per million

$$= \frac{No.of\ the\ part\ of\ the\ component \times 10^6}{Total\ no.of\ parts\ of\ all\ components\ of\ the\ solution}$$

USE -

1. The concentration of pollutants in water or atmosphere is often expressed in terms of μ g **mL^{-1} or ppm.**

2. Degree of hardness of water is expressed in ppm.

PERCENTAGE COMPOSITION

$$\text{Percentage of the element or constituent} = \frac{\textit{No. of parts by mass of the element or constituent}}{\textit{Mol. mass of the compound}} \times 100$$

Empirical and Molecular Formulae

EMPIRICAL FORMULA

The empirical formula of a compound is the chemical formula which expresses the simplest whole number ratio of the atoms of the various elements present in one molecule of the compound.

MOLECULAR FORMULA

The molecular formula of a compound is the chemical formula which represents the true formula of its molecule. It expresses the actual number of atoms of various elements present in one molecule of the compound.

M.F	E.F
C_6H_6	CH
$C_6H_{12}O_6$	CH_2O
H_2O_2	HO
$H_2S_2O_8$	HSO_4

CALCULATION OF Empirical and Molecular Formulae

Molecular formula = $n\times$ Empirical formula

Molecular mass = n × Vapour density

where n is any integer such as 1, 2, 3… etc.
When $n=1$, Molecular Formula $=$ Empirical Formula
When $n=2$, Molecular Formula $= 2\times$ Empirical Formula and so on.

The value of 'n' can be obtained from the following relation, $n = \frac{\textit{Molecular mass}}{\textit{Empirical formula mass}}$

Mole Concept

1. The value 6.022×10^{23} is called as 'Avogadro's number' or 'Avogadro's constant' in honour of Amedeo Avogadro, a great pioneer in this field.
2. It is usually represented by N_A. Hence,
   Avogadro's Number $(N_A) = \mathbf{6.022\times10^{23}}$
   Avogadro's number may be defined as the number of atoms present in one gram atom of the element or the number of molecules present in one gram molecule of the substance.

Limiting reagent

It is the reactant that is consumed completely during a chemical reaction. If the supplied mass ratio of reactants are not stoichiometric ratio. One of the reactant is consumed completely leaving parts of the others unreacted. One that is consumed completely is known as limiting reactant.
"Limiting reactant determine the amount of product in a given chemical reaction."

Significant Figures

The total number of digits in a number including the last digit whose value is uncertain is called the number of significant figures.
For example, in the above value, i.e., 23.4567 g, there are six significant figures.

THE INTERNATIONAL SYSTEM OF UNIT (SI)

The SI system has seven fundamental unit.

Physical Quantity	Symbol	Unit	Symbol
Length	l	Meter	m
Mass	m	Kilogram	kg
Time	t	second	S
Electric current	I	ampere	A
Temperature	T	Kelvin	K
Amount of substance	n	Mole	mol
Intensity	Iv	Candela	Cd

Mass

Mass of a substance is the amount of matter present in it.

Weight

Weight is the force exerted by gravity an object.

$$W = mg$$

Volume

It is the amount of space occupiedby substance. It's unit m^3

$$V = (\text{lenth})^3$$

Density

Mass per unit volume is known as density.

$D = \frac{\text{mass}}{\text{vol}}$, unit = Kgm^{-3}

Temperature

There are 3 scale

$k = {}^{\circ}C + 273K \qquad f = \frac{9}{5}({}^{\circ}C) + 32 \qquad C = K - 273.15$

RULES FOR DETERMINING THE NUMBER OF SIGNIFICANT FIGURES

The following rules are applied in determining the number of significant figures in any reported quantity :

1. *All non-zero digits as well as the zeros between the non-zero digits are significant.*
   e.g., 576 cm has three significant figures, 0.95 g has two significant figures, 4001 has four significant figures, 7.03 has three significant figures
2. *Zeros to the left of the first non-zero digit in a number are not significant. (They simply indicate the position of the decimal point).*
   e.g., 0.09 m has only one significant figure, 0.065 kg has two significant figures.
3. *If a number ends zeros but these zeros are to the right of the decimal point, then these zeros are significant*
   e.g., 3.0 m has two significant figures, 3.80 cm has three significant figures, 3.800 g has four significant figures, 0.0900 kg has three significant figures.
4. *If a number ends in zeros but these zeros are not to the right of a decimal point, these zeros may or may not be significant.*
   For example, 10700 (g) may have three, four or five significant figures. This ambiguity is removed by expressing the value in an exponential form.
   For example, the above mass may be written in three different exponential forms as follows :
   $1.07 \times 10^4\ g$, which has three significant figures or $1.070 \times 10^4\ g$, which has four significant figures or $1.0700 \times 10^4\ g$, which has five significant figures
   Thus, in such cases, the general notation is: $N \times 10^n$
   where N = a number with a single non-zero digit to the left of the decimal point
   and n = an integer called exponent.

The above method of expressing a number is called **Scientific or Exponential Notation.**

Rounding off

The general procedure for rounding off is as follows :

(i) If the digit just next to the last digit to be retained is less than 5, the last digit is taken as such and all other digits on its right are dropped.

(ii) If the digit is greater than 5, the last digit to be retained is increased by 1 and all other digits on its right are dropped.

(iii) If the digit is equal to 5, the last significant figure is left unchanged if it is even and is increased by 1 if it is odd.

RULES APPLIED IN DETERMINING THE NUMBER OF SIGNIFICANT FIGURES IN THE ANSWER OF ANY PARTICULAR CALCULATION

A. The result of ***an addition or subtraction*** should be reported to the same number of decimal places as that of the term with least number of decimal places. The numbers of significant figures of different numbers have no role to play.

1.
4.523
2.3
6.24
Actual sum = 13.063
Reported sum = 13.1*

2.
7.621
6.243
1.020
Actual sum = 14.884
Reported sum = 14.884

3.
18.4215
−6.01
Actual Diff. = 12.4115
Reported Diff. = 12.41

4.
29.25
−12.0234
Actual Diff. = 17.2266
Reported Diff. = 17.23

B. The result of a ***multiplication or division*** should be reported to the same number of significant figures as is possessed by the least precise term used in the calculation.

1.
4.327
× 2.8
Actual Product = 12.1156
Reported Product = 12

2. $0.46 \div 15.734$ gives Actual quotient $= 0.029236$, Reported quotient 0.029

C. If a calculation involves a number of steps, the result should contain the same number of significant figures as that of the least precise number involved, other than the exact numbers.

QUESTIONS

NCERT EXERCISE & EXAMPLES

LAWS OF CHEMICAL COMBINATION

1. The following data are obtained when dinitrogen and dioxygen react together to form different compounds :

	Mass of dinitrogen	Mass of dioxygen
(i)	14 g	16 g
(ii)	14 g	32 g
(iii)	28 g	32 g
(iv)	28 g	80 g

(a) Which law of chemical combination is obeyed by the above experimental data ? Give its statement.

PERCENT DETERMINATION AND MOLECULAR WEIGHT

2. Calculate the molecule mass of the following :
(i) H_2O (ii) CO_2
(iii) CH_4

3. Calculate the mass percent of different elements present in sodium sulphate (Na_2SO_4).

4. How much copper can be obtained from 100 g of copper sulphate ($CuSO_4$) ?

AVERAGE ATOMIC MASS

5. Calculate the atomic mass (average) of chlorine using the following data :

	% Natural Abundance	Molar mass
^{35}Cl	75.77	34.9689
^{37}Cl	24.23	36.9659

6. Use the data given in the following table to calculate the molar mass of naturally occurring argon isotopes :

Isotope	Isotopic molar mass	Abundance
^{36}Ar	35.96755 g mol^{-1}	0.337%
^{38}Ar	37.96272 g mol^{-1}	0.063%
^{40}Ar	39.9624 g mol^{-1}	99.600%

MOLARITY

7. Calculate the mass of sodium acetate (CH_3COONa) required to make 500 mL of 0.375 molar aqueous solution. Molar mass of sodium acetate is 82.0245 g mol^{-1}.

8. Calculate the concentration of nitric acid in moles per litre in a sample which has a density, 1.41 g mL^{-1} and the mass percent of nitric acid in it being 69%.

9. What is the concentration of sugar ($C_{12}H_{22}O_{11}$) in mol L^{-1} if its 20 g are dissolved in enough water to make a final volume upto 2L ?

10. If the density of methanol is 0.793 kg L^{-1}, What is its volume needed for making 2.5 L of its 0.25 M solution?

MISCELLANEOUS QUESTIONS

11. Calculate the molarity of a solution of ethanol in water in which the mole fraction of ethanol is 0.040 ?

12. A sample of drinking water was found to be severely contaminated with chloroform, $CHCl_3$, supposed to be carcinogenic in nature. The level of contamination was 15 ppm (by mass)
(i) Express this in percent by mass.
(ii) Determine the molality of chloroform in the water sample.

EMPIRICAL AND MOLECULAR FORMULAE

13. Determine the empirical formula of an oxide of iron which has 69.9% iron and 30.1% dioxygen by mass.

14. Determine the molecular formula of an oxide of iron in which the mass percent of iron and oxygen are 69.9 and 30.1 respectively.

15. A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide, 0.690 g of water and no other products. A volume of 10.0 L (measured at STP) of this welding gas is found to weigh 11.6 g. Calculate (i) empirical formula (ii) molar mass of the gas, and (iii) molecular formula.

MOLE CONCEPT

16. Which one of the following will have largest number of atoms ?
(i) 1g Au (s) (ii) 1 g Na (s)
(iii) 1 g Li (s) (iv) 1 g of Cl_2 (g).

17. Calculate the number of atoms in each of the following (i) 52 moles of Ar (ii) 52 u of He (iii) 52 g of He.

18. In three moles of ethane (C_2H_6), calculate the following :
(i) number of moles of carbon atoms
(ii) no. of moles of hydrogen atoms
(iii) no. of molecules of ethane.

19. What will be the mass of one ^{12}C atom in g ?

20. Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction, $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$
What mass of $CaCO_3$ is required to react completely with 25 mL of 0.75 M HCl ?

21. Chlorine is prepared in the laboratory by treating manganese dioxide (MnO_2) with aqueous hydrochloric acid according to the reaction
$4HCl(aq) + MnO_2(s) \rightarrow 2H_2O(l) + MnCl_2(aq) + Cl_2(g)$
How many grams of HCl react with 5.0 g of manganese dioxide ?

LIMITING REAGENT

22. Calculate the amount of carbon dioxide that could be produced when.
(i) Mole of carbon is burnt in air.
(ii) 1 mole of carbon is burnt in 16 g of dioxygen
(iii) 2 moles of carbon are burnt in 16 g dioxygen.

23. In a reaction $A + B_2 \rightarrow AB_2$, Identify the limiting reagent, if any, in the following reaction mixtures :
(i) 300 atoms of A + 200 molecules of B
(ii) 2 mol A + 3 mol B
(iii) 100 atoms of A + 100 molecules of B
(iv) 5 mol A + 2.5 mol B
(v) 2.5 mol A + 5 mol B.

24. Dinitrogen and dihydrogen react with each other to produce ammonia according to the following chemical equation : $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
(i) Calculate the mass of ammonia produced if 2.00×10^3 g dinitrogen reacts with 1.00×10^3 g of dihydrogen.
(ii) Will any of the two reactants remain uncreated?
(iii) If yes, which one and what would be its mass ?

25. How are 0.50 mol Na_2CO_3 and 0.50 M Na_2CO_3 different ?

26. If ten volumes of dihydrogen gas reacts with five volumes of dioxygen gas, how many volumes of water vapour would be produced ?

LAWS OF CHEMICAL COMBINATION

27. What do you mean by significant figures.

28. Express the following in the scientific notation
(i) 0.0048 (ii) 234,000
(iii) 8008 (iv) 500.0
(v) 6.0012

29. How many significant figures should be present in the answer of the following calculations ?
(i) $\dfrac{0.02856 \times 298.15 \times 0.112}{0.5785}$
(ii) 5×5.364
(iii) 0.0125 + 0.7864 + 0.0215.

30. How many significant figures are present in the following ?
(i) 0.0025 (ii) 208
(iii) 5005 (iv) 126,000
(v) 500.0 (vi) 2.0034

31. Round up the following upto three significance figures :
(i) 34.216 (ii) 10.4107
(iii) 0.04597 (iv) 2808

UNITS AND CONVERSION

32. Pressure is determined as force per unit area of the surface. The SI unit of pressure, pascal is as shown below:
$1\ Pa = 1\ N\ m^{-2}$
If mass of air at sea level is 1034 g cm^{-2}, calculate the pressure in pascal.

33. What is the SI unit of mass ? How is it defined ?

34. Match the following prefixes with their multiples.

	Prefixes	Multiples
(i)	micro	10^6
(ii)	deca	10^9
(iii)	mega	10^{-6}
(iv)	giga	10^{-15}
(v)	femto	10

35. Fill in the blanks in the following conversions :
(i) 1 km = ... mm = ... pm
(ii) 1 mg = ... kg = ... ng
(iii) 1 mL = ... L = ... dm^3

36. Convert the following into basic units :
(i) 28.7 pm (ii) 15.15 μs
(iii) 25365 mg

37. If the speed of light is $3.0 \times 10^8\ ms^{-1}$, calculate the distance covered by light in 2.00 ns.

SOLUTIONS

NCERT EXERCISE & EXAMPLES

Sol.1 (a) The given data is in accordance with the law of multiple proportions, which states : When two elements combine to form two or more than two compounds, the weights of one of the two elements which combines with the fixed weight of the other, bears a simple ratio to one another.

In the said question, if we fix the weight of dinitrogen at 14 g, then the weights of dioxygen which combines with the fixed weight (= 14 g) of dinitrogen will be 16.32, 16, 40 which are in the simple whole number ratio of 1 : 2 : 1 : 2.5 or 2 : 4 : 2 : 5.

Sol.2 (i) Molecular mass of H_2O = 2 × Atomic mass of H + Atomic mass of O
$= 2 \times 1 + 16 = 18.0$ amu.

(ii) Molecular mass of CO_2 = 2 × Atomic mass of C + 2 × Atomic mass of O
$= 12 + 2 \times 16 = 44.0$ amu.

(iii) Molecular mass of CH_4 = Atomic mass of C + 4 × Atomic mass of H
$= 12 + 4 \times 1 = 12 + 4 = 16$ amu.

Sol.3 Mass percent of Na = 32.39
Mass percent of S = 22.53
Mass percent of O = 45.07

Sol.4 Molar mass of $CuSO_4$ = Atomic mass of Cu + Atomic mass of S + 4 × Atomic mass of O
$= 63.5 + 32.0 + 4 \times 16.0 = 159.5 \text{ g M}^{-1}$.
159.5 g of $CuSO_4 \equiv 63.5$ g of Cu

$$100 \text{ g of } CuSO_4 \equiv \frac{63.5}{159.5} \times 100 = 39.81 \text{ g}$$

∴ Mass of Cu that can be obtained = 39.81 g.

Sol.5 Average atomic mass of chlorine is

$$= \frac{75.77 \times 34.9689 + 24.23 \times 36.9659}{75.77 + 24.23} = \frac{3545.277}{100} = 35.45$$

Sol.6 Molar mass of naturally occurring Argon

$$= \frac{35.96755 \times 0.377 + 37.96272 \times 0.063 + 39.9624 \times 99.600}{100.000}$$

$$= \frac{12.12106 + 2.39165 + 3980.255}{100}$$

$$= \frac{3994.76}{100} = 39.948 \text{ g mol}^{-1}.$$

Sol.7 15.38 g.

Sol.8 ∴ Concentration of nitric acid is = 15.44 mol L^{-1}.

Sol.9 Concentration of sugar in mol L^{-1}
Molar mass of sugar $= 12 \times 12 + 22 \times 1 + 11 \times 16$
$= 342 \text{ g mol}^{-1}$

No. of moles of sugar in 20 g of it $= \frac{20}{342}$

Concentration in mol L^{-1} = No. of moles per litre of the solution

$$= \frac{20}{342 \times 2} \qquad [\because \text{Vol. of solution} = 2L]$$

$= 0.029 \text{ mol L}^{-1}$.

Sol.10 Molar mass of methanol (CH_3OH)
$= 1 \times 12 + 4 \times 1 + 1 \times 16$
$= 32 \text{ g mol}^{-1}$.
moles of methanol in 2.5 L of its 0.25 m solution
$= 2.5 \times 0.25 = 0.625$ mole
Mass of methanol $= 32 \times 0.625$ g $= 20.0$ g
Density of methanol = 0.793 kg L^{-1}
∴ Volume of methanol required

$$= \frac{20.0}{793} = 0.025 \text{L}.$$

Sol.11 Let us calculate the mass of ethanol in which its mole fraction is 0.040.
Mole fraction of ethanol

$$= \frac{\text{no. of moles of ethanol}}{\text{no. of moles of water} + \text{no. of moles of ethanol}}$$

$$0.040 = \frac{\frac{w}{46}}{\frac{1000}{18} + \frac{w}{46}} \quad \text{where w = wt. of ethanol}$$

Solving for w = wt. of ethanol $\left[V = \frac{M}{d}\right]$
density is 1 gm cm^{-3}

= 106.48 g

∴ Molarity of the solution $= \frac{106.48}{46} = 2.315$m

Sol.12 (i) 10^6 gm of solution contains 15 g of $CHCl_3$

1 gm of solution contain $= \frac{15}{10^6}$

100 gm of solution contain $= \frac{15}{10^6} \times 10^2$
$= 15 \times 10^{-4}$ g
∴ Percent by mass $= \sim 15 \times 10^{-4}$ g

(ii) **Molality of $CHCl_3$:** 10^6 gm of the solution contains 15 g of $CHCl_3$
∴ wt. of water = 1000000 − 15 = 999985 gm

Now 999985 g of water contains 15 g of $CHCl_3$

1000 of water contains $= \frac{15}{999985} \times 1000$ g of $CHCl_3$

Molar mass of $CHCl_3 = 12 + 1 + 3 \times 35.5$ $= 119.5 \text{ g mol}^{-1}$

$\therefore$Molality $= \frac{15}{999985} \times \frac{1000}{119.5} \text{m} = 1.25 \times 10^{-4}$ m.

Sol.13

Element	%	Atomic Mass	$\frac{\%}{\text{Atomic Mass}}$	Simple whole no. ratio
Fe	= 69.9	56	$\frac{69.9}{56} = 1.248$	1
O	= 30.1	16	$\frac{30.1}{16} = 1.88$	1.5

The ratio between Fe and O is Fe : O
1 : 1.5
2 : 3

The empirical formula = Fe_2O_3

Sol.14 **Step I :** To calculate the empirical formula

Element	%	At. Mass	% At. Mass	Simplest at. ratio	Simple whole no. at. ratio
Iron (Fe)	69.9	56	$\frac{69.9}{56} = 1.248$	$\frac{1.248}{1.248} = 1.0$	2
Oxygen (O)	30.1	16	$\frac{30.1}{16} = 1.881$	$\frac{1.881}{1.248} = 1.5$	3

Hence the empirical formula of oxide of Iron = Fe_2O_3

Step II : The molecular formula of the oxide of Iron is the same empirical formula, *i.e.*, Fe_2O_3.

Sol.15 Welding fuel gas is made up of C and H only i.e., C_xH_y

10.0 L of this gas at STP weigh = 11.6 g

22.4 L of this gas at STP weighs $= \frac{11.6}{10.0} \times 22.4\text{g}$

= 25.98

Since 22.4 L of any gas at STP weighs = Molecular mass

$\therefore$ Molar mass of the welding fuel gas = 26.0 [near to whole no.]

$\therefore$ It must contain 2 atoms of C and 2 atoms of hydrogen

$\therefore$ Its molecular formula is C_2H_2
[x = y = 2]

Its empirical formula is CH.

Sol.16 (i) 1 gm atom of Au (s) = 197 g have 6.023×10^{23} atoms of Au

$$1\text{g of Au} = \frac{6.023 \times 10^{23}}{197}$$

$= \mathbf{3.057 \times 10^{21}}$ **atoms**

(ii) 23.0 g of Na = 6.023×10^{23} atoms of N

$$1\text{g of Na} = \frac{6.023 \times 10^{23}}{23}$$

$= \mathbf{2.618 \times 10^{22}}$ **atoms**

(iii) 7.0 g of Li = 6.023×10^{23} atoms of Li

$$1\text{g of Li} = \frac{6.023 \times 10^{23}}{7}$$

$= \mathbf{8.604 \times 10^{22}}$ **atoms**

(iv) 71.0 g of $Cl_2 = 2 \times 6.023 \times 10^{23}$ atoms of Cl

$$1\text{g of } Cl_2 = \frac{2 \times 6.023 \times 10^{23}}{71}$$

$= \mathbf{1.697 \times 10^{22}}$ **atoms**

By comparison (iii) i.e., 1g Li (s) will have max. no. of atoms, viz., 8.604×10^{22} atoms.

Sol.17 (i) 1 mole of Argon (Ar) contains 6.023×10^{23} atoms

52 moles of Ar contains $6.023 \times 10^{-23} \times 52$ atoms

$= 3.13 \times 10^{-25}$ atoms

(ii) 4 u of Helium (He) = 1 atom of He

$$52 \text{ u of He} = \frac{1}{4} \times 52 = 13 \text{ atom}$$

(iii) 4 g of He contains = 6.023×10^{-23} atoms

$$52 \text{ g of He contains} = \frac{6.023 \times 10^{23} \times 52}{4}$$

$= 7.8286 \times 10^{-24}$ atoms.

Sol.18 (i) 1 Mole of ethane (C_2H_6) contain 2 moles of carbon atoms

$\therefore$ 3 Mole of C_2H_6 will contain 6 moles of carbon (C) atoms.

(ii) 1 Mole of C_2H_6 contain 6 moles of hydrogen (H) atoms

$\therefore$ 3 Moles of C_2H_6 will contain $3 \times 6 = 18$ moles of H atoms.

(iii) 1 Mole of C_2H_6 contains 6.023×10^{23} molecules of ethane

$\therefore$ 3 Moles of C_2H_6 will contain $3 \times 6.023 \times 10^{23}$

$= 1.8069 \times 10^{24}$ molecules.

Sol.19 We want to calculate the mass of one atom of ^{12}C.

1 gm atom of $^{12}C = 12.0$ g

6.023×10^{23} atoms of ^{12}C weigh = 12.0 g

1 atoms of ^{12}C weigh $= \frac{12}{6.023 \times 10^{23}}$ g

$\therefore$ wt. of 1 atoms of $^{12}C = 1.99265 \times 10^{-23}$ g

Sol.20 The given reaction is

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

Let us find out the weight of HCl present in 25 mL of 0.75 M HCl

1000 mL of 1.0 M HCl contains = 36.5 g of it

25 mL of 0.75 M HCl contains

$= \frac{36.5}{1000} \times 25 \times 0.75$

= 0.6844 g of HCl

According to the equation;

73 g of HCl [2 (1 + 35.5)] reacts with 100.0 g of $CaCO_3$

0.6844 g of HCl reacts with $= \frac{100}{73} \times 0.6844$

= 0.94 g of $CaCO_3$.

Sol.21 The chemical equation is

$MnO_2(s) + 4HCl\ (aq) \rightarrow MnCl_2(aq) + 2H_2O(l) + Cl_2(g)$

1 mol 4 mol [At. Wt. of Mn = 55]

$[55 + 2 \times 16]$ $4\,[1 + 35.5]$

= 87.0 g = 146 g

87.0 g of MnO_2 react with 146.0 g of HCl

5.0 g of MnO_2 react with $= \frac{146.0}{87.0} \times 5.0$

= 8.40 g of HCl

$\therefore$Amount of HCl in grams which will react with 5.0 g of manganese dioxide = 8.40 g.

Sol.22 (i) $C(s) + O_2(g) \rightarrow CO_2(g)$

1 mole air 1 mole

= 12.0 g $= 12 + 2 \times 16 = 44.0$ g

Amount of CO_2 produced = 44.0 g

(ii) $C(s) + O_2(g) \rightarrow CO_2(g)$

1 mole 1 mole 1 mole

= 12 g = 32 g = 44.0 g

32.0 g of O_2 produce 44.0 g of CO_2

16.0 g of O_2 produce $= \frac{44}{32} \times 16$ = 22.0 g of CO_2

Amount of CO_2 produced = 22.0 g

(iii) Amount of CO_2 produced when 2 mols (= 24 g) of C are burnt in 16.0 g [limited amount] of O_2

= 22.0 g

Sol.23 (i) The given reaction is $A + B_2 \rightarrow AB_2$

Here 300 atoms of A requires 300 molecules of B

Since there are only 200 molecules of B provided

$\therefore$ B is the limiting reagent.

(ii) 3 mol B requpires 3 mol A. Since only 2 mol of A are provided, therefore A is the limiting reagent.

(iii) 100 atoms of A + 100 molecules of B constitute a STOICHIOMETRIC mixture. Neither A nor B is the limiting reagent.

(iv) B is the limiting reagent as 5 mol A requires 5 mol B but only 2.5 mol B are given.

(v) A is the limiting reagent as 5 mol B requires 5 mol A, but only 2.5 mol B are provided.

Sol.24 $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

1 mol 3 mol 2 mol

= 28.0 g = 6.0 g = 34.0 g

(i) 28.0 g of N_2 require 6.0 g of H_2 to produce 34.0 g of NH_3

2.00×10^3 g of N_2 will produce $\frac{34}{28} \times 2.00 \times 10^3$ g of NH_3

$= 2.43 \times 10^3$ g of NH_3

= 2430 g NH_3

(ii) Yes. Dihydrogen will remain uncreated to same extent.

(iii) Amount of hydrogen that remains unreacted

28.0 g of N_2 require 6.0 g of H_2

28.0 g of N_2 will require $\frac{6.0}{28.0} \times 2.00 \times 10^3$ g of H_2

= 428.5 g of H_2

$\therefore$ Amount of hydrogen = $[1.00 \times 10^3 - 428.5]$ g that remains unreacted = 571.5 g

Sol.25 0.50 mol Na_2CO_3 means $\frac{1}{2}$ the molar mass of Na_2CO_3

$= \frac{2 \times 23 + 12 + 3 \times 16}{2} = 53.0$g

$\therefore$ 0.50 mol Na_2CO_3 represents the mass = 53.0 g of it whereas 0.50 M Na_2CO_3 represents its molarity in solution. 0.50 M Na_2CO_3 indicates that 53.0 g of Na_2CO_3 have been dissolved in 1L of its solution.

Sol.26 $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

2 Volumes 1 Volume 2 Volumes

(experimentally)

$\therefore$ The ratio by volumes is

2 : 1 : 2

$\therefore$ 10 volumes of dihydrogen will react with 5 volumes of dioxygen to produce 10 volumes of water vapours.

Sol.27 Significant figures refer to the number of digit in a number which has some importance in the magnitude of a given number.
Example : 30.4560
n is equal to 5
Example : 16708.4300
n is equal to 7.

Sol.28 (i) $0.0048 = \frac{48}{10000} = 48 \times 10^{-4} = 4.8 \times 10^{-3}$

(ii) $234{,}000 = 2.34 \times 10^5$
(iii) $8008 = 8.008 \times 10^3$
(iv) $500.0 = 5.000 \times 10^2$
(v) $6.0012 = 6.0012 \times 10^{-0}$

Sol.29 $\frac{0.02856 \times 298.15 \times 0.112}{0.5785} = \frac{0.953698}{0.5785} = 1.65$
It should have 3 significant figures.
(ii) 5×5.364
$5 \times 5.364 = 26.82$
It should have 4 significant figures.
(iii) $0.0125 + 0.7864 + 0.0215$
$0.0125 + 0.7864 + 0.0215 = 0.8204$
It should have 4 significant figures.

Sol.30 (i) 2 (ii) 3 (iii) 4 (iv) 3 (iv) 4 (vi) 5

Sol.31 (i) 34.216 ~ 34.2 (ii) 10.4107 ~ 10.4
(iii) 0.04597 ~ 0.0460 (iv) 2808 ~ 2810

Sol.32 Acceleration due to gravity (g) = 9.806 m s^{-2}
mass of air = 1.034 kg $cm^{-2} = \frac{1.034}{10^{-4}}$
Pressure $= \frac{\text{Force}}{\text{Area}} = \frac{1.034 \times 9.806}{10^{-4}}$ Pa
$= 10.138 \times 10^4$ Pa
Pressure of air at sea level = 1.0138×10^5 Pa.

Sol.33 SI unit of mass is kg. [kilogram]
It is defined as the mass of platinum-iridium (Pt-Ir) cylinder that is stored in an air-tight jar at International Bureau of Weights and Measures in France.

Sol.34

	Prefixes	Multiples
(i)	micro	10^{-6}
(ii)	deca	10
(iii)	mega	10^6
(iv)	giga	10^9
(v)	femto	10^{-15}

Sol.35 (i) 1 km = 10^6 mm = 10^{15} pm
(ii) 1 mg = 10^{-6} kg = 10^6 ng.
(iii) 1 mL = 0.001 L = 0.001 dm^3

Sol.36 (i) 28.7 pm = 28.7×10^{-11} m
(ii) 15.15 µs = 15.15×10^{-6} s = 1.515×10^{-5} s
(iii) 25365 mg = 2.5365×10^{-2} kg.

Sol.37 Distance covered by light in one second
$= 3.0 \times 10^8$ m
∴ Distance covered by light in 2.00 ns or 2×10^{-9} second $= 3.0 \times 10^8 \times 2 \times 10^{-9}$ m
∴ Distance covered in 2.00 ns = 6.0×10^{-1} m
= 0.6 m.

QUESTION ALIKE

GENERAL TERMS

1. Convert the following temperatures into degrees Fahrenheit :
   (i) 25°C, the room temperature
   (ii) 37°C, the human body (physiological) temperature.

2. On a particular day, the temperature recorded in New York was 60°F. What would be the equivalent temperature in °C ?

3. At what temperature will both the Celsius and Fahrenheit scales read the same value ?

SIGNIFICANT FIGURES

4. How many significant figures are there in each of the following numbers ?
   (i) 6.200 (ii) 0.052
   (iii) 7.5×10^4 (iv) 0.00050
   (v) $67.32-6.3$ (vi) $4.2+7.589$
   (vii) $(5.56)^2(8.24)/(3.6)$
   (viii) $18.567/(8.1\times2)$

5. Express the number 45000 in exponential notation to show
   (i) two significant figures
   (ii) four significant figures.

6. Convert 16.1 km to miles using the following units equivalents :
   $1\,\text{km}=1000\,\text{m}$, $1\,\text{ft}=12\,\text{inches}$
   $1\,\text{m}=100\,\text{cm}$, $1\,\text{mile}=1760\,\text{yd}$
   $1\,\text{inch}=2.54\,\text{cm}$, $1\,\text{yd}=3\,\text{ft}$

LAW OF CONSERVATION OF MASS

7. 490 g of $KClO_3$ when heated produced 1.92 g of oxygen and the residue (KCl) left behind weight 2.96 g. Show that these results illustrate the law of conservation of mass.

8. What mass of silver nitrate will react with 5.85 g of sodium chloride to produce 14.35 g of silver chloride and 8.5 g of sodium nitrate, if the law of conservation of mass is true?

9. When 4.2 g of $NaHCO_3$ is added to a solution of acetic acid (CH_3COOH) weighing 10.0 g, it is observed that 2.2 g of CO_2 is released into the atmosphere. The residue left behind is found to weigh 12.0 g. Show that these observations are in agreement with the law of conservation of mass.

10. If 6.3 g of $NaHCO_3$ are added to 15.0 g of CH_3COOH solution, the residue is found to weigh 18.0 g. What is the mass of CO_2 released in the reaction ?

LAW OF CONSTANT COMPOSITION

11. 6.488 g of lead combine directly with 1.002 g of oxygen to form lead peroxide (PbO_2). Lead peroxide is also produced by heating and nitrate and it was found that the percentage of oxygen present in lead peroxide is 13.38 percent. Use these data to illustrate the law of constant composition.

12. 2.16 g of copper metal when treated with nitric acid followed by ignition of the nitrate gave 2.70 g of copper oxide. In another experiment 1.15 g of copper oxide upon reduction with hydrogen gave 0.92 g of copper. Show that the above data illustrate the Law of Definite Proportions.

13. Silver chloride is prepared by
    (i) dissolving 0.5 g of silver wire in nitric acid and adding excess of hydrochloric acid to silver nitrate formed. The silver chloride precipitated is separated, washed and dried. The weight of silver chloride is 0.66 g.
    (ii) heating 1 g of silver metal in a current of dry chlorine gas till the metal is completely converted into its chloride. It is found to weigh 1.32 g.
    Illustrate the law of constant composition by the above data.

AVOGADRO'S NUMBER AND MOLE CONCEPTS

14. Calculate the mass of (i) an atom of silver (ii) a molecule of carbon dioxide.

15. How many atoms and molecules of sulphur are present in 64.0 g of sulphur (S_8) ?

16. Calculate the number of molecules present
    (i) in 34.20 grams of cane sugar $(C_{12}H_{22}O_{11})$
    (ii) in one litre of water assuming that the density of water is $1\ g/cm^3$.
    (iii) in one drop of water having mass 0.05 g.

16. Calculate the number of atoms of the constituent elements in 53 g of Na_2CO_3.

17. Calculate the number of molecules present in

350 cm^3 of NH_3 gas at 273 K and 2 atmosphere pressure.

THE CALCULATION OF EMPIRICAL FORMULAS

18. An inorganic salt gave the following percentage composition :
$Na = 29.11$, $S = 40.51$ and $O = 30.38$
Calculate the empirical formula of the salt.

19. 2.38 g uranium was heated strongly in a current of air. The resulting oxide weighed 2.806 g. Determine the empirical of the oxide. (At. mass $U = 238$; $O = 16$).

20. 2.746 g of a compound gave on analysis 1.94 g of silver, 0.268 g of sulphur and 0.538 g of oxygen. Calculate the empirical formula of the compound (At. masses : $Ag = 108$, $S = 32$, $O = 16$)

21. A crystalline salt on being rendered anhydrous loses 45.6% of its weight. The percentage composition of the anhydrous salt is
Aluminium = 10.50%; Potassium = 15.1%; Sulphur = 24.96%; Oxygen = 49.92%.
Find the simplest formula of the anhydrous and crystalline salt.

THE CALCULATION OF MOLECULAR FORMULAS

22. A compound containing sodium, sulphur, hydrogen and oxygen gave the following results on analysis :
$Na = 14.28\%$, $S = 9.92\%$, $H = 6.02\%$
Calculate the molecular formula of the anhydrous compound. If all the atoms of hydrogen in the compound are present in the combination with oxygen as water of crystallization, what is the structure of the crystalline salt? The molecular mass of the crystalline salt is 322.

23. An organic substance containing carbon, hydrogen and oxygen gave the following percentage composition
$C = 40.687\%$, $H = 5.085\%$ and $O = 54.228\%$
The vapour density of the compound is 59. Calculate the molecular formula of the compound.

24. A crystalline salt when heated becomes anhydrous and loses 51.2% of its weight. The anhydrous salt on analysis gave the following percentage composition.
$Mg = 20.0\%; S = 26.6\%$ and $O = 53.3\%$
Calculate the molecular formula of the anhydrous salt and the crystalline salt. Molecular mass of the anhydrous salt is 120.

25. A chemical compound is found to have the following composition :
$C = 19.57\%; Fe = 15.2\%; N = 22.83\%; K = 42.39\%$
Calculate the empirical formula of the compound. What will be its molecular formula if the molecular mass of the compound is 368 ? Name the compound and describe the action of hydrogen peroxide on it.

26. Butyric acid contains only C, H and O. A 4.24 mg sample of butyric acid is completely burned. It gives 8.45 mg of CO_2 and 3.46 mg of H_2O. The molecular mass of butyric acid was determined by experiment to 88 amu. What is molecular formula ?

INVOLVING MASS - MASS RELATIONSHIP

27. In the commercial manufacture of nitric acid, how many moles of NO_2 produce 7.33 mol of HNO_3 in the reaction :
$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$?

28. How many of Fe can be theoretically obtained by the reduction of 1 kg of Fe_2O_3 ?

29. Calculate the mass of 60% H_2SO_4 required to decompose 50 g of chalk (calcium carbonate).

INVOLVING MASS - VOLUME RELATIONSHIP

30. What volume of oxygen at 18°C and 750mm pressure can be obtained from 10g of potassium chlorate ?

31. What mass of iodine is liberated from a solution of potassium iodide when 1 litre of chlorine gas at 10°C and 750mm pressure is passed through it ?

32. 1.4 g of a sample of chalk $(CaCO_3)$ containing clay as impurity were treated with excess of dilute hydrochloric acid. Volume of CO_2 evolved when measured at 15°C and 768 mm pressure was 282 cm^3. Calculate the percentage purity of the sample.

33. How much marble of 96.5% purity would be required to prepare 10 litres of carbon dioxide STP when the marble is acted upon by dilute hydrochloric acid ?

QUESTION ALIKE SOLUTIONS

Sol.1 (i) $°F = \frac{9}{5}(°C) + 32 = \frac{9}{5}(25) + 32$

$= 45 + 32 = 77°$

(ii) $°F = \frac{9}{5}(37) + 32 = 66.6 + 32 = 98.6°$

Sol.2 $°C = \frac{5}{9}(°F - 32)$

$= \frac{5}{9}(60 - 32) = \frac{5 \times 28}{9} = 15.55 = 15.6°$

Sol.3 Suppose both read the same value as 'x'.

Then as $°C = \frac{5}{9}(°F - 32)$.

$\therefore\ x = \frac{5}{9}(x - 2)$

or $9x = 5x - 160$

or $4x = -160$ or $x = \mathbf{-40°}$

Sol.4 (i) Zeros to the right of the decimal point are significant.

(ii) Zeros to the left of the first non-zero digit are not significant.

(iii) When expressed as 7.5×10^4, only significant figures of 7.5 are to be considered.

(iv) Apply rules given in Hints (i) and (ii) above.

(v) $67.32 - 6.3 = 61.02$. The result is to be reported to same number of decimal places as that of the term with least number of decimal places (viz 6.3 with only one decimal place). Hence after rounding off, reported result = 61.0, (which has there significant figures).

(vi) $4.2 + 7.589 = 11.789$. As is to be reported to one decimal place (as in (v) above), after rounding off, reported result = 11.8 (having three significant figures).

(vii) As least precise term (viz 3.6) has two significant figures, the reported result should have two significant figures.

(viii) Leaving exact number 2, the least precise term (8.1) has two significant figures

Sol.5 (i) 4.5×10^4

(ii) 4.500×10^4

When expressed as 7.5×10^4, only significant figures of 7.5 are to be considered.

Sol.6 $16.1\,\text{km} = 16.1\,\text{km} \times \frac{1000\,\text{m}}{1\,\text{km}} \times \frac{100\,\text{cm}}{1\,\text{m}} \times \frac{1\,\text{inch}}{2.54\,\text{cm}}$

$\times \frac{1\,\text{ft}}{12\,\text{inches}} \times \frac{1\,\text{yd}}{3\,\text{ft}} \times \frac{1\,\text{mile}}{1760\,\text{yd}}$

$= 10.0\,\text{miles}.$

Note that the least precise term (2.54) has three significant figures.

Sol.7 Mass of $KClO_3$ taken $= 4.90\,g$

Total mass of the product $(KCl + O_2)$

$= 2.96 + 1.92 = 4.88\,g$

Difference between the mass of the reactant and the total mass of the products

$= 4.90 - 4.88$

$= 0.02\,g$.

This small difference may be due to experimental error.

Thus, law of conservation of mass holds good within experimental errors.

Sol.8 $\underset{x\,g}{AgNO_3} + \underset{5.85\,g}{NaCl} \longrightarrow \underset{14.35\,g}{AgCl} + \underset{8.5\,g}{NaNO_3}$

$x + 5.85 = 14.35 + 8.5$

or $x = 17.0\,g$

Sol.9 $\underset{4.2\,g}{NaHCO_3} + \underset{10.0g}{CH_3COOH} \longrightarrow$

$\underset{\text{Residue} = 12.0\,g}{CH_3COONa + H_2O} + \underset{2.2\,g}{CO_2} \uparrow$

Total mass of reactants $= 4.2 + 10.0\,g = 14.2\,g$

Total mass of products $= 12.0 + 2.2\,g = 14.2\,g$

Sol.10 3.3 g

Sol.11 **Step 1.** To calculate the percentage of oxygen in first experiment.

Mass of peroxide formed

$= 6.488 + 1.002 = 7.490\,g$.

$7.490\,g$ of lead peroxide contain $1.002\,g$ of oxygen

$\therefore$ 100 g of lead peroxide will contain oxygen

$= \frac{1.002}{7.490} \times 100 = 13.38\,g$

i.e., oxygen present $= 13.38\%$

Step 2. To compare the percentage of oxygen in both the experiments.

Percentage of oxygen in PbO_2 in the first experiment $= 13.38$

Percentage of oxygen in PbO_2 in the second experiment $= 13.38$

Since the percentage composition of oxygen in both the samples of PbO_2 is identical, the above data illustrate the law of constant composition.

Sol.12 % of Cu in copper oxide in 1st case

$=\dfrac{2.16}{2.70}\times100=80\%$

% of oxygen $=20\%$

% of Cu in copper in 2nd case

$=\dfrac{0.92}{1.15}\times100=80\%$

% of oxygen $=20\%$

Sol.13 % of Ag in AgCl in 1st cast.

$=\dfrac{0.5}{0.66}\times100=75.76\%$

% of $\mathrm{Cl}=24.25\%$

% of Ag in AgCl in 2nd case

$=\dfrac{1}{1.32}\times100=75.76\%$

% of $\mathrm{Cl}=24.4\%$.

Sol.14 (i) 1 mole of Ag atoms $=108\,\mathrm{g}$

(∵ atomic mass of silver $=108\,\mathrm{u}$)

$=6.022\times10^{23}$ atoms.

$=6.022\times10^{23}$ atoms of silver mass $=108\,\mathrm{g}$

∴ Mass of one atom of silver

$=\dfrac{108}{6.022\times10^{23}}=1.793\times10^{-22}\,\mathrm{g}$

(ii) 1 mole of $CO_2=44\,\mathrm{g}$

(∵ Molecular mass of $CO_2=1\times12+2\times16=44\,\mathrm{u}$)

$=6.022\times10^{23}$ molecules

Thus, $=6.022\times10^{23}$ molecules CO_2 have mass $=44\,\mathrm{g}$

∴ 1 molecule of CO_2 has mass

$=\dfrac{44}{6.022\times10^{23}}=\dfrac{44\times10^{-23}}{6.022}\,\mathrm{g}$

$=7.307\times10^{-23}\,\mathrm{g}$

Sol.15 Molecular formula of sulphur $=S_8$

∴ Molecular mass of sulphur $(S_8)=32\times8=256.0\,\mathrm{u}$

1 mole of sulphur molecules $=256\,\mathrm{g}$

$=6.022\times10^{23}$ molecular of sulphur

Now, $256\,\mathrm{g}$ of sulphur contain 6.022×10^{23} molecules

∴ $64\,\mathrm{g}$ of sulphur will contain $=\dfrac{6.022\times10^{23}\times64}{256}$

$=1.506\times10^{23}$ **molecules.**

1 molecule of sulphur (S_8) contains 8 atoms of sulphur

∴ 1.506×10^{23} molecules of sulphur will contain sulphur atoms $=8\times1.506\times10^{23}$

$=1.2048\times10^{24}$ **atoms.**

Sol.16 (i) 1 mole of $C_{12}H_{22}O_{11}=342\,\mathrm{g}$

[∵ Molecular mass of cane sugar $(C_{12}H_{22}O_{11})$

$=12\times12+22\times1+11\times16=342\,\mathrm{amu}$]

$=6.022\times10^{23}$ molecules

Now, $342\,\mathrm{g}$ of cane sugar contain 6.022×10^{23} molecules

∴ $34.2\,\mathrm{g}$ of cane sugar will contain

$=\dfrac{6.022\times10^{23}}{342}\times34.2$

$=6.022\times10^{22}$ **molecules**

(ii) 1 mole of water $=18\,\mathrm{g}=6.022\times10^{23}$ molecules

Mass of 1 litre of water = Volume × density

$=1000\,\mathrm{mL}\times1\,\mathrm{g\,L^{-1}}=1000\,\mathrm{g}$

Now, $18\,\mathrm{g}$ of water contains $=6.022\times10^{23}$ molecules

∴ $1000\,\mathrm{g}$ of water will contain

$=\dfrac{6.022\times10^{23}\times1000}{18}$

$=3.346\times10^{25}$ **molecules**.

(iii) 1 mole of $H_2O=18\,\mathrm{g}=6.022\times10^{23}$ molecules

Mass of 1 drop of water $=0.05\,\mathrm{g}$

Now, $18\,\mathrm{g}$ of H_2O contain $=6.022\times10^{23}$ molecules

∴ $0.05\,\mathrm{g}$ of H_2O will contain

$=\dfrac{6.022\times10^{23}}{18}\times0.05$

$=6.073\times10^{21}$ **molecules**

Sol.17 First of all, we have to determine the volume of the gas at STP.

Given conditions	At STP
$V_1=350\,\mathrm{cm}^3$	$V_2=?$
$T_1=273\,\mathrm{K}$	$T_2=273\,\mathrm{K}$
$P_1=2$ atmospheres	$P_2=1\,\mathrm{atm}$

Applying gas equation : $\dfrac{P_1V_1}{T_1}=\dfrac{P_2V_2}{T_2}$

we get $\dfrac{350\times2}{273}=\dfrac{1\times V_2}{273}$

or $V_2=\dfrac{350\times2}{273}\times\dfrac{273}{1}=700\,\mathrm{cm}^3$

By mole concept,

1 mole of $NH_3=6.022\times10^{23}$ molecules

$=22400\,\mathrm{cm}^3$ at STP

Thus, $22400\,\mathrm{cm}^3$ of NH_3 at STP contains 6.022×10^{23} molecules

∴ $700\,\mathrm{cm}^3$ of NH_3 at STP will contain

$=\dfrac{6.022\times10^{23}}{22400}\times700$

$= 1.882 \times 10^{22}$ **molecules**

Sol.18 Calculation of empirical formula

Element	Symbol	Percentage of elements	At. mass of elements
Sodium	Na	29.11	23
Sulphur	S	40.51	32
Oxygen	O	30.38	16

Moles of the elements $= \frac{\%}{\text{At.mass}}$ (Relative no. of moles)	Simplest molar ratio	Simplest whole no. molar ratio
$\frac{29.11}{23} = 1.266$	$\frac{1.266}{1.266} = 1$	2
$\frac{40.51}{32} = 1.266$	$\frac{1.266}{1.266} = 1$	2
$\frac{30.38}{16} = 1.897$	$\frac{1.89}{1.266} = 1.5$	2

Thus, the Empirical Formula is $Na_2S_2O_3$.

Sol.19 **Step 1.** *To calculate the percentage of uranium and oxygen in the oxide.*

2.806 g of the oxide contain uranium $= 2.38$ g.

$\therefore$ Percentage of uranium $= \frac{2.38}{2.806} \times 100 = 84.82$

Hence, the percentage of oxygen in the oxide $= 100.00 - 84.32 = 15.18$

Step 2. *To calculate the empirical formula*

Element	Symbol	Percentage of elements	At. mass of elements
Uranium	U	84.82	238
Oxygen	O	15.18	16

Moles of the elements $= \frac{\%}{\text{At.mass}}$ (Relative no. of moles)	Simplest molar ratio	Simplest whole no. molar ratio
$\frac{84.82}{238} = 0.3562$	$\frac{0.3562}{0.3562} = 1$	3
$\frac{15.18}{16} = 0.94875$	$\frac{0.94875}{0.3562} = 2.666$	8

Hence, the empirical formula of the oxide is U_3O_8.

Sol.20 Calculation of Empirical Formula

Element	Mass	At. mass	No. of g atoms (moles) (Relative no. of moles)
Ag	1.94 g	108	$\frac{1.94}{108} = 0.0179$
S	0.268 g	32	$\frac{0.268}{32} = 8.375 \times 10^{-3}$
O	0.538 g	16	$\frac{0.538}{16} = 0.0336$

Simplest molar ratio	Simplest whole no. molar ratio
$\frac{0.0179}{8.375 \times 10^{-3}} = 2.12$	2
$\frac{8.375 \times 10^{-3}}{8.375 \times 10^{-3}} = 1$	1
$\frac{0.0336}{8.375 \times 10^{-3}} = 4.01$	4

$\therefore$ Empirical formula $= Ag_2SO_4$.

Sol.21 **Step 1.** To calculate the empirical formula of the anhydrous salt

Element	Symbol	Percentage of elements	At. mass of elements
Potassium	K	15.1	39
Aluminum	Al	10.50	27
Sulphur	S	24.96	32
Oxygen	O	49.92	16

Moles of the elements $= \frac{\%}{\text{At.mass}}$ (Relative no. of moles)	Simplest molar ratio	Simplest whole no. molar ratio
$\frac{15.10}{39} = 0.39$	$\frac{0.39}{0.39} = 1$	1
$\frac{10.50}{27} = 0.39$	$\frac{0.39}{0.39} = 1$	1
$\frac{24.96}{32} = 0.78$	$\frac{0.78}{6.39} = 2$	2
$\frac{49.92}{16} = 3.12$	$\frac{3.12}{0.39} = 8$	8

Thus, the empirical formula of the anhydrous salt is $K\ Al\ S_2O_8$

Step 2. To calculate the empirical formula mass of the hydraous salt $(KAlS_2O_8)$
$= 1 \times 39.0 + 1 \times 27.0 + 2 \times 32.0 + 8 \times 16.0 = 258.0u$.

Step 3. To calculate the empirical formula mass of the hydrated salt.
Let the empirical formula amass of the hydrated salt = 100.0 u.
Loss of weight due to dehydration = 45.6%
$\therefore$ Empirical formula mass of the anhydrous salt $= 100 - 45.6 = 54.4u$.
Now, if the empirical formula mass of the anhydrous salt is 54.4, then that of hydrated salt $= \frac{100}{54.4} \times 258 = 474.3u$.

Step 4. To calculate the number of molecules of water in the hydrated salt.
Total loss in mass due to dehydration $= 474.3 - 258.0 = 216.3u$
Loss in mass due to one molecule of water = 18.0 u
$\therefore$ No. of molecules of water in the hydrated sample $= \frac{216.3}{18} = 12$

Step 5. To calculate the empirical formula of the hydrated salt.
Empirical formula of the anhydrous salt $= KAlS_2O_8$
No. of molecules of water of crystallization = 12
$\therefore$ Empirical formula of the hydrated salt $= KAlS_2O_8.12H_2O$

Sol.22 **Step 1.** To calculate the percentage of oxygen. The given compound contains oxygen but its percentage is not given. This can, however, be calculated by subtracting the sum of percentages of Na,S and H from 100 as shown below:
Sum of percentage composition of Na, S and H
$= 14.28 + 9.92 + 6.20$
$= 30.40$
$\therefore$ Percentage of oxygen $= 100.00 - 30.40$
$= 69.60$

Step 2. To calculate the empirical formula

Element	**symbol**	**Percentage of elements**	**At. mass of elements**
Sodium	Na	14.28	23
Sulphur	S	9.92	32
Hydrogen	H	6.20	1
Oxygen	O	69.60	16

Moles of the elements $= \frac{\%}{\text{At.mass}}$ **(Relative no. of moles)**	**Simplest molar ratio**	**Simplest whole no. molar ratio**
$\frac{14.28}{23} = 0.62$	$\frac{0.62}{0.31} = 2$	2
$\frac{9.92}{32} = 0.31$	$\frac{0.31}{3.0} = 1$	1
$\frac{6.2}{1} = 6.20$	$\frac{6.20}{0.31} = 20$	20
$\frac{69.60}{16} = 4.35$	$\frac{4.35}{0.31} = 14$	14

Hence, the empirical formula of the compound is $Na_2SH_{20}O_{14}$

Step 3. To calculate the empirical formula mass. Empirical formula mass of the compound $(Na_2SH_{20}O_{14})$
$= 2 \times 23.0 + 1 \times 32.0 + 20 \times 1.0 + 14 \times 16.0 = 322$

Step 4. To calculate the value of 'n'
$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{322}{322} = 1$$

Step 5. To calculate the formula of the compound.
Molecular formula $= n \times$ Empirical formula
$= 1 \times Na_2SH_{20}O_{14} = Na_2SH_{20}O_{14}$.

Step 6. To calculate the number of molecules of water of crystallization. Since all the H-atoms are present in the form of H_2O, 20 atoms of hydrogen would combine with 10 oxygen atoms to produce 10 molecules of H_2O. Thus, the number of molecules of water of crystallization present in the salt $Na_2SH_{20}O_{14}$ is 10.

Step 7. To determine the structure of the crystalline salt. Out of the 14 oxgyen atoms, 10 are present in the form of H_2O. The remaining 4 must be a part of the salt consisting of Na and S. Hence, molecular formula for the anhydrous salt is Na_2SO_4 and that of crystalline salt will be $Na_2SO_4.10H_2O$

Sol.23 **Step 1.** To calculate the empirical formula of the compound.

Element	**Symbol**	**Percentage of elements**	**At. mass of elements**
Carbon	C	40.687	12
Hydrogen	H	5.085	1
Oxygen	O	54.228	16

Moles of the elements $=\dfrac{\%}{\text{At.mass}}$ **(Relative no. of moles)**	**Simplest molar ratio**	**Simplest whole no. molar ratio**
$\dfrac{40.687}{12}=3.390$	$\dfrac{3.390}{3.389}=1$	2
$\dfrac{5.085}{1}=5.085$	$\dfrac{5.085}{3.389}=1.5$	3
$\dfrac{54.228}{16}=3.389$	$\dfrac{3.389}{3.389}=1$	2

Step 2. To calculate the empirical formula mass. The empirical formula of the compound is $C_2H_3O_2$.
$\therefore$ Empirical formula mass
$=(2\times12)+(3\times1)+(2\times16)=59$.

Step 3. To calculate the molecular mass of the salt.
The vapour density of the compound $=59$. (Given)
Using the relation between the vapour density and molecular mass –
$\text{Molecular mass}=2\times\text{vapour density}$
$=2\times59=118$.

Step 4. To calculate the value of 'n'

$$n=\frac{\text{Molecular mass}}{\text{Empirical formula mass}}=\frac{118}{59}=2$$

Step 5. To calculate the molecular formula of the salt.
$\text{Molecular formula}=\text{Empirical formula}$
$=2\times C_2H_3O_2=C_4H_6O_4$
Thus, the molecular formula is $C_4H_6O_4$.

Sol.24 To Calculate the empirical formula of the anhydrous salt. It comes out to be $MgSO_4$. E.F. mass $=120$. Mol. mass $=$ 120. Hence, molecular formula $=$ $MgSO_4$.
As crystalline salt on becoming anhydrous loses 51.2% by mass, this means
43.8 g of anhydrous salt contains $H_2O=51.2$ g
$\therefore$ 120 g of anhydrous salt contains H_2O

$$=\frac{51.2}{48.8}\times120\,g=126\,g=\frac{126}{18}\text{ molecules }=7$$

molecules.
Hence, mol. formula of crystalline salt $=MgSO_4.7H_2O$.

Sol.25 The molecular formula $K_4FeC_6N_6$ suggests that it is Potassium ferrocyanide. It is oxidised by H_2O_2 to potassium ferricyanide.

$$H_2O_2\longrightarrow H_2O+O$$
$$2K_4\left[Fe(CN)_6\right]+O+H_2O\longrightarrow$$
$$2K_3\left[Fe(CN)_6\right]+2KOH$$

Sol.26 1 mole CO_2 contains 1 g atom of C i.e., 44 g CO_2 contains C $=12$ g

$\therefore$ 8.45 mg CO_2 will contain $C=\dfrac{12}{44}\times8.45$ mg

This is present in 4.24 mg of the compound.
$\therefore$ % of C in the compound

$=\dfrac{12}{44}\times\dfrac{8.45}{4.24}\times100=54.4\%$ or use the formula directly

$$\%\text{ of C}=\frac{12}{44}\times\frac{\text{Mass of }CO_2}{\text{Mass of the compound}}\times100$$

Similarly, % of H

$$=\frac{2}{18}\times\frac{\text{Mass of }H_2O}{\text{Mass of the compound}}\times100$$

$$=\frac{2}{18}\times\frac{3.46}{4.24}\times100=9.1\%$$

$\therefore$ % of $O=100-(54.4+9.1)=36.5\%$
Calculate E.F. It comes out to be C_2H_4O.
E.F. $=44$u, Mol mass $=88$ u.
Hence, $n=$ Mol. mass/E.F. mass $=2$
$\therefore$ Mol. formula $=2\times$ E.F. $=C_4H_8O_2$

Sol.27 2 moles of HNO_3 are produced from 3 moles of NO_2. Hence, 7.33 moles of HNO_3 will be produced from $NO_2=\dfrac{3}{2}\times7.33=10.995$ moles.

Sol.28 700 g

$$\underset{\substack{2\times56+3\times16\\=16\,g}}{Fe_2O_3}\equiv\underset{\substack{2\times56\\=112\,g}}{2Fe}$$

Sol.29 $\underset{100\,g}{CaCO_3}+\underset{98\,g}{H_2SO_4}\longrightarrow CaSO_4+H_2O+CO_2$

50 g chalk will require pure $H_2SO_4=49$ g

$\therefore$ 60% H_2SO_4 required $=\dfrac{100}{60}\times49=81.67$ g

Sol.30 2.963 litres

$$\underset{\substack{2(39+35.5+48)\\=245\,g}}{2KClO_3}\longrightarrow2KCl+\underset{3\times22.4\text{ L at STP}}{3O_2}$$

Sol.31 10.78g

$$2KI+\underset{22.4\text{ L at STP}}{Cl_2}\longrightarrow2KCl+\underset{254\,g}{I_2}$$

First convert the given volume to volume at STP.

Sol.32 86.1%

$$\underset{100\,g}{CaCO_3}+2HCl\longrightarrow CaCl_2+H_2O+\underset{22400\text{ c.c. at S.T.P.}}{CO_2}$$

First convert the given volume to volume at

S.T.P. Calculate the mass of $CaCO_3$ from which this volume of CO_2 at S.T.P. is obtained. Then calculate %age purity.

Sol.33 $\underset{100\,g}{CaCO_3} + 2HCl \longrightarrow CaCl_2 + H_2O + \underset{22.4\ L\ at\ STP}{CO_2}$

10 L of CO_2 at STP will be obtained from pure

$CaCO_3 = \frac{100}{22.4} \times 10 = 44.64\,g$

Impure marble required $= \frac{100}{96.5} \times 44.64$

$= 46.26\,g$

Objective Questions

1. How many significant figures, respectively, are there in 73.000 g, 0.0503 g and 2.001 s?
(a) 3, 3, 4 (b) 3, 4, 5
(c) 2, 5, 4 (d) 5, 3, 4

2. Which of the following pairs of substances illustrate the law of multiple proportions
(a) CO and CO_2
(b) H_2O and D_2O
(c) NaCl and NaBr
(d) MgO and $Mg(OH)_2$

3. 1.0 g of an oxide of A contained 0.5 g of A. 4.0 g of another oxide of A contained 1.6 g of A. The data indicate the law of
(a) Reciprocal proportions
(b) Constant proportions
(c) Conservation of energy
(d) Multiple proportions

4. An oxide of iodine (I = 27) contains 25.4 g of iodine for 8 g of oxygen. Its formula could be
(a) I_2O_3 (b) I_2O
(c) I_2O_5 (d) I_2O_7

5. X and Y are two elements which form X_2Y_3 and X_3Y_4. If 0.20 mol of X_2Y_3 weighs 32.0 g and 0.4 mol of X_3Y_4 weighs 92.8 g, the atomic masses of X and Y are, respectively
(a) 16.0 and 56.0 u.
(b) 8.0 and 28.0 u.
(c) 56.0 and 16.0 u.
(d) 28.0 and 8.0 u.

6. The mass of a molecule of water is
(a) $3 \times 10^{-26}\,kg$ (b) $3 \times 10^{-25}\,kg$
(c) $1.5 \times 10^{-26}\,kg$ (d) $2.5 \times 10^{-26}\,kg$

7. The atomic weights of two elements A and B are 40 and 80 respectively. If x g of A contains y atoms, how many atoms are present in $2x$ g of B
(a) $\frac{y}{2}$ (b) $\frac{y}{4}$
(c) y (d) $2y$

8. How many atoms are contained in one mole of sucrose ($C_{12}H_{22}O_{11}$)
(a) $45 \times 6.02 \times 10^{23}$ atoms/mole
(b) $5 \times 6.62 \times 10^{23}$ atoms/mole
(c) $5 \times 6.02 \times 10^{23}$ atoms/mole
(d) None of these

9. A sample of phosphorus trichloride (PCl_3) contains 1.4 moles of the substance. How many atoms are there in the sample
(a) 4 (b) 5.6
(c) 8.431×10^{23} (d) 3.372×10^{24}

10. A compound (80 g) on analysis gave $C = 24$ g, $H = 4\ g$, $O = 32\ g$. Its empirical formula is
(a) $C_2H_2O_2$ (b) C_2H_2O
(c) CH_2O_2 (d) CH_2O

11. The number of moles of oxygen in 1 L of air containing 21% oxygen by volume, in standard conditions, is
(a) 0.186 *mol* (b) 0.21 *mol*
(c) 2.10 *mol* (d) 0.0093 *mol*

12. On reduction with hydrogen, 3.6 g of an oxide of metal left 3.2 g of metal. If the vapour density of metal is 32, the simplest formula of the oxide would be
(a) MO (b) M_2O_3
(c) M_2O (d) M_2O_5

13. When potassium permanganate is titrated against ferrous ammonium sulphate, the equivalent weight of potassium permanganate is
(a) Molecular weight /10
(b) Molecular weight /5
(c) Molecular weight /2
(d) Molecular weight

14. Equivalent weight of crystalline oxalic acid is
(a) 30 (b) 63
(c) 53 (d) 45

15. 1.25 g of a solid dibasic acid is completely neutralised by 25 ml of 0.25 molar $Ba(OH)_2$ solution. Molecular mass of the acid is
(a) 100 (b) 150
(c) 120 (d) 200

16. A solution contains Na_2CO_3 and $NaHCO_3$. About 10 mL of the solution required 2.5 mL of 0.1 M H_2SO_4 for neutralization using phenolphthalein as indicator. Methyl orange is then added when a further 2.5 mL of 0.2 M H_2SO_4 was required. The amount of Na_2CO_3 and $NaHCO_3$ in 1 L of the solution is
(a) 5.3 g and 4.2 g (b) 3.3 g and 6.2 g
(c) 4.2 g and 5.3 g (d) 6.2 g and 3.3 g

17. One mole of chlorine combines with certain weight of a metal giving 111 g of its chloride. The same amount of metal can displace 2 g of hydrogen from an acid. The atomic mass of the metal is

(a) 40 (b) 20
(c) 80 (d) None of these.

18. The NH_3 evolved due to complete conversion of N from 1.12 g sample of protein was absorbed in 45 mL of 0.4 N HNO_3. The excess acid required 20 mL of 0.1 N NaOH. The % N in the sample is

(a) 8 (b) 16
(c) 20 (d) 25

19. In the mixture of ($NaHCO_3$ + Na_2CO_3), volume of HCl required is x mL with phenolphthalein indicator and y mL with methyl orange indicator in the same titration. Hence, the volume of HCl for complete reaction of Na_2CO_3 is

(a) 2x (b) y
(c) x/2 (d) (y – x)

20. 3.92 *g* of ferrous ammonium sulphate crystals are dissolved in 100 *ml* of water, 20 *ml* of this solution requires 18 *ml* of $KMnO_4$ during titration for complete oxidation. The weight of $KMnO_4$ present in one *litre* of the solution is

(a) 3.476 *g* (b) 12.38 *g*
(c) 34.76 *g* (d) 1.238 *g*

21. If $1\frac{1}{2}$ moles of oxygen combine with *Al* to form Al_2O_3 the weight of *Al* used in the reaction is (*Al*=27)

(a) 27 *g* (b) 54 *g*
(c) 49.5 *g* (d) 31 *g*

22. What weight of SO_2 can be made by burning sulphur in 5.0 moles of oxygen

(a) 640 *grams* (b) 160 *grams*
(c) 80 *grams* (d) 320 *grams*

23. How many moles of $MgIn_2S_4$ can be made from 1 g each of Mg, In and S? (Atomic masses: Mg = 24 u, In = 114.8 u, S = 32 u)

(a) 6.47×10^{-4} (b) 3.0×10^{-1}
(c) 9.17×10^{-2} (d) 4.35×10^{-3}

24. If 30 mol of a gaseous hydrocarbon requires 90 mL of O_2 for complete combustion and 60 mL of CO_2 is formed in the process, the molecular formula of hydrocarbon will be

(a) C_2H_2 (b) CH_4
(c) C_2H_4 (d) C_2H_6

25. The composition of residual mixture will be if 30 g of Mg combines with 30 g of oxygen

(a) 40 g MgO + 20 g O_2
(b) 45 g MgO + 15 g O_2
(c) 50 g MgO + 10 g O_2
(d) 60 g MgO only

Answer Key

1. (d)	2. (a)	3. (d)
4. (c)	5. (c)	6. (a)
7. (c)	8. (a)	9. (d)
10. (d)	11. (d)	12. (c)
13. (b)	14. (b)	15. (d)
16. (a)	17. (a)	18. (c)
19. (a)	20. (a)	21. (b)
22. (d)	23. (d)	24. (c)
25. (c)		

Examplar Questions

1. Two students performed the same experiment separately and each one of them recorded two readings of mass which are given below. Correct reading of mass is 3.0 g. On the basis of given data, mark the correct option out of the following statements.

Student	**Readings**	
	(i)	(ii)
A	3.01	2.99
B	3.05	2.95

(i) Results of both the students are neither accurate nor precise.
(ii) Results of student A are both precise and accurate.
(iii) Results of student B are neither precise nor accurate.
(iv) Results of student B are both precise and accurate.

2. A measured temperature on Fahrenheit scale is 200 °F. What will this reading be on Celsius scale?
(i) 40 °C (ii) 94 °C
(iii) 93.3 °C (iv) 30 °C

3. What will be the molarity of a solution, which contains 5.85 g of NaCl(s) per 500 mL?
(i) 4 mol L^{-1} (ii) 20 mol L^{-1}
(iii) 0.2 mol L^{-1} (iv) 2 mol L^{-1}

4. If 500 mL of a 5M solution is diluted to 1500 mL, what will be the molarity of the solution obtained?
(i) 1.5 M (ii) 1.66 M
(iii) 0.017 M (iv) 1.59 M

5. The number of atoms present in one mole of an element is equal to Avogadro number. Which of the following element contains the greatest number of atoms?
(i) 4g He (ii) 46g Na
(iii) 0.40g Ca (iv) 12g He

6. If the concentration of glucose ($C_6H_{12}O_6$) in blood is 0.9 g L^{-1}, what will be the molarity of glucose in blood?
(i) 5 M (ii) 50 M
(iii) 0.005 M (iv) 0.5 M

7. What will be the molality of the solution containing 18.25 g of HCl gas in 500 g of water?
(i) 0.1 m (ii) 1 M
(iii) 0.5 m (iv) 1 m

8. One mole of any substance contains 6.022×10^{23} atoms/molecules. Number of molecules of H_2SO_4 present in 100 mL of 0.02M H_2SO_4 solution is _______.
(i) 12.044×10^{20} molecules (ii) 6.022×10^{23} molecules
(iii) 1×10^{23} molecules (iv) 12.044×10^{23} molecules

9. What is the mass percent of carbon in carbon dioxide?
(i) 0.034% (ii) 27.27%
(iii) 3.4% (iv) 28.7%

10. The empirical formula and molecular mass of a compound are CH_2O and 180 g respectively. What will be the molecular formula of the compound?
(i) $C_9H_{18}O_9$ (ii) CH_2O
(iii) $C_6H_{12}O_6$ (iv) $C_2H_4O_2$

11. If the density of a solution is 3.12 g mL^{-1}, the mass of 1.5 mL solution in significant figures is _______.

(i) 4.7g (ii) 4680×10^{-3}g
(iii) 4.680g (iv) 46.80g

12. Which of the following statements about a compound is incorrect?
(i) A molecule of a compound has atoms of different elements.
(ii) A compound cannot be separated into its constituent elements by physical methods of separation.
(iii) A compound retains the physical properties of its constituent elements.
(iv) The ratio of atoms of different elements in a compound is fixed.

13. Which of the following statements is correct about the reaction given below:
$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(g)$
(i) Total mass of iron and oxygen in reactants = total mass of iron and oxygen in product therefore it follows law of conservation of mass.
(ii) Total mass of reactants = total mass of product; therefore, law of multiple proportions is followed.
(iii) Amount of Fe_2O_3 can be increased by taking any one of the reactants (iron or oxygen) in excess.
(iv) Amount of Fe_2O_3 produced will decrease if the amount of any one of the reactants (iron or oxygen) is taken in excess.

14. Which of the following reactions is not correct according to the law of conservation of mass.
(i) $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$
(ii) $C_3H_8(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$
(iii) $P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$
(iv) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O\,(g)$

15. Which of the following statements indicates that law of multiple proportion is being followed.
(i) Sample of carbon dioxide taken from any source will always have carbon and oxygen in the ratio 1:2.
(ii) Carbon forms two oxides namely CO_2 and CO, where masses of oxygen which combine with fixed mass of carbon are in the simple ratio 2:1.
(iii) When magnesium burns in oxygen, the amount of magnesium taken for the reaction is equal to the amount of magnesium in magnesium oxide formed.
(iv) At constant temperature and pressure 200 mL of hydrogen will combine with 100 mL oxygen to produce 200 mL of water vapour.

Examplar Solutions

1. (ii)
2. (iii)
3. (iii)
4. (ii)
5. (iv)
6. (iii)
7. (iv)
8. (i)
9. (ii)
10. (iii)
11. (i)
12. (iii)
13. (i)
14. (ii)
15. (ii)

JEE and NEET Previous Year

Jee Previous Year

Q.1. 0.6 g of urea on strong heating with NaOH evolves NH_3. Liberated NH_3 will combine completely with which of the following HCl solution? **[2020 Mains]**

(a) 100 mL of 0.2 N HCl
(b) 400 mL of 0.2 N HCl
(c) 100 mL, 0.1 N HCl
(d) 200 mL, 0.2 N HCl

Q.2. The ratio of mass per cent of C and H of an organic compound ($C_XH_YO_Z$) is 6:1. If one molecule of the above compound ($C_XH_YO_Z$) contains half as much oxygen as required to burn one molecule of compound C_XH_Y completely to CO_2 and H_2O . The empirical formula of compound is $C_XH_YO_Z$ **[2018 Mains]**

(a) $C_3H_6O_3$ (b) C_2H_4O
(c) $C_3H_4O_2$ (d) $C_2H_4O_3$

Q.3. The most abundant elements by mass in the body of a healthy human adult are Oxygen (61.4%) Carbon (22.9%), Hydrogen (10.0%) and Nitrogen (2.6%). The weight which a 75 kg person would gain if all ^1H atoms are replaced by ^2H atoms is **[2017 Mains]**

(a) 15 kg (b) 37.5 kg
(c) 7.5 kg (d) 10 kg

Q.4. 1 g of carbonate (M_2CO_3) on treatment with excess HCI produces 0.01186 mole of CO_2. The molar mass of M_2CO_3 is **[2017 Mains]**

(a) 1186 (b) 84.3
(c) 118.6 (d) 11.86

Q.5. The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of the solution is the same as its molality. Density of this solution at 298 K is 2.0 gm^{-3}. The ratio of the molecular weights of the solute & solvent, $\left(\frac{m_{solute}}{m_{solvent}}\right)$ is **[2016 Adv.]**

Q.6. The molecular formula of commercial resin used for exchanging ions in water softening is $C_8H_7SO_3Na$ (molecular weight = 206). What would be the maximum uptake of Ca^{2+} ions by the resin when expressed inmole per gram resin? **[2015 Mains]**

(a) $\frac{1}{103}$ (b) $\frac{1}{206}$
(c) $\frac{2}{309}$ (d) $\frac{1}{412}$

Q.7. 3 g of activated charcoal was added to 50 mL of acetic acid solution (0.06 N) in a flask. After an hour it was filtered and the strength of the filtrate was found to be 0.042 N. The amount of acetic acid adsorbed (per gram of charcoal is **[2015]**

(a) 18 mg (b) 36 mg
(c) 42 mg (d) 54 mg

Q.8. A compound H_2X with molar weight of 80 g is dissolved in a solvent having density of 0.4 g mL^{-1}. Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is **[2014 Adv.]**

Q.9. The molarity of a solution obtained by mixing 750 mL of 0.5 M HCI with 250 mL of 2 M HCI will be **[2013 Mains]**

(a) 0.875 M (b) 1.00 M
(c) 1.75 M (d) 0.0975 M

Q.10. 29.2% (w/W) HCI stock solution has density of 1.25 gmL^{-1}. The molecular weight of HCI is 36.5 g. The volume (mL) of stock solution required to prepare a 200 mL solution 4.0 M HCI is **[2012]**

Q.11. Dissolving 120 g of urea (mol. wt. 60) in 1000 g of water gave a solution of density 1.15 g/mL. The molarity of the solution is **[2011 Mains]**

(a) 1.78 M (b) 2.00 M
(c) 2.05 M (d) 2.22 M

Q.12. The difference in the oxidation number of the two types of sulphur atoms in $Na_2S_4O_6$ is **[2011]**

Q.13. Among the following, the number of elements showing only one non-zero oxidation state O, CI, F, N, P, Sn, TI, Na, Ti, **[2010]**

Q.14. A student performs a titration with different burettes and finds titrate values of 25.2 mL, 25.25 mL, and 25.0 mL. The number of significant figures in the average titrate value is **[2010]**

Q.15. Consider a titration of potassium dichromate solutionwith acidified Mohr's salt solution using diphenylamine as indicator. The nuber of moles of Mohr's salt required per mole of dichromate is **[2007 Mains]**

(a) 3 (b) 4
(c) 5 (d) 6

Q.16. Mixture X = 0.02 mole of $[Co(NH_3)_5SO_4]Br$ and 0.02 mole of $[Co(NH_3)_5 Br]SO_4$ was prepared in 2 L solution. 1 L of mixture X + excess of $AgNO_3$ solution→ Y L of mixture X + excess of $BaCI_2$ solution → Z Number of moles of Y and Z are **[2003 Mains]**

(a) 0.01, 0.01 (b) 0.02, 0.01
(c) 0.01, 0.02 (d) 0.02, 0.02

Q.17. Which has maximum number of atoms? **[2003 Mains]**

(a) 24 g of C (12) (b) 56 g of Fe (56)
(c) 27 g of AI (27) (d) 108 g of Ag (108)

Q.18. In the standardization of $Na_2S_2O_3$ using $k_2Cr_2O_7$by iodometry, the equivalent weight of $k_2Cr_2O_7$is **[2001]**

(a) (molecular weight)/2
(b) (molecular weight)/6
(c) (molecular weight)/3
(d) Same as molecular weight

Q.19. An aqueous solution of 6.3 g oxalic acid dehydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralize 10 mL of this solution is **[2001]**

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

NEET Previous Year

Q.20. A compound is formed by cation C and anion A. The anions form hexagonal close packed (hep) lattice and the cations occupy 75% of octahedral voids. The formula of the compound is: **[2019]**

(a) C_3A_4 (b) C_4A_3
(c) C_2A_3 (d) C_3A_2

Q.21. A mixture of 2.3 g formic acid and 4.5g oxalic acid is treated with conc. H_2SO_4. The evolved gaseous mixture is passed through KOH pellets. Weigh(in g) of the remaining product at STP will be **[2018]**

(a) 1.4 (b) 3.0
(c) 4.4 (d) 2.8

Q.22. In which case is number of molecules of water maximum? **[2018]**

(a) 18 mL of water
(b) 0.18 g of water
(c) 10^{-3} mol of water
(d) 0.00224 L of water vapours at 1 atm and 273 K

Q.23. When 22.4 L of $H_2(g)$ is mixed with 11.2 L of $Cl_2(g)$, each at STP, the moles of HCl(g) formed is equal to **[2014]**

(a) 1 mole of HCl (g)
(b) 2 moles of HCl (g)
(c) 0.5 mole of HCl (g)
(d) 1.5 moles of HCl (g)

Q.24. 1.0g of magnesium is burnt with 0.56 g of oxygen in a closed vessel. Which reactant is left in excess and how much? **[2014]**

(a) Mg. 0.16g (b) O_2,0.16g
(c) Mg, 0.44g (d) O_2,0.28g

Q.25. How many grams of concentrated nitric acid solution should be used to prepare 250 mL of 2.0 M HNO_3 ? **[2013]**

(a) 45.0g conc. HNO_3
(b) 90.0g conc. HNO_3
(c) 70.0g conc. HNO_3
(d) 54.0g conc. HNO_3

Q.26. 6.02×10^{20} molecules of area are present in 100 mL of its solution. The concentrartion of solution is **[2013]**

(a) 0.2 M (b) 0.01 M
(c) 0.001 M (d) 0.1 M

Q.27. Mole fraction of the solute in a 1.00 molal aqueous solution is **[2011]**

(a) 0.0177 (b) 0.0344
(c) 1.7700 (d) 0.1770

Q.28. 10 g of hydrogen and 64 g of oxygen were filled in a steel vessel and exploded. Amount of water produced in this reaction will be

(a) 2 moles (b) 3 moles
(c) 4 moles (d) 1 mole

Q.29. Volume occupied by one molecule of water (density =1g cm^{-3}) is **[2008]**

(a) 9.0×10^{-23} cm^3 (b) 6.023×10^{-23} cm^3
(c) 3.0×10^{-23} cm^3 (d) 5.5×10^{-23} cm^3

Q.30. What volume of oxygen gas (O_2) measured at 0^0 C and 1 atm, is needed to burn completely 1L of propane gas (C_3H_8) measured under the same conditions? **[2008]**

(a) 7 L (b) 6 L
(c) 5 L (d) 10 L

Q.31. How many moles of lead (II) chloride will be formed from a reaction between 6.5g of PbO and 3.2g of HCl? **[2008]**

(a) 0.044 (b) 0.333

(c) 0.011 (d) 0.029

Q.32. Number if moles of MNO_4^- required to oxidize one mole of ferrous oxalate completely in acidic medium will be **[2007]**
(a) 0.6 mole (b) 0.4 mole
(c) 7.5 mole (d) 0.2 mole

Q.33. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ion in acidic solution is **[2007]**
(a) 4/5 (b) 2/5
(c) 1 (d) 3/5

Q.34. An element, X has the following isotopic composition:
$^{200}X : 90\%$, $^{199}X : 8.0\%$, $^{202}X : 2.0\%$
The weighted average atomic mass of naturally occurring element X is closest to **[2007]**
(a) 201 u (b) 202 u
(c) 199 u (d) 200 u

Q.35. The number of moles of $KMnO_4$ reduced by one mole of KI in alkaline medium is **[2005]**
(a) one fifth (b) five
(c) one (d) two

Q.36. The mass of carbon anode consumed (giving only carbon dioxide) in the production of 270 kg of aluminium metal from bauxite by the Hall process is (at. Mass of Al = 27) **[2005]**
(a) 180 kg (b) 270 kg
(c) 540 kg (d) 90 kg

Q.37. The maximum number of molecules are present in **[2005]**
(a) 15 L of H_2 gas at STP
(b) 5 L OF H_2 gas at STP
(c) 0.5 g of H_2 gas
(d) 10 g of O_2 gas

Q.38. In Haber process 30L of dihydrogen and 30 L of dinitrogen were taken for reaction which yielded only 50% of the expected product. What will be the composition of gaseous mixture under the aforesaid condition in the end? **[2003]**
(a) 20 L ammonia, 10 L nitrogen, 30 L hydrogen
(b) 20 L ammonia 25 L nitrogen, 15 L hydrogen
(c) 20 L ammonia, 20 L nitrogen, 20 L hydrogen
(d) 10 L ammonia, 25 L nitrogen, 15 L hydrogen

Q.39. Specific volume of cylindrical virus particles is 6.02×10^{-2} cc / g, whose radius and length are 7A and 10 A respectively. If $N_A = 6.023\times10^{23}$, find molecular weight of virus. **[2001]**
(a) 15.4 kg/mol (b) 1.54×10^4kg/mol
(c) 3.08×10^4 kg/mol (d) 3.08×10^3 kg/mol

Answer Key

1. (a)
2. (d)
3. (c)
4. (d)
5. (9)
6. (d)
7. (d)
8. (8)
9. (a)
10. (8.8 mL)
11. (c)
12. (5)
13. (2)
14. (3)
15. (b)
16. (a)
17. (a)
18. (b)
19. (a)
20. (a)
21. (d)
22. (a)
23. (a)
24. (a)
25. (a)
26. (b)
27. (a)
28. (c)
29. (c)
30. (c)
31. (d)
32. (a)
33. (b)
34. (d)
35. (c)
36. (d)
37. (a)
38. (d)
39. (a)

3

CLASSIFICATION OF ELEMENTS PERIODICITY IN PROPERTIES

CLASSIFICATION OF ELEEMENTS AND PERIODICITY IN PROPERITES

PERIODIC TABLE

Periodic table may be defined as the table which classifies all the known elements in accordance with their properties in such a way that elements with similar properties are grouped together in the same vertical column and dissimilar elements are separated from one another

PERIODICITY

The repetition of properties of elements after certain regular intervals is called periodicity of elements.

GENESIS OF PERIODIC CLASSIFICATION

1. Dobereiner's Triads
2. Telluric screw
3. Newlands's Law Of Octaves
4. Lothar-Meyer arrangement

1. DOBEREINER'S TRIADS

Noticed that the middle element of each of the **Triads** had an atomic weight about half way between the atomic weights of the other two. Also the properties of the middle element were in between those of the other two members. Since Dobereiner's relationship, referred to as the **Law of Triads**, seemed to work only for a few elements, it was dismissed as coincidence.

Element	Atomic	Element	Atomic	Element	Atomic
Li	7	*Ca*	40	*Cl*	35.5
Na	23	*Sr*	88	*Br*	80
K	39	*Ba*	137	*I*	127

LIMITATION OF DOBEREINER:

1. There are only three traids.
2. It is valid only for 9 elements.

2. TELLURIC SCREW

The next reported attempt to classify elements was made by a French geologist, A.E.B. de Chancourtois.

He arranged the known elements in order of increasing atomic weights and made a cylindrical table of elements to display the periodic recurrence of properties. This also did not attract much attention.

3. NEWLANDS'S LAW OF OCTAVES

John Alexander Newlands profounded the **Law of Octaves**.

He arranged the elements in increasing order of their atomic weights and noted that every eighth element has properties similar to the first element

The relationship was just like every eighth note that resembles the first in octaves of music. Newlands's Law of Octaves seemed to be true only for elements up to calcium.

	Li	*Be*	*B*	*C*	*N*	*O*	*F*
At. wt.	7	9	11	12	14	16	19
	Na	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*
At. wt.	23	24	27	29	31	32	35.5
	K	*Ca*					
At. wt.	39	40					

4. Lothar-Meyer arrangement

Lothar Meyer plotted the physical properties such as atomic volume, melting point and boiling point against atomic weight and obtained a periodically repeated pattern.

Lothar Meyer developed a table of the elements that closely resembles the Modern Periodic Table. However, his work was not published until after the work of Dmitri Mendeleev, the scientist who is generally credited with the development of the Modern Periodic Table.

MENDELEEV'S PERIODIC LAW

The properties of the elements are a periodic function of their atomic weights.

SIGNIFICANCE OF MENDELEEV'S PERIODIC TABLE

1. **Systematic study of the elements.** The Mendeleev's periodic table simplified and systematized the study of the elements and their compounds since their properties could now be studied as groups or families rather than individuals.
2. **Prediction of new elements.** At the time when Mendeleev's periodic table was formulated, only **63 elements** were known. Therefore, while arranging the elements according to their properties, Mendeleev left some **blank spaces or gaps**. These gaps represented unknown elements. Further, Mendeleev predicted the properties of these unknown elements on the basis of their positions.
3. **Correction of doubtful atomic weights.** Mendeleev's periodic table has helped in correcting the doubtful atomic weights of some elements.

LIMITATIONS OF MENDELEEV PERIODIC TABLE

1. In Mendeleev Perodic Table position of H is not fixed.
2. Position of isotopes can not explain.
3. Some dissimilar elements are grouped together while some similar elements are placed in different groups.
4. Regular atomic mass increases not follow.

MODERN PERIODIC LAW

When Mendeleev developed his **Periodic Table**, chemists knew nothing about the internal structure of atom. However, the beginning of the 20th century witnessed profound developments in theories about sub-atomic particles.

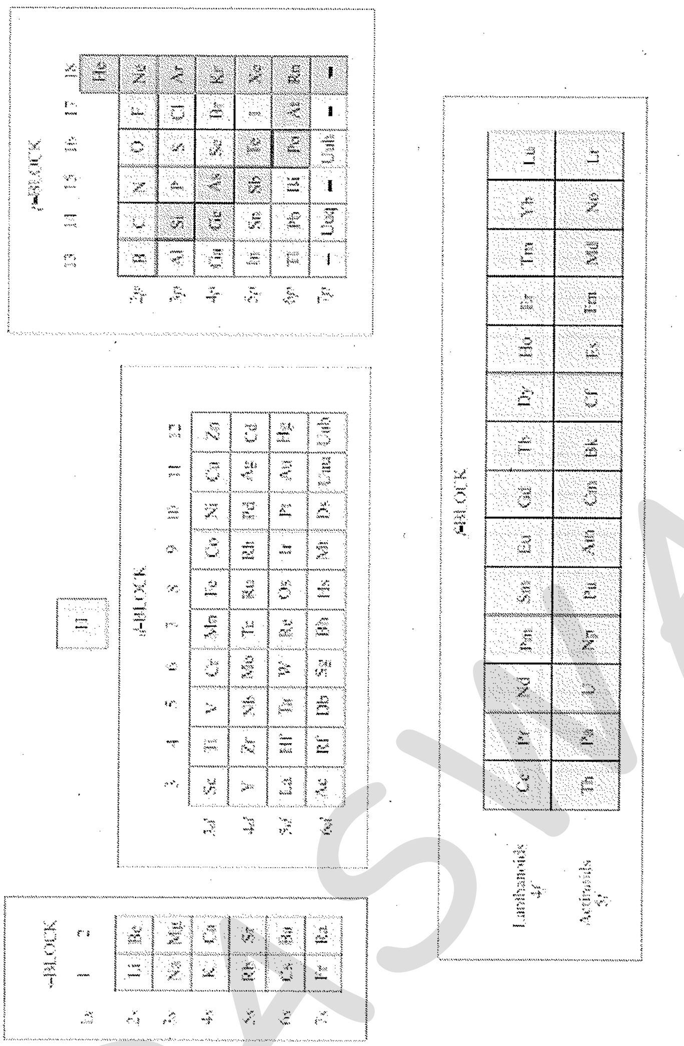
He thereby showed that the atomic number is a more fundamental property of an element than its atomic mass. **Mendeleev's Periodic Law** was, therefore, accordingly modified. This is known as the **Modern Periodic Law** and can be stated as :

The physical and chemical properties of the elements are periodic functions of their atomic numbers.

LONG FORM OF THE PERIODIC TABLE
BOHR'S TABLE

The table which is most commonly used these days and which is based upon the **electronic configuration** of elements is called the **Present form** or the **Long form of the periodic table.**

This is also called **Bohr's table** since it follows Bohr's scheme for the arrangement of various electrons around the nucleus.



The types of elements in the Periodic Table based on the orbitals that are being filled. Also shown is the broader division of elements into METALS (▭▭▭▭), NON-METALS (▭▨) and METALLOIDS (▨).

NOMENCLATURE OF ELEMENTS WITH ATOMIC NUMBERS > 100

The roots for the numbers 0 – 9 are :

Digit	Name	Abbreviation
0	Nil	n
1	Un	u
2	Bi	b
3	Tri	t
4	Quad	q
5	Pent	p
6	Hex	h
7	Sept	s
8	Oct	o
9	Enn	e

Recommended and Official names of element with Z > 100

Z	Recommended Name	Symbol	IUPAC Official Name	IUPAC Symbol
101	Unnilunium	**Unu**	Mendelevium	**Md**
102	Unnilbium	**Unb**	Nobelium	**No**
103	Unniltrium	**Unt**	Lawrencium	**Lr**
104	Unnilquadium	**Unq**	Rutherfordium	**Rf**
105	Unnilpentium	**Unp**	Dubnium	**Db**
106	Unnilhexium	**Unh**	Seaborgium	**Sg**
107	Unnilseptium	**Uns**	Bohrium	**Bh**
108	Unniloctium	**Uno**	Hassnium	**Hs**
109	Unnilennium	**Une**	Meitnerium	**Mt**
110	Ununnilium	**Uun**	Darmstadtium	**Ds**
111	Unununium	**Uuu**	Rontgenium	**Rg***
112	Ununbium	**Uub**	*	*
113	Ununtrium	**Uut**	+	—
114	Ununquadium	**Uuq**	*	*
115	Ununpentium	**Uup**	+	—
116	Ununhexium	**Uuh**	*	*
117	Ununseptium	**Uus**	+	—
118	Ununoctium	**Uuo**	+	—
119	Ununennium	**Uue**	+	—
120	Unbinilium	**Ubn**	+	—

DIVISION OF ELEMENTS INTO s-, p-, d-AND f-BLOCK AND THEIR ELECTRONIC CONFIGURATION :
Elements in the long form of the periodic table have been divided into four blocks, i.e., s, p, d and f.
This division is based upon the name of the orbital which receives the last electron.

1. s-Block Elements.

(a) The elements of Group 1 (alkali metals) and Group 2 (alkaline earth metals) **in which the last electron enters the s-orbital.**

(b) **General outer shell electronic configuration of s-block elements :** ns^{1-2} **where n = 2 – 7.**

General characteristics of s-Block Elements

(i) They are soft metals with low melting and boiling points.
(ii) They have low ionization enthalpies (energies) and are highly electropositive .
(iii) They lose the valence (outermost) electron(s) readily to form + 1 (in case of alkali metals) and + 2 ions (in the case of alkaline metals) and + 2 ions (in the case of alkaline earth metals).

2. p-Block Elements.

(a) The **p-Block Elements** comprise those belonging to Group 13 to 18 .
(b) Elements in which the last electron enters any one of the three p-orbitals of their respective outermost shells are called **p-block elements.**
(c) These together with the *s*-**Block Elements** are called the **Representative Elements or Main Group Elements.**
(d) **General outer shell electronic configuration of p-block elements :** $ns^2 np^{1-6}$ **where n = 2 – 6.**

General characteristics of p-Block Elements

(i) p-Block elements include both metals and non-metals but the number of non-metals is much higher than that of metals. Further, the metallic character increase from top to bottom within a group and non-metallic character increases from left to right along a period in this block.

(ii) Their ionization enthalpies are relatively higher as compared to those of s-block elements.

3. d-Block Elements [Transition Element]

(a) Elements in which the last electron enters any one of the five d-orbitals of their respective penultimate shells are called **d-block elements.**

(b) General outer shell electronic configuration of d-block elements : $(n-1)d^{1-10}ns^{1-2}$ where n = 4 + 7.

General characteristics of d-Block Elements

(i) They are hard, malleable (*i.e.,* can be converted into sheets) and ductile (*i.e,* can be drawn into wires) metals with high melting and boiling points.

(ii) They are good conductors of heat and electricity.

(iii) Their ionization enthalpies are between *s*-and *p*-block elements.

(iv) They show variable oxidation states.

4. The *f*-Block Elements (*Inner-Transition Elements*)

(a) The elements in which the last electron enters in the f-subshell of Innerpenaltimate (n–2) shell are called f-block elements.

(b) **General outer shell electronic configuration of f-block elements : $(n-2)\ f^{1-14}\ (n-1)\ d^{0-1}\ ns^2$ where n = 6 – 7.**

(c) The elements of the first series, i.e., Cerium to lutetium $({}_{58}Ce - {}_{71}Lu)$ which form a part of the sixth period are collectively called as **lanthanides** or **lanthanoids.**
These are also called **rare earth elements** since they occur scarcely in the earth's crust.

General characteristics of f-block Elements

(i) They are heavy metals.

(ii) They have generally high melting and boiling points.

(iii) They show variable oxidation states.

(iv) Their compounds are generally coloured.

METALS, NON-METALS AND METALLOIDS

The elements can be divided into **Metals** and **Non-Metals**.

(A) METALS

1. Metals comprise more than 78% of all known elements and appear on the left side of the **Periodic Table**.
2. Metals are usually solids at room temperature [**mercury is an exception;** gallium and caesium also have very low melting points (303K and 302K, respectively)].
3. Metals usually have high melting and boiling points.

(B) NON-METALS

1. Non-metals are usually solids or gases at room temperature with low melting and boiling points (boron and carbon are exceptions).
2. They are poor conductors of heat and electricity. Most nonmetallic solids are brittle and are neither malleable nor ductile.
3. The elements become more metallic as we go down a group; the nonmetallic character increases as one goes from left to right across the **Periodic Table**.

(C) METALLOIDS

The elements (e.g., silicon, germanium, arsenic, antimony and tellurium) bordering the line and running diagonally across the **Periodic Table** show properties that are characteristic of both metals and nonmetals. These elements are called **Semi-metals** or **Metalloids (Si, Ge, As, Sb, Te, Po, At)**.

PERIODIC TRENDS IN PROPERTIES OF ELEMENTS

(a) Trends in Physical Properties :

1. Atomic Radius
2. Ionic Radius
3. Ionization Enthalpy
4. Electron Gain Enthalpy
5. Electronegativity

(b) Trends in Chemical Properties :

1. **Periodicity of Valence or Oxidation States**
2. **Anomalous Properties of Second Period Elements**

ATOMIC RADIUS

The distance from the centre of the nucleus to the outermost shell containing electrons.

Types of atomic radii :

Depending upon whether an element is non-metal or a metal, three different types of atomic radii are used. These are as follows :

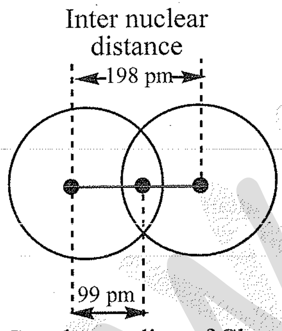
(a) Covalent radius **(b)** van der Waals radius **(c)** Metallic radius

In case of non-metals, atomic radius refers to either covalent or van der Waals radius.

(a) Covalent radius.

It is defined as one-half the distance between the nuclei of two covalently bonded atoms of the same element in a molecule.

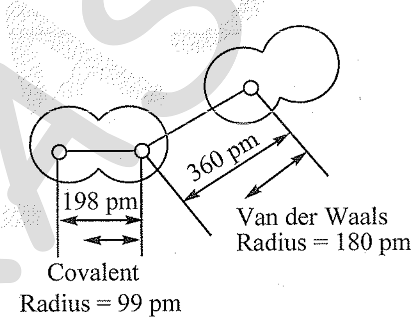
The covalent bond must be single covalent bond.



Covalent radius of Cl_2

(b) Van der Waals radius

It is defined as one-half of internuclear distance of two non bonded adjacent atoms of two nearest molecules of an element in solid state.



Van der Waals radii of chlorine

FACTORS AFFECTING THE MAGNITUDE OF ATOMIC RADII

1. **Nuclear Charge :**
   Greater the magnitude of positive nuclear charge, greater is the electrostatic force of attraction exerted by the nucleus on the negative electron cloud surrounding the nucleus.Consequently smaller is the atomic radius.
2. **Number of Shells :**
   With the increase in the number of shells the atomic radii also increases because the size of atom also increases as the electrons get farther and farther from the nucleus.

VARIATION OF ATOMIC RADII IN THE PERIODIC TABLE

(a) Variation along a period :

The atomic size generally decreases across a period for the elements of the second period.

It is because within the period the outer electrons are in the same valence shell and the effective nuclear charge increases as the atomic number increases resulting in the increased attraction of electrons to the nucleus. Hence atom will contact and size decreases.

Atom (period 2)	*Li*	*Be*	*B*	*C*	*N*	*O*	*F*	*Ne*
Atomic radius	152	111	88	77	70	74	72	160
Atom (Period 3)	*Na*	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*	*Ar*
Atomic radius	186	160	143	117	110	104	99	191

(b) Variation within a group :

The atomic (covalent) radii of elements increase with increase in atomic number as we move from top to bottom in a group due to increases the number of shell. For example, consider the atomic (covalent) radii of the members of the alkali metals group.

Alkali metals (Group I)	**Atomic radius**	**Halogens (Group 17)**	**Atomic radius**
Li	152	*F*	72
Na	186	*Cl*	99
K	231	*Br*	114
Rb	244	*I*	133
Cs	262	*At*	140

IONIC RADIUS

The ionic radii can be estimated by measuring the distances between cations and anions in ionic crystals.

Comparision of the ionic radii with corresponding atomic radii:

A study of ionic radii of cations and anions reveals the following two generalizations :

(a) The radius of the cation is always smaller than that of its parent atom.

$$\underset{1s^2 2p^2 2p^6 3s^1}{Na} \longrightarrow \underset{1s^2 2s^2 2p^6}{Na^+} + e^-$$

The size of a cation is always smaller than that of the corresponding atom due to

(i) decrease in the number of shells

(ii) increase in the effective nuclear charge resulting in greater force of attraction by the nucleus on the electrons.

Comparative sizes of atoms and their cations :

Atoms	*Li*	*Na*	*K*	*Be*	*Mg*	*Al*	*Mn*
Atomic radii (pm)	152	186	231	111	160	143	126
Corres. Cations	Li^+	Na^+	K^+	Be^{2+}	Mg^{2+}	Al^+	Mn^{4+}
Ionic radii (pm)	60	95	133	39	65	50	46

(b) **The radius of the anion is always large than that of its parent atom.** The size of an anion will be larger than that of the parent atom because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge.

Comparative sizes of atoms and their anions :

Atom	*F*	*Cl*	*Br*	*I*	*O*	*S*	*N*
Atomic radii (pm)	72	99	114	133	74	102	75
Corres. anion	F^-	Cl^-	Br^-	I^-	O^{2-}	S^{2-}	N^{3-}
Ionic radii (pm)	136	181	196	219	142	184	171

ISOELECTRONIC SPECIES AND IONS

Isoelectronic species may be defined as neutral or ionic species which have the same number of electrons but different nuclear charges.

Variation of ionic size among isoelectronic ions

The ionic radii of isoelectronic ions decrease with the increase in the magnitude of the nuclear charge.

For example, consider the isoelectronic ions : $N^{3-}, O^{2-}, F^-, Na^+,$ Mg^{2+} and Al^{3+}.

All these ions have 10 electrons but their nuclear charges vary *i.e.,* there are + 7, + 8 + 9, + 11, + 12 and + 13 .Therefore, their ionic radii increase in the order :

$Al^{3+} < Mg^{+} < Na^{+} < F^{-} < O^{2-} < N^{3-}$.

Variation of ionic radii in an isoelectronic series :

Ions	N^{3-}	O^{2-}	F^{-}	Na^{+}	Mg^{2+}	Al^{3+}
Nuclear charge	+7	+8	+9	+11	+12	+13
Ionic radius (pm)	171	140	136	95	65	50

IONISATION ENTHALPY

Minimum amount of energy required to remove outermost electrons from an ioslated gasious atom in its ground state.

It is represented by $\Delta_i H$

This is process may be represented as

$M(g)+\Delta_i H \longrightarrow M^{+}(g)+e^{-}(g)$

where M(g) and M^{+} (g) represent the gaseous atom and the resultant gaseous cation (a positive ion).

Ionization enthalpy is also known as ionization potential since it is the minimum potential difference (in a discharge tube) required to remove the most loosely bound electron from an isolated gaseous atom to form gaseous cation.

Units of I.E./I.P.

The ionization enthalpy is expressed in units of **kJ mol^{-1}**

Successive Ionization Enthalpies

The energy required to remove the most loosely bound electron from the isolated gaseous atom is called its first ionization enthalpy and is denoted by $\Delta_i H_1$

$M(g)+\Delta_i H_1 \longrightarrow M^{+}(g)+e^{-}(g)$

Similarly, the energies required to knock out second and third electrons are called second and third ionization energies respectively, e.g.,

$M^{+}(g)+\Delta_i H_2 \longrightarrow M^{2+}(g)+e^{-}(g)$

$M^{2+}(g)+\Delta_i H_3 \longrightarrow M^{3+}(g)+e^{-}(g)$

where $\Delta_i H_2$ and $\Delta_i H_3$ are the second and the third ionization enthalpies respectively.

FACTORS GOVERNING IONISATIION ENTHALPY

Ionization enthalpy depends upon following factors :

(a) Nuclear charge **(b)** Atomic size

(c) Penetration effect of the electrons **(d)** Screening effect of inner electrons

(e) Effect of arrangement of electrons, i.e., Effect of exactly half filled or completely filled orbitals.

(a) **NUCLEAR CHARGE : The ionization enthalpy increases with increase in nuclear charge.** This is due to the fact that with increase in nuclear charge, the electrons of the outer shell are more firmly held by the nucleus and thus greater energy is required to pull out an electron from the atom.

(b) **ATOMIC SIZE OR RADIUS :** Ionization enthalpy decreases as the atomic size increases. As the distance of the outer electrons from the nucleus increases with increase in atomic radius, the attractive force on the outer electrons decreases.

(c) **PENETRATION EFFECT OF THE ELECTRONS : Ionization enthalpy increases as the penetration effect of the electrons increases.** within the same shell, the penetration effect decreases in the order :

$$s > p > d > f$$

Thus, **the ionization enthalpy will be more to knockout a s-electron than a p-electron of the same shell, which in turn, will be more than that required to remove a d-electron and so on.**

(d) **Shielding or Screening effect of the inner shell electrons :** As the shielding or the screening effect of the inner electrons increases, the ionization enthalpy decreases.

The actual charge felt by the valence shell electrons is called effective nuclear charge

The repulsive force felt by the valence shell electrons from the electrons present in the inner shells

is called the shielding effect or screening effect.

(e) Electronic configuration, *i.e.*, Effect of exactly half-filled or completely filled orbitals

(i) **Be** $(1s^2 2s^2)$ **has higher ionization enthalpy than B** $(1s^2 2s^2 2p^1)$. This is because Be has fully filled orbitals which is a stable electronic arrangement. Similarly Mg $(1s^2 2s^2 2p^6 3s^2)$ has higher ionization enthalpy than aluminium $(1s^2 2s^2 2p^6 3s^2 3p_x^1)$.

(ii) N$(1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1)$ **has higher ionization enthalpy than oxygen** $(1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1)$. This is because N contains exactly half filled *p*-orbitals. Such an arrangement gives extra stability to the atom. As a result, the removal of electron becomes difficult and hence the ionization enthalpy is high. For similar reasons, **ionization enthalpy of P** $(1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1)$ is **higher than that of S** $(1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1)$.

(iii) **Noble gases have the highest ionization enthalpy in their respective periods.** For example, ionization enthalpy of Ne is more than any other element of the second period.

Variation of Ionization Enthalpy in the Periodic Table

(a) **Variation along a period :**

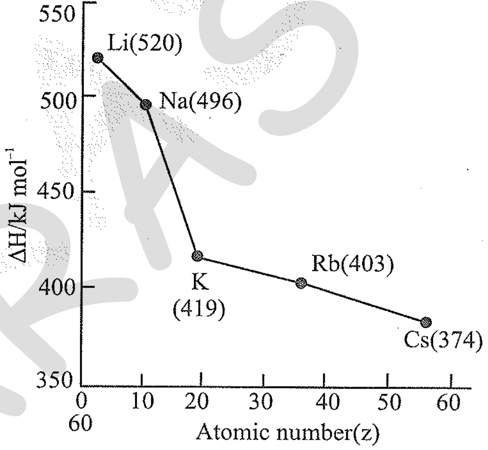
In general, on moving left to right in a period, the ionization enthalpy increases with increasing atomic numbers.

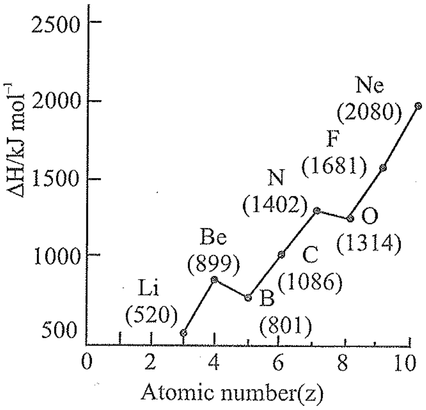
The observed trends can be easily explained on the basis of increased nuclear charge and smaller atomic radii.

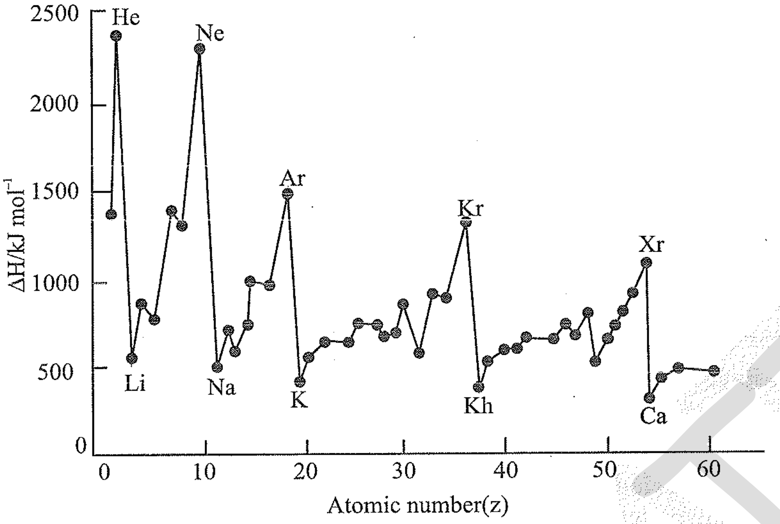
(b) **Variation within a group :**

The ionization enthalpies keep on decreasing regularly as we move down a group from one element to the other. **The above trend can be easily explained on the basis of increasing atomic size and screening effect.**

The combined effect of the increase in the atomic size and the screening effect more than compensates the effect of the increased nuclear charge. Consequently, the valence electrons become less and less firmly held by the nucleus and hence the ionization enthalpies gradually decrease as we move down the group.







Variation of first ionization enthaplpies ($\Delta_i H$) with atomic number for elements with Z = 1 to 60

ELECTRON GAIN ENTHALPY

When an electron is added to a neutral gaseous atom (X) to convert it into a negative ion, the enthalpy change accompanying the process is defined as the **Electron Gain Enthalpy** $\Delta_{eg}H$.

This process may be presented as :

$$\underset{\text{neutral gaseous atom}}{X(g)} + e^- \rightarrow \underset{\text{anion}}{X^-(g)};\ \Delta H = \Delta_{eg}H \qquad \ldots(i)$$

Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion .

Depending on the element, **the process of adding an electron to the atom can be either endothermic or exothermic.**

Electron Gain Enthalpies (in kJ mol^{-1}) of Some Main Group Elements :

Group 1	*H*	*Li*	*Na*	*K*	*Rb*	*Cs*
Ä$_{eg}$H	-73	-60	-53	-48	-47	-46
Group 16		*O*	*S*	*Se*	Te	Po
Ä$_{eg}$H		-141	-200	-195	-190	-174
Group 17		*F*	*Cl*	*Br*	*I*	*At*
Ä$_{eg}$H		-328	-349	-325	-295	-270
Group 18	*He*	*Ne*	*Ar*	*Kr*	*Xe*	*Rn*
Ä$_{eg}$H	+48	+116	+96	+96	+77	+68

The negative of the enthalpy change accompanying the addition of an electron to an isolated gaseous atom is defined as **electron affinity** (A_e). The electron affinity is said to be **positive**, if energy is released when an isolated gaseous atom accepts an electron and it is assigned a **negative sign** if energy is to be supplied to add an extra electron to the isolated gaseous atom. This is, however, contrary to the thermodynamic convention. Further, since electron affinity is defined at absolute zero, therefore, at any other temperature heat capacity instead of electron affinity of the reactants and products should be considered. Therefore, in view of these two reasons, **the term electron gain enthalpy is used instead of electron-affinity.** The two terms are related to each other as

$$\Delta H_{eg} = -A_e - (5/2RT)$$

Thus numerically electrons gain enthalpy is higher than that of electron affinity by 5/2 RT. Since the value of 5/2 RT at 298K is just 2.477 kJ mol^{-1}. Therefore, this small difference is often ignored and the two terms are used indistinguishably with the only difference that **electron gain enthalpy is just the negative electron affinity.**

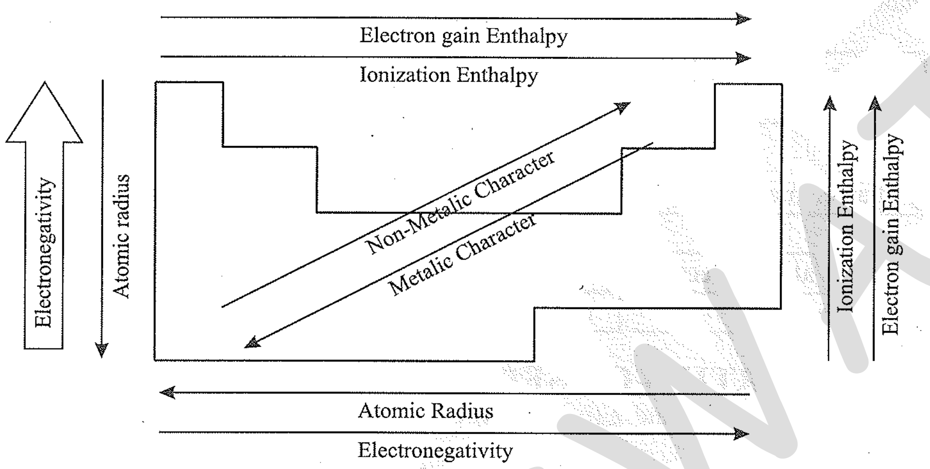
FACTORS AFFECTING ELECTRON GAIN ENTHALPY

- **(i)** Atomic size
- **(ii)** Nuclear charge
- **(iii)** Electronic configuration

Some Important Trends in Electron Gain Enthalpies.

- **(i)** **Halogens have the most negative electron gain enthalpies.**
- **(ii)** **The electron gain enthalpy of noble gases is positive.**
- **(iii)** **The electron gain enthalpies of some of the element second period i.e., O and F are however, less negative than the corresponding elements (i.e., S and Cl) of the third period.**

THE PERIODIC TRENDS OF ELEMENTS IN PERIODIC TABLE:



ELECTRONEGATIVITY

A qualitative measure of the ability of an atom in a chemical compound to attract shared electrons to itself is called electronegativity.Unlike ionization enthalpy and electron gain enthalpy, it is not a measureable quantity.

NOTE: The electronegativity of any given element is not constant; it varies depending on the element to which it is bound. Though it is not a measurable quantity, it does provide a means of predicting the nature of force that holds a pair of atoms together.
It is represented by, X

Trends in groups and periods

(a) **Variation within a group**
The electronegativity values decrease down a group. This is because when on moving down the group, atomic radius as well as screening effect increases. **Caesium is the least electronegative element.**

(b) **Variation within a period**
The electronegativity values for the representative elements increase along a period from left to right This is because on moving along the period from left to right nuclear charge increases and atomic radius decreases Thus, **fluorine is most electronegative element** and is given a value of 4.0 (Pauling scale)

Some Important Electronegativity Value:

Atom	Li	Be	B	C	N	O	F	Na	Mg	Al	Si	P	S	Cl
Electro negativity	1.0	1.5	2	2.5	3	3.5	4	0.9	1.2	1.5	1.8	2.1	2.5	3.0

APPLICATION OF ELECTRONEGATIVITY

Application of electronegativity. The concept of electronegativity is very useful in predicting metallic, non-metallic character of elements and polarity, of bonds.

(i) **Metallic and non-metallic character.** As the electronegativity increases, the non-metallic character increases.

Differences between electron gain enthalpy and electronegativity

S.No.	Electron gain enthalpy	Electronegativity
1	It is the tendency of an isolated gaseous atom to attracted an electron.	It is the tendency of an atom to attract the shared pair of electron.
2	It can be experimentally measured and is usually expressed in kJ mol^{-1} or electron volts/atom.	It cannot be measured, experimentally. It is only a relative number w.r.t. fluorine taken as 4.0 .
3	It is the property of as isolated atom.	It is the property of a bonded atom.
4	The electron gain enthalpy of an atom is constant.	The electronegativity of an atom is not constant.
5	It does not change regularly in a period or group.	It changes regularly in a period but there are certain exceptions in a group.

VALENCY:

The combining capacity of an element is known as valency.

Group	1	2	13	14	15	16	17	18
No. of Valence electron	1	2	3	4	5	6	7	8
Valency	1	2	3	4	3,5	2,6	1,7	0,8

ANOMALOUS PROPERTIES OF SECOND PERIOD ELEMENT:

The first element of each group 1-(lithium) and 2 (beryllium) and group 13-17 (Boron to Flourin) differ in many respect from the other member which is

- Small size, high ionization enthalpy, non-availability of d-orbital, high electronegativity.
- First member of p-Block element display greater ability to form $P\pi - P\pi$ multiple bond to itself
  Eg: ($C=C$, $C\equiv C$, $N\equiv N$, $N=N$)
  And to other second period element
  ($C=O$, $C=N$, $C\equiv N$, $N=O$)

QUESTIONS

NCERT EXERCISE & EXAMPLES

Genesis of Periodic Classification

1. What is the basic theme of organisation in the periodic table ?

Mendeleev's Periodic Table and Modern Periodic Table

2. Which important property did Mendeleev use to classify the elements in his periodic table and did he stick to that ?

3. What is the basic difference in approach between the Mendeleev Periodic law and the Modern Periodic Law ?

4. What are the major differences between metals and non-metals ?

5. Considering the elements B, Al, Mg and K, the correct order of their metallic character is :
(a) $B > Al > Mg > K$ (b) $Al > Mg > B > K$
(c) $Mg > Al > K > B$ (d) $K > Mg > Al > B$

6. Considering the elements B, C, N, F and Si, the correct order of their non-metallic character is :
(a) $B > C > Si > N > F$
(b) $Si > C > B > N > F$
(c) $F > N > C > B > Si$
(d) $F > N > C > Si > B$

Period, Group, Block

7. On the basis of quantum numbers, justify that the sixth period of the periodic table should have 32 elements ?

8. In terms of period and group where would you locate the element with Z = 114 ?

9. Write the atomic number of the element present in the third period and seventeenth group of the periodic table.

10. Which element do you think would have been named by
(i) Lawrence Berkeley laboratory ?
(ii) Seaborg's group ?

11. Use the periodic table to answer the following questions ?
(a) Identify an element with five electrons in the outer subshell.
(b) Identify an element that would tend to lose two electrons.
(c) Identify an element that would tend to gain two electrons.
(d) Identify group having metal, non-metal, liquid as well as gas at the room temperature.

12. Assign the position of the element having outer electronic configuration (i) ns^2np^4 for n = 3 (ii) $(n-1)\,d^2ns^2$ for n = 4, and (iii) $(n-2)\,f^1(n-1)\,d^1ns^2$ for n = 6, in the periodic table.

13. In the modern periodic table, the period indicates the value of :
(a) atomic number
(b) atomic mass
(c) principal quantum number
(d) azimuthal quantum number

14. Which of the following statements related to the modern periodic table is incorrect ?
(a) The p-block has 6 columns, because a maximum of 6 electrons can occupy all the orbitals in a p-shell.
(b) The d-block has 8 columns, because a maximum of 8 electrons can occupy all the orbitals in a d-subshell.
(c) Each block contains a number of columns equal to the number of electrons that can occupy that can occupy that subshell.
(d) The block indicates value of azimuthal quantum number (ℓ) for the last subshell that received electrons in building up the electronic configuration.

15. Anything that influences the valence electrons will affect the chemistry of the element. Which one of the following factors does not affect the valence shell ?
(a) Valence principal quantum number (n)
(b) Nuclear charge (Z)
(c) Nuclear mass
(d) Number of core electrons

16. Predict the formulae of the stable binary compounds that would be formed by the combination of the following pairs of elements.
(a) Lithium and oxygen
(b) Magnesium and nitrogen
(c) Aluminium and iodine
(d) Silicon and oxygen
(e) Phosphorus and fluorine
(f) Element 7 and fluorine

Atomic Radius and Ionic Radius

17. What does atomic radius and ionic radius really mean to you ?

18. How does atomic radius vary in a period and in a group ? How do you explain the variation ?

19. What do you understand by isoelectronic species ? Name a species that will be isoelectronic with each of the following atom or ions.
(i) F^- (ii) Ar
(iii) Mg^{2+} (iv) Rb^+

20. Consider the following species :
N^{-3}, O^{-2}, F^-, Na^+, Al^{3+}
(a) What is common in them ?
(b) Arrange them in the order of increasing ionic radii.

21. Explain why cations are smaller and anions larger in radii than their parent atoms ?

22. The size of isoelectronic species $-F^-$. Ne and Na^+ is affected by
(a) nuclear charge (Z)
(b) valence principal quantum number (n)
(c) electron-electron interaction in the outer orbitals.
(d) none of the factors because their size is the same.

23. Describe the theory associated with the radius of an atom as it (a) gains an electron (b) loses an electron.

Ionization Enthalpy

24. Energy of an electron in the ground state of the hydrogen atom is -2.18×10^{-18} J. Calculate the ionization enthalpy of atomic hydrogen in terms of J mol^{-1}.

25. Among the second period elements, the actual ionization enthalpies are in the order.
Li < B < Be < C < O < N < F < Ne
Explain why
(i) Be has higher Δ_iH than B
(ii) O has lower Δ_iH than N and F ?

26. How will you explain the fact that first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium ?

27. What are various factors due to which the ionization enthalpy of the main group elements tends to decrease down a group ?

28. The first ionization enthalpy values (in kJ mol^{-1}) of group 13 elements are :

B	Al	Ga	In	Tl
801	577	579	558	589

How would you explain this deviation from the general trend ?

29. Would you expect the first ionization enthalpies for two isotopes of the same element to be the same or different ? Justify you answer.

30. Which one of the following statements is incorrect in relation to ionization enthalpy ?
(a) Ionization enthalpy increases for each successively electron.
(b) The greatest increase in ionization enthalpy is experienced on removal of electron from core noble gas configuration.
(c) End of valence electrons is marked by a big jump is ionization enthalpy.
(d) Removal of electron from orbitals bearing lower value is easier than from orbital having higher n value.

Electron Gain Enthalpy

31. Which of the following pairs of elements would have a more negative electron gain enthalpy?
(i) O or F (ii) F or Cl

32. Would you expect the second electron gain enthalpy of O as positive, more negative or less negative than the first ? Justify your answer.

Electronegativity

33. What is the basic difference between the terms electron gain enthalpy and electronegativity ?

34. How would you react to the statement that the electronegativity of N on Pauling scale is 3.0 in all the nitrogen compounds ?

Reactivity

35. The increasing order of reactivity among group I elements is Li < Na < K < Rb < Cs whereas that among group 17 elements is F > Cl > Br > I. Explain.

36. Considering the elements F, Cl, O and N, the correct order of their chemical reactivity in terms of oxidizing property is :
(a) F > Cl > O > N (b) F > O > Cl > N
(c) Cl > F > O > N (d) O > F > N > Cl

37. Why do elements in the same group have similar physical and chemical properties ?

Miscellaneous Questions

38. The first (Δ_iH_1) and the second (Δ_iH_2) ionization enthalpies (in kJ mol^{-1}) and the ($\Delta_{eg}H$) electron gain enthalpy (in kJ mol^{-1}) of a few elements are a given below :

Elements	**IE**	**IE_2**	**$\Delta_{eg}H$**
I	520	7300	−60
II	419	3051	−48
III	1681	3374	−328
IV	1008	1846	−295
V	2372	5251	+48
VI	738	1451	−40

Which of the above element is likely to be :

(a) the least reactive element.
(b) the most reactive metal.
(c) the most reactive non-metal.
(d) the least reactive non-metal ?
(e) The metal which can form a stable binary halide of the formulae MX_2 (X = halogen).
(f) The metal which can form a stable covalent halide of the formula MX (X = halogen).

39. What is the significance of the terms-'isolated gaseous atom' and 'ground state' while defining the ionization enthalpy and electron gain enthalpy ?

SOLUTIONS

NCERT EXERCISE & EXAMPLES

Sol.1 The basic theme of organization in the periodic classification of elements is the electronic configuration of their atoms.

Sol.2 Mendeleev used the atomic weights of the elements as the main property to classify the elements. He arranged elements in horizontal rows and vertical columns of a table in order of their increasing atomic weights in such a way that the elements with similar properties occupied the same vertical column or group.
He realized that some of the elements did not fit in with his scheme of classification of the order of atomic weight was strictly followed. In such cases, he ignored the order of atomic weights. For example iodine with lower atomic weight (= 127) than that of tellurium (= 127.6) (Group VI) was placed in Group VII along with other halogens because of similarities in properties.

Sol.3 Mendeleev Periodic Law was based up on **atomic weights** of elements, whereas Modern Periodic Law is based upon **atomic numbers** of elements.
Mendeleev stated : "The properties of the elements are a periodic function of their **atomic weights.**"
Modern Periodic Law states : "The physical and chemical properties of the elements are periodic functions of their **atomic numbers.**"

Sol.4 Elements which have a strong tendency to lose electrons to forms cations are called metals while those which have a strong tendency to accept electrons to form anions are called non-metals. Thus, metals are strong reducing agents, they have low ionization enthalpies, have less negative electron gain enthalpies, low electronegativity, form basic oxides and ionic compounds.
Non-metals, on the other hand, are strong oxidising agents, they have high ionisation enthalpies, have high negative electron gain enthalpies, high electronegatively, form acidic oxides and covalent compounds.

Sol.5 **(d)** K > Mg > Al > B

Sol.6 **(c)** F > N > C > B > Si

Sol.7 When n = 6, l = 0, 1, 2, 3, 4, 5. The order in which the energy of the orbitals increases is 6s < 4f < 5d < 6p. The total number of orbitals available are 16 [s = 1, p = 3, d = 5; f = 7]. The maximum number of electrons which an orbital can contain is 2. Therefore the sixth period can accommodate 32 elements.

Sol.8 Since Z = 114; Its probable symbol is Uuq. It will lie in the 7th period and 14th group. Its structure will be $7s^2\ 7p^2$.

Sol.9 The atomic number of the element present in the third period and seventeenth group is 17 [2, 8, 7]. It is Chlorine.

Sol.10 **(i)** Berkelium (Bk) with atomic number 97.
(ii) Seaborgium (Sg) with atomic number 106.

Sol.11 **(a)** Fluorine F = $1s^2, 2s^2, 2p^5$ [$5e^-$ in 2p subshell]
(b) Calcium Ca = $1s^2, 2s^2, 2p^6\ 3s^2\ 3p^6\ 4s^2$ [It can lose $2e^-$]
(c) Oxygen O = $1s^2, 2s^2\ 2p^4$ [It can lose $2e^-$]
(d) Group I, if we include Hydrogen in it. H is Non-metal as well as H_2 gas. Cs is a liquid. Li, Na, K, Rb are solids and metals.

Sol.12 **(i)** $ns^2\, np^4$ is $3s^2\, 3p^4$
The complete electronic configuration is $1s^2, 2s^2\, 2p^6, 3s^2\, 3p^4$
Atomic Number = 2 + 2 + 6 + 2 + 4 = 16.
The element is sulphur in the 3rd period and in Group 16 (p-block)
(ii) $(n-1)\, d^2\, ns^2$ for n = 4; It is $3d^2\, 4s^2$
The complete electronic configuration is $1s^2, 2s^2\, 2p^6, 3s^2\, 3p^6 3d^2 4s^2$
Atomic Number is 22. The element is Titanium.
It is a transition element present in the 4th period and Group 4.
(iii) $(n-2)\, f^1\, (n-1)\, d^1\, ns^2$ for n = 6
$4f^1\, 5d^1\, 6s^2$
Its complete electronic configuration is $1s^2, 2s^2\, 2p^6, 3s^2\, 3p^6 3d^{10} 4s^2 4p^6\, 4d^{10}\, 4f^7\, 5s^2\, 5p^6\, 5d^1\, 6s^2$
It is Gadolium (Gd)
It is an inner transition element, belongs to Lanthanoid series or 4f series. It is an f-block element.

Sol.13 **(c)** Principal quantum number

Sol.14 **(b)** The d-block has 10 columns, because a maximum of 10 electrons can occupy all the five d-orbitals of the d-subshell.

Sol.15 **(d)** Number of core electrons.

Sol.16 **(a)** Lithium oxide .... Li_2O
(b) Magnesium nitride .... Mg_3N_2
(c) Aluminium iodide .... AlI_3
(d) Silicon oxide or silica .... SiO_2

(e) Phosphorus fluoride .... PF_5
(f) Element (Lu) fluoride .... EF_3 [LuF_3]

Sol.17 In the case of non-metals like chlorine atomic radius actually covalent radius and it is half the bond distance between atoms in chlorine molecule Cl_2.
Bond distance in Cl_2 molecule = 198 pm

Atomic or **covalent radius** $= \frac{198}{2} = 99$ pm...

In the case of metals, atomic radius is actually metallic radius which is taken as half the internuclear distance separating the metal in solid copper is 256 pm; hence the metallic radius (or atomic radius) of copper is 128 pm.
On the other hand, the ionic radius is the radius of its ion (cation or anion). It is actually estimated by measuring the distances between cations and anions in ionic crystals.

Sol.18 Variation of Atomic radius across a period.
Atomic radii of elements generally decrease in going from left to right in a period. It is because within the same period, the outer electrons are in crease the same valence shell and the effective nuclear charge increases as the atomic number increases resulting in the increased attraction of electrons to the nucleus. Hence atom will contract.

Variation of Atomic radius within a group
Atomic radii of elements within a group increase from top to bottom.
In moving down a group, nuclear charge increases with increase to atomic number but at the same time, there is a progressive increase in the principal quantum level, the number of electrons in the outermost shell, however, remains the same. Consequently the distance of the outermost electrons from the nucleus gradually increases down the group because the effect of additional energy level is more pronounced than the effect of increased nuclear charge.

Sol.19 Isoelectronic species (atoms or ions) are those which contain the same number of electrons.
For example, O^{2-}, F^-, Na^+, Mg^{2+} have 10 electrons each. They constitute isoelectronic series.

(i) F^- is isoelectronic with Na^+ (10 e^-)
(ii) Ar is isoelectronic with K^+ (18 e^-)
(iii) Mg^{2+} is isoelectronic with O^{2-} (10 e^-)
(iv) Rb^+ is isoelectronic with Br^- (36e^-)

Sol.20 (a) The species N^{-3}, O^{-2}, F^-, Na^+, Al^{3+} are all isoelectronic containing 10 electrons each.

(b) The species N^{-3}, O^{-2}, F^-, Na^+, Al^{3+} in the increasing order of ionic radii are $Al^{3+} < Na^+ < F^- < O^{-2} < N^{-3}$.

Sol.21 Cations are always smaller than their parent atoms, because they have fewer electrons, while their nuclear charge remains the same. The remaining electrons are held more tightly by the protons in the nucleus and thus their radii are smaller than the parent atoms.
Anions are always larger than their parent atoms because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in the effective nuclear charge.

Sol.22 **(a)** nuclear charge (Z)

Sol.23 **(a)** When an atom gains one or more electrons, it becomes negatively charged ion called ANION. The radius of an anion will be larger than that of its parent atom, because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge. As a result electron cloud expands, i.e., ionic radius increases.

(b) When an atom loses one or more electrons it becomes positively charged ion called CATION. The radius of a cation is **always less** than that of its parent atom. This may be due to the following reasons.

(i) **Disappearance of the valence shell.** In certain cases the loss of electrons leads to a complete disappearance of the valence shell. Removal of the outer most shell decreases the size.

(ii) **Increase of effective nuclear charge.** In a cation, the no. of electrons is less than in the corresponding atom. The total nuclear charge remains the same. This increases the effective nuclear charge. As a result, the electrons are attracted towards the nucleus more tightly, thereby leading to the decrease in ionic radius.

Sol.24 A ground state electron has $E = -2.18 \times 10^{-18}$ J
Energy required for the removal of electron is $+2.18\times10^{-18} J$
$H(g) \rightarrow H^+(g) + e^-$ $\Delta E = IE = 2.18 \times 10^{-18}$ J/e
We have to apply the idea of mole concept :
In terms of per mole, it will be
2.18×10^{-18} J $\times$ 6.022×10^{23} = 13.12×10^5 J mol^{-1}
[1 mole of electrons = 6.022×10^{23} electrons]

Sol.25 **(i)** $\Delta_i H$ of Be is higher than that of B.

Electronic donfiguration of Be is $1s^2, 2s^2$ whereas that of B is $1s^2, 2s^2 2p^1x$

In the case of Be, electron has to be removed from an s-orbital, whereas in the case of B, it has to be removed from a p-orbital. It is difficult to remove an s-electron because it is closer to the nucleus than a p-electron hence more energy is required to remove an electron from 2s of Be than 2p-electron in the case of B. Hence IE of Be is higher than that of B.

(ii) Electronic configuration of O is $1s^2, 2s^2 2p_x^2 2p_y^1 2p_z^1$ (neither exactly half-filled nor completely filled).

whereas N is $1s^2, 2s^2 2p_x^1 2p_y^1 2p_z^1$ (exactly half-filled).

It is difficult to remove an electron from the valence shell of N because its p-subshell is exactly half-filled and so has more stability, whereas O has electronic configuration which is neither completely filled nor exactly half-filled. Therefore, it is easier to remove one electron from O atom. F, due to increased nuclear charge, has more IE than either O or N.

Sol.26 The first electron in both the cases has to be removed from 3s-orbital, but nuclear charge of Na is less than that of Mg. Hence IE of Na is lower than that of Mg.

$$Na = 1s^2, 2s^2 2p^6, 3s^1 \xrightarrow{IE_1} Na^+ (= 1s^2, 2s^2 2p^6)$$

$$Mg = 1s^2, 2s^2 2p^6, 3s^2 \xrightarrow{IE_1} Mg^+ (= 1s^2, 2s^2 2p^6, 3s^1)$$

After the loss if first electron the electronic configuration of Na^+ is $1s^2, 2s^2 2p^6$, i.e., that of noble gas which is very stable and hence the removal of 2nd electron from Na^+ is very difficult. In the case of Mg, after the loss of first electron, electronic configuration of Mg^+ ion is $1s^2, 2s^2 2p^6, 3s^1$. The second electron to be removed is from 3s orbital which is easier.

Hence IE_2 of sodium is much larger than IE_2 of Mg.

Sol.27 **(i)** On moving **down the group, the atomic size increases** gradually due to the addition of one new principal energy shell at each succeeding element. As a result, the distance of the valence electrons from the nucleus increases. Consequently, the force of attraction of the nucleus for the valence electrons decreases and **thus IE should decrease.**

(ii) With the addition of new shells the number of inner shell electrons which shield the valence electrons from the nucleus increases. In other words, **shielding or screening effect increases.** As a result, the force of attraction of the nucleus for the valence electrons further decreases and hence the **ionization enthalpy should decrease.**

(iii) **Nuclear charge increases down the** group with increase in atomic number. As a result the force of attraction of the nucleus for the valence electrons should increase thus, **ionization enthalpy should increase.**

The combined effect of the increase in the atomic size and the screening effect more than compensates, the effect of the increased nuclear charge. Consequently the valence electrons become less and less firmly held by the nucleus hence the ionization enthalpies gradually decrease as we move down the group.

Sol.28 On moving down the group 13 from B to Al, the first ionization enthalpies $[IE_1]$ decreases due to an increase in atomic size and screening effect which outweigh the effect of increased nuclear charge. However the IE_1, of Ga is only slightly higher than that of Al [2kJ mol^{-1}] while that of Tl is much higher than those of Al, Ga and In. This is due to the fact that Al follows immediately after s-block elements while Ga, and In follow after d-block elements and Tl after *d*- and *f*-block elements. These extra *d* and *f* electrons do no shield or screen the outer shell electrons from the nucleus effectively.

As a result, the valence shell electrons remain more tightly held by the nucleus and hence larger amount of energy is required to remove them. This explains why Ga has higher IE_1, than Al. In moving down from Ga to In, the increased shielding effect [due to the presence of additional 4d-electrons] outweighs the effect of increased nuclear charge (49 – 31 = 18 units) and hence IE_1 of In is lower than that of Ga, Thereafter, the effect of increased nuclear charge (81 – 49 = 32 units) outweighs the shielding effect due to the presence of additional 4f and 5d electrons and hence IE_1, of Tl is higher than that of In.

Sol.29 Isotopes of the same element differ only in the number of neutrons. Isotopes of the same element have the same no. of protons and electrons. IE values depend largely upon (i) nuclear charge (ii) size of the atom. IE does not depend upon the number of neutrons. Hence the value of IE remains the same for different isotopes of the same element.

Sol.30 **(d)** It is easier to remove an electron from orbitals bearing higher principal quantum value than from orbital having lower n_0 value.

Sol.31 **(i)** F (-328 kJ mol^{-1}) has more negative electron gain enthalpy than O (-141 kJ mol^{-1}).

(ii) Cl (-349 kJ mol^{-1}) has more negative electron gain enthalpy than F (-328 kJ mol^{-1}).

Sol.32 When an electron is added to Oxygen atom to form O^- ion energy is released. But when another electron is added to O^- ion to from O^{2-} ion energy is absorbed to overcome the strong electrostatic repulsion between the negatively charged O^- ion and the new electron being added. The second electron gain enthalpy of O is positive.

Thus, **first electron gain enthalpy :**

$$O(g) + e^-(g) \rightarrow O^-(g); \Delta H_{eg} = -141 \text{ kJ mol}^{-1}$$

(energy is released)

Second electron gain enthalpy :

$$O^-(g) + e^-(g) \rightarrow O^{2-}(g); \ \Delta H_{eg} = +780 \text{ kJ mol}^{-1}$$

(energy is obsorbed)

Sol.33 Electronegativity differs from electron gain affinity in the sense that the latter is related to atoms in their isolated states, whereas former is a property of an atom in a bonded state, i.e., in a molecule. Electronegativity is only qualitative and is not a measurable quantity.

Sol.34 Though the value of electronegativity of N on Pauling scale is 3.0, yet **electronegativity** of any given element is not constant. It varies depending upon the element to which it is bound. The value of electronegativity of 3.0 assigned to N is only arbitrary since it is not a measurable quantity.

Sol.35 The group I elements are alkali metals. They form unipositive ions M^+ by losing one electron from their valence shells

$$M \rightarrow M^+ + e^-$$

As Ionisation enthalpy decreases from top to bottom in group I, the tendency to form unipositive ions increases from top to bottom. Therefore the reactivity increases down the group from Li to Cs. In other words the order the reactivity in group I elements is Li < Na < K < Rb < Cs.

The group 17 elements are halogens with electronic configuration of ns^2np^5 in their valence shells, they try to become ns^2np^6 by acquiring one electron.

All the halogens are highly reactive elements due to the following two reasons.

(i) **Low bond dissociation energy :** ($X_2 \rightarrow 2X$) Halogens have low bond dissociation energy. F_2 has lowest bond dissociations energy which makes it the most reactive.

(ii) **High electron affinity :** Due to high electron enthalpy these elements have a strong tendency to gain an electron and thus are highly reactive.

Sol.36 **(b)** F > O > Cl > N

Sol.37 Elements in the same vertical column or group have similar valence shell electronic configurations, have the same number of electrons in the outer orbitals hence similar properties.

Thus the similarities in properties are due to similarity in the electronic configuration of the valence shells of atoms of the elements. For example of the Group I elements (alkali-metals) all have 1s valence shell electronic configuration.

Sol.38 (a) The least reactive element is V.

It is Helium. It has no tendency to lose electrons [as is clear from its high IE_1 and its higher IE_2], nor can it gain electrons [positive value of electron gain enthalpy – energy has to be absorbed to gain or add an electron].

(b) the most reactive metal is II, It is K,

Its IE_1 is lowest and IE_2 is very high; i.e., it can lose one electron readily from its valance shell [4th] to become K. It cannot lose 2nd electron readily because of stable Ar core.

(c) the most reactive non-metal is III, It is Fluorine. Its IE_1 and IE_2 are very high, meaning it cannot lose electrons readily. On the other hand, its electron gain enthalpy has a large negative value indicating it can accept an electron readily.

(d) the least reactive non-metal is IV. It is iodine. Its IE_1 and IE_2 are very high, meaning it cannot lose electrons readily. On the other hand, its electron gain enthalpy has a large negative value but not as large negative value as F above indicating it can accept an electron readily.

(e) The metal which can form a stable binary halide of the formulae MX_2 (X = halogen) is VI. It is Magnesium

$$Mg + X_2 \rightarrow MgX_2$$

Its IE_1 and IE_2 are not very high, but its electron gain enthalpy is very small, IE_2 is

not very large as compound to IE_1.
Because of its electro positive nature and tendency to lose two electrons, it can form a stable binary halide MX_2.

(f) The metal which can form a stable covalent halide is I. It is Lithium its $IE_2 >> E_1$, meaning it can lose one electron readily but not the second. Due to its small size, its forms stable covalent halide of the formula MX.

Sol.39 While defining ionization enthalpy, energy is required to remove the most loosely bound electron from an isolated gaseous atom in its ground state resulting in the formation of a positive ion

$$X(g) + \text{energy} \rightarrow X^+(g) + e^-$$

While defining electron gain enthalpy, there is enthalpy charge accompanying the process

$$X(g) + e^- \rightarrow X^-(g); \Delta H = \Delta H_{eg}$$

Again energy is released when one electron is added to a natural gaseous atom X to convert it into a negative ion. This is requirement for comparison purposes.

QUESTION ALIKE

Based on Predicting Relative Ionisation Enthalpies

1. The electronic configurations for the following neutral atoms are given for use in question.

(a) $1s^2, 2s^2, 2p^6, 3s^2$; (b) $1s^2, 2s^2, 2p^6, 3s^1$;
(c) $1s^2, 2s^2, 2p^4$; (d) $1s^2, 2s^2, 2p^5$;
(e) $1s^2, 2s^2, 2p^6$.

(i) Which of the electronic configuration given above would you expect for the noble gas ?
(ii) Which of the electronic configuration given above would you expect to have the lowest ionization enthalpy?
(iii) List the above configurations in order of increasing enthalpy.

2. The first $\Delta_i H_1$ and the second $(\Delta_i H_2)$ ionization enthalpies (kJ mol^{-1}) of a few elements designed by Roman numerals are shown below :

Elements	IE_1	IE_2
I	**2372**	**5251**
II	**520**	**7300**
III	**900**	**1760**
IV	**1680**	**3380**

Which of the above elements is likely to be
(b) a reactive metal (b) a reactive non-metal
(c) a noble gas (d) a metal that forms a stable binary halide of the formula AX_2 (X = halogen).

3. The first ionization enthalpy (Δ_{iH}) values of the third period element, Na, Mg and is are respectively 496, 737 and 786 kJ mol^{-1} predict whether the Δ_{H} value for Al will be more close to 575 or 760 kJ mol^{-1}. Justify your answer.

4. Arrange the following in the order of increasing ionization enthalpy :

(i) $1s^2 2s^2 2p^6 3s^2$ (ii) $1s^2 2s^2 2p^6 3s^1$
(iii) $1s^2 2s^2 2p^6$ (iv) $1s^2 2s^2 2p^2$
(v) $1s^2 2s^2 2p^3$

5. The electronic configurations of some neutral atoms are given below :

(i) $1s^2 2s^2$ (ii) $1s^2 2s^2 2p^1$
(iii) $1s^2 2s^2 2p^4$ (iv) $1s^2 2s^2 2p^3$.

Which of these electronic configuration would be expected to have the highest
(a) Δ_{iH_1} (b) Δ_{iH_2}
(c) Δ_{iH_3} (d) Δ_{iH_4} ?

Based on The Calculation Ionization Enthalpies

6. Calculate the energy required to convert all the atoms of magnesium to magnesium ions present in 24 mg of magnesium vapours ? First and second ionization enthalpies of Mg are 737.6 and 1450 kJ mol^{-1} respectively.

7. Calculate the energy in joules required to convert all the atoms of sodium to sodium ions present in 2.3 mg of sodium vapours ? Ionization enthalpy of sodium vapours ? Ionization enthalpy of sodium is 495 kJ mol^{-1} (Atomic mass of Na = 23).

8. The ionization potential of hydrogen is 13.60 eV. Calculate the energy in kJ required to produce 0.1 mole of H^+ ions. Given, 1 eV = 96.49 kJ mol^{-1}

Based on Predicting Electron Gain Enthalpy

9. Arrange the elements with the following electronic configurations in order of increasing electron gain enthalpy.

(i) $1s^2 2s^2 2p^5$ (ii) $1s^2 2s^2 2p^4$
(iii) $1s^2 2s^2 2p^3$ (iv) $1s^2 2s^2 2p^6 3s^2 3p^4$

10. Arrange the following elements in order of decreasing electron gain enthalpy : B, C, N, O.

11. Which one (atom/ion) in the following pairs has higher electron gain enthalpy ?

(i) O^-, S (ii) O, S^-
(iii) O^-, S^- (iv) N^-, P

12. The electron gain enthalpies of halogens decrease in the order F > Cl > Br > I. Comment upon the statement.

Based on Predicting Period, Group and Block of Elements

13. Considering the atomic number and position in the periodic table, arrange the following elements in the increasing order of metallic character : Si Be, Mg, Na, P.

14. Write the names and atomic numbers of the following elements :

(i) The fourth alkali metal
(ii) The third alkaline earth metal
(iii) The fifth element of the first transition series
(iv) The first inner transition element and
(v) The sixth noble gas.

15. The outer electronic configuration of some elements are given below :

(i) $3s^2 3p^3$ (ii) $3d^5 4s^1$
(iii) $3s^2 3p^6 4s^2$ (iv) $5d^1 6s^2$

(v) $4f^1 5d^1 6s^1$
State to which block of the periodic table each of these elements belongs.

16. An element 'X' with atomic number 112 has recently been discovered. Predict its electronic configuration and suggest the group in which this element would be placed.

17. Arrange the following elements in the increasing order of metallic character : B, Al, Mg K.

18. Write the electronic configuration and the block to which an element with Z = 90 belongs.

Based on The Calculation of Electron Gain Enthalpy

19. The electron gain enthalpy of chlorine is – 349 kJ mol^{-1}. How much energy in kJ is released when 3.55 g of chlorine is converted completely into Cl^- ion in the gaseous state ?

20. The amount of energy released when 1×10^{10} atoms of chlorine in vapour state are converted to Cl^- ions according to the equation,
$Cl(g)+e^-(g)\longrightarrow Cl^-(g)$ **is** 57.86×10^{-10} J.
Calculate the electron gain enthalpy of chlorine atom in terms of kJ mol^{-1} and eV per atom.

21. The electron affinity of bromine is 3.36 eV. How much energy in kcal is released when 8g of bromine is completely converted to Br^- ions in the gaseous state ?

22. The amount of energy released when one million atoms of iodine are completely converted into I^- ions in the vapour state according to the equation,
$I(g)+e^-(g)\longrightarrow I^-(g)$ is 4.9×10^{-13} J.
Calculate the electron affinity of iodine in
(i) kJ/mol and
(ii) in eV per atom

Based on Valence and Chemical Reactivity

23. **Are the oxidation state and covalency of Al in $[AlCl(H_2O)_6]^{2+}$ same.**

24. Show by a chemical reaction with water that Na_2O is a basic oxide and Cl_2O_7 is an acidic oxide.

25. Predict the formulae of the stable binary compounds that would be formed by the following pairs of elements :
(a) silicon and bromine
(b) aluminium and sulphur
(c) calcium and oxygen
(d) aluminium and carbon

Based on Finding Isoelectronic Species and Comparison of their Relative Radii

26. Name the species that will be isoelectronic with the following atoms or ions :
(i) Ne (ii) Cl^-
(iii) Ca^{2+} (iv) Rb^+

27. Which of following species are isoelectronic?
(i) O^{2-} (ii) Na
(iii) F (iv) Mg^{2+}
(v) Cl^- (vi) Al^{3+}
(vii) Ne
Arrange them in decreasing order of their size.

28. Which of the following species has the largest and the smallest size. Mg, Mg^{2+} , Al, Al^{3+}.

29. Which one of the following pairs would have large size ? Explain.
(i) K or K^+ (ii) Br or Br^-
(iii) O^{2-} or F^- (iv) Li^+ or Na^+
(v) P or As (vi) Na^+ or Mg^{2+}

30. Arrange the following in order of increasing radii ?
(i) I, I^+, I^- (ii) C, N, Si, P
(iii) $O^{2-}, N^{3-}, S^{2-}, F^-$

QUESTION ALIKE SOLUTIONS

Sol.1 (i) Arrange the electronic configuration of all the atoms in order of increasing atomic number in such a way that atoms containing the same outer energy shell are grouped together. Thus, we have

$\underset{(c)}{1s^2 2s^2 2p^4}$ $\underset{(d)}{1s^2 2s^2 2p^5}$ $\underset{(e)}{1s^2 2s^2 2p^6}$ ...L-shell

$\underset{(a)}{1s^2 2s^2 2p^6 3s^2}$ $\underset{(b)}{1s^2 2s^2 2p^6 3s^1}$ ...M-shell

Since the M-shell is more distant from the nucleus than L-shell, so lesser amount of energy is required to remove an electron from M-shell than from the L-shell. In other words, ionization enthalpy (IE) of atoms (a) and (b) should be lower than that of atoms (c), (d) and (e).

Further, in case of atom (a), the electron is to be removed from the more stable completely filled 3*s*-orbital whereas in case of atom (b) it is not so. Therefore, the IE of atom (b) should be lower than that of atom (a).

The nuclear charge on atoms (c), (d) and (e) is + 8, + 9 and + 10 respectively. Since the IE increases with increase in nuclear charge so the IEs atoms (c), (d) and (e) follow the sequence : c < d < e .

From The above discussion, we conclude that the ionization enthalpies of the five atoms increase in the following order

b < a < c < d < e

i.e., $1s^2 2s^2 2p^6 3s^1 < 1s^2 2s^2 2p^6 3s^2$

$< 1s^2 2s^2 2p^4 < 1s^2 2s^2 2p^5 < 1s^2 2s^2 2p^6$

(ii) Evidently, atom (b) with electronic configuration, $1s^2 2s^2 2p^6 3s^1$ has the lowest ionization enthalpy.

(iii) Since the outer electronic configuration of noble gases is $ns^2 np^6$, therefore, the electronic configuration, $1s^2 2s^2 2p^6$ [atom (e)] represents an noble gas.

Sol.2 (a) Since element II has a very low Δ_{iH_1} but a very high Δ_{iH_2}, therefore, it has only one electron in the valence shell and hence is likely to be a *reactive metal (i.e., an alkali metal).*

(b) Since the Δ_{iH_1} of element IV is very high and its Δ_{iH_2} is not so high (actually almost double), it is likely to be a *reactive non-metal (i.e., a halogen).*

(c) Among the elements listed, Δ_{iH_1} of element I si the highest and its Δ_{iH_2} is also not so high, therefore, it must be *a noble gas.*

(d) The Δ_{iH_1} of element III is higher than that of element II, but unlike element II, its Δ_{iH_2} is only about twice its Δ_{iH_1}, therefore, it is likely that element III has two electrons in the valence shell (*i.e., alkaline earth metal).* As such it will form a stable binary halide of the formula AX_2 where A is the metal and X is the halogen.

Sol.3 Arrange the elements Na, Mg, and Si into different groups and periods in order of their increasing atomic numbers, we have,

1	2	13	14
Na	Mg	Al	Si
–	–		

Since in case of Al, a 3*p*-electron is to be lost while in Mg, a 2*s*-electron is to be lost, therefore, value for Al will be lower than that of Mg (737 kJ mol^{-1}) because of the effective shielding of the 3*p*-electron from the nucleus by 3*s*-electrons. Therefore Δ_{iH} for all Al will be more close to 575 kJ mol^{-1}.

Sol.4 **1.** In a period noble gas *i.e.,* $1s^2 2s^2 2p^6$ (iii) has the highest Δ_{iH_1}. Out of C, $1s^2 2s^2 2p^2$ (iv) and N, $1s^2 2s^2 2p^3$ (v), N has higher Δ_{iH_1} due to higher nuclear change and stable exactly half-filled electronic configuration. Because of bigger size both Mg, $1s^2 2s^2 2p^6 3s^2$ (i) and Na, $1s^2 2s^2 2p^6 3s^1$ (ii) have lower Δ_{iH_1} than C, N, O. Out (i) and (ii), (i) has higher Δ_{iH_1} due to higher nuclear charge and completely filled *s*-orbital. Thus, the overall order of increasing Δ_{iH_1} is (ii) < (i) < (iv) < (v) < (iii).

Sol.5 (a) – (iv) has highest Δ_{iH_1} due to stable exactly half-filled electronic configuration

(b) – (iii) has highest Δ_{iH_2} since the second electron has to be removed from the stable exactly half filled electronic configuration left after removal of 1st electron, i.e.,

$1s^2 2s^2 2p^4 \xrightarrow{\Delta_i H_1} 1s^2 2s^2 2p^3 \xrightarrow{\Delta_i H_2}$

(c) – (i) has the highest Δ_{iH_3} since the third electron has to be removed from the stable inert gas configuration,

$1s^2 2s^2 \xrightarrow{\Delta_i H_1} 1s^2 2s^1 \xrightarrow{\Delta_i H_2} 1s^2 \xrightarrow{\Delta_i H_3}$

(d) – (ii) has the highest Δ_{iH_4} since the fourth electron has to be removed from the stable inert gas configuration,

$1s^2 2s^2 2p^1 \xrightarrow{\Delta_i H_1} 1s^2 2s^1 \xrightarrow{\Delta_i H_2} 1s^2 2s^1 \xrightarrow{\Delta_i H_3}$
$1s^2 \xrightarrow{\Delta_i H_4}$

Sol.6 According to the definition of successive ionization enthalpies.

$$M(g)+\Delta_i H \longrightarrow M^+(g)+e^-(g);$$
$$\Delta_i H_1 = 737.76 \text{ kJ mol}^{-1}$$
$$M^+(g)+\Delta_i H_2 \longrightarrow M^{2+}(g)+e^-(g)$$
$$\Delta_i H_2\ 1450.73 \text{ kJ mol}^{-1}$$

∴ Total amount of energy needed to convert Mg (g) atom into $M^{2+}(g)$ ion = $\Delta_i H_1 + \Delta_i H_2$ = $737.76 - 1450.73$ kJ mol^{-1} = 2188.49 kJ mol^{-1}

24 mg of Mg $= \frac{24}{1000} g = \frac{24}{1000 \times 24}$ mole

$= 10^{-3}$ mole

∴ Amount of energy needed to ionize 10^{-3} mole of Mg vapours

$= 2.188.49 \times 10^{-3}$ **= 2.188 kJ.**

Sol.7 No. of moles of Na present is 2.3 mg of Na

$= \frac{23}{10} \times \frac{1}{1000} \times \frac{1}{23} = 1 \times 10^{-4}$ mole

∴ Required energy $= 1 \times 10^{-4} \times 495 \times 10^3$ **= 49.5 J**

Sol.8 Required energy $= 0.1 \times 13.60 \times 96.49$

= 131.226 kJ

Sol.9 Out of F ($1s^2 2s^2 2p^5$), O ($1s^2 2s^2 2p^4$), N ($1s^2 2s^2 2p^3$) and S ($1s^2 2s^2 2p^6 3s^2 3p^4$), only N because of its stable exactly half-filled electronic configuration has +ve electron gain enthalpy while all others have –ve electron gain enthalpies. Since F needs only one more electron to acquire the nearest inert gas configuration, therefore, it has the most –ve electron gain enthalpy. Out of O and S, O has less negative electron gain enthalpy than S because of electron-electron repulsions present in its small compact 2*p*-orbital. Thus, overall order of increasing electron gain enthalpy is : (i) < (iv) < (ii) < (iii).

Sol.10 N has +ve electron gain enthalpy while all others have –ve electron gain enthalpies. Since size decreases in moving from $B \longrightarrow C \longrightarrow O$, therefore, electron gain enthalpies become more and more negative from $B \longrightarrow C \longrightarrow O$. Thus, the overall decreasing order of electron gain enthalpies is N, B, C, O.

Sol.11 (i) Due to repulsions between the electron on O^- and the additional incoming electron, the electron gain enthalpy of O^- is positive while that O a-ve.

(ii) On similar grounds, the electron gain enthalpy of S^- is +ve while that O is – ve.

(iii) Due to small size, repulsions between O^- and the incoming electron is much more than in S^-. Therefore, electron gain enthalpy of O^- is more +ve than that of S^-.

(iv) Due to repulsions between N^- and the incoming gain enthalpy of N^- is positive while that P is – ve.

Sol.12 The statement is wrong. The actual order is I > Br > F > Cl.

Sol.13 Arranging the elements into different groups and periods in order of their increasing atomic numbers, we have,

1	2	13	14	15
-	Be	-	-	-
Na	Mg	-	Si	P

We know that the metallic character increases down a group and decreases along a period as we move from left to right. Therefore, Na is the most metallic element, followed by Mg and Si while P is the least metallic element. Among Be and Mg, Mg is more metallic than Be. Therefore, the overall increasing order of metallic character is $P < Si < Be < Mg < Na$.

Sol.14 (i) $Rb(Z=37)$ (ii) $Ca(Z=20)$
(iii) $Mn(Z=35)$ (iv) $Ce(Z=58)$
(v) $Rn(Z=86)$

Sol.15 (i) p (ii) d
(iii) s (iv) d
(v) f

Sol.16 $[Rn]5f^{14}6d^{10}7s^2$, 12th group.

Sol.17 $B < Al < Mg < K$

Sol.18 $[Rn]6d^2, 7s^2$, f-block element.

Sol.19 According to the definition of electron gain enthalpy.

$$Cl(g)+e^-(g) \longrightarrow Cl^-(g) + 349 \text{ kJ mol}^{-1}$$

∴ Energy released when 1 mole (= 35.5 g) of chlorine atoms change completely into $Cl^-(g)$ = 349 kJ

Energy released when 3.55 g of chlorine atoms change completely into $Cl^-(g)$

$= \frac{349}{35.5} \times 3.55$ **= 34.9 kJ.**

Sol.20 The amount of energy released when 1×10^{10} atoms of chlorine in vapour state are converted to Cl^- ions, according to the equation.

$Cl(g)+e^-(g) \longrightarrow Cl^-(g)$ is 57.86×10^{-10} J.

∴ The electron gain enthalpy of chlorine *i.e.*, the amount of energy released when 1 mole (6.023×10^{23}) atoms of chlorine are converted into Cl^- ions according to the above equation will be

$$=-\frac{57.86\times10^{-10}}{1\times10^{10}}\times6.023\times10^{23}$$

$=-348.49\times10^{3}\ \text{J / mol}$ **= 348.49 kJ/mol**

Now 1 eV/atom = 96.49 kJ mol^{-1}

∴ Electron gain enthalpy of chlorine

$=-\frac{348.49}{96.49}$ **= 3.61 eV/atom**

Sol.21 No. of moles of Br = 8/80 = 0.1

Required energy $=0.1\times3.36\times23.06$ = **7.748 kcal**

Sol.22 Electron affinity

$=6.023\times10^{23}\times4.9\times10^{-13}\times10^{-6}$

$=29.5\times10^{4}\times10^{-3}\ \text{kJ}$

$=295\ \text{kJ mol}^{-1}$

$=295/96.49\ \text{eV / atom}$

$=3.06\ \text{eV / atom}$

Sol.23 The oxidation state of Cl is – 1. Let us suppose that oxidation state of Al is x

∴ $x-1+6\times0=+2$ or $x=+3$

Thus, the oxidation state of Al is +3

Since six ligands (which can donate a pair of electrons), *i.e.,* H_2O molecules are attached to the aluminium atom, therefore, its covalency is 6.

Sol.24 Na_2O reacts with water to form sodium oxide which turns red litmus blue,

$$\underset{\text{Sod.oxide}}{Na_2O}+H_2O\longrightarrow\underset{\text{Sod.hydroxide}}{2\,NaOH}$$

Therefore, Na_2O *is a basic oxide.*

In contrast, Cl_2O_7 reacts with water to form perchloric acid which turns blue litmus red.

$$\underset{\text{Chlorine(VII) oxide}}{Cl_2O_7}+H_2O\longrightarrow\underset{\text{Perchloric acid}}{2HClO_4}$$

Therefore, Cl_2O_7 *is an acidic oxides.*

Sol.25 (a) $SiBr_4$ (b) Al_2S_3

(c) CaO (d) Al_4C_3

Sol.26 Isoelectronic species are those which have same number of electrons.

(i) Ne has 10 electrons. Therefore, the species $N^{3-},O^{2-}\ F^{-},Na^{+},Al^{3+}$ etc. each of which has also 10 electrons, are isoelectronic with it.

(ii) Cl^{-} has 18 electrons. Therefore, the species p^{3-},S^{2-},Ar,K^{+} and Ca^{2+}, each one of the which contains 18 electrons are isoelectronic with it.

(iii) Ca^{2+} has 18 electrons. Therefore, the species p^{3-},S^{2-},Ar and K^{+}, each one of which also contain 18 electrons, are isoelectronic with it.

(iv) Rb^{+} has 36 electrons. Therefore, the species Br^{-}, or Sr^{2+}, each one of which also contain 36 electrons, are isoelectronic with it.

Sol.27 The number of electrons in these species are :

Atoms or ion	No. of electrons
O^{2-}	8 + 2 = 10
Na	= 9
F	= 11
Mg^{2+}	12 – 2 = 10
Cl^{-}	17 + 1 = 18
Al^{3+}	13 – 3 = 10
Ne	= 10

Thus, O^{2-}, Mg^{2+}, Al^{3+} and Ne (each one of which has 10 electrons) are isoelectronic species. Now nuclear charge on O^{2-} is + 8. Mg^{2+} is + 12, Al^{3+} is + 13 and Ne is + 10. Since the size of the species decreases as he nuclear charge increases, therefore, their size decreases in the order:

$O^{2-}>Ne>Mg^{2+}>Al^{3+}$.

Sol.28 (i) Mg and Al belong to the third period. Across a period, atomic radii decrease due to increased nuclear charge. Therefore, atomic size of Al is smaller than that of Mg.

(ii) Further, cations are smaller than their parent atoms. Therefore, Mg^{2+} is smaller than Mg and Al^{3+} is smaller than Al.

(iii) Mg^{2+} and Al^{3+} are isoelectronic ions. Among isoelectronic ions, higher the + ve charge, smaller the size. Therefore, ionic radius of Al^{3+} is smaller than that of Mg^{2+}.

From the above discussion, it follows that Mg has the largest while Al^{3+} has the smallest size.

Sol.29 (i) Due to higher effective nuclear charge, K^{+} has lower atomic size than K.

(ii) Due to lower effective nuclear charge, the size of Br^{-} is higher than that of Br.

(iii) O^{2-} or F^{-} are isoelectronic species. Since effective nuclear charge of O^{2-} is lower than that of F^{-}, therefore, O^{2-} has higher atomic size than F^{-}.

(iv) Li^{+} and Na^{+} both belong to group 1. because of greater number of shells (2 in case of Na^{+} and 1 in case of Li^{+}), Na^{+} has bigger atomic size than Li^{+}.

(v) As has four shells while P has three. Therefore, atomic size of As is higher than that of P.

(vi) Na^{+} and Mg^{2+} are isoelectronic ions. Therefore, due to lower effective nuclear charge ionic radius of Na^{+} is higher than that of Mg^{2+}.

Sol.30 (i) Size of a cation is always smaller while that of an anion is always bigger than the neutral atom, *i.e.*, I, I^+, I^-.

(ii) C and N lie in 2nd period while Si and P lie below them in the 3rd period. Since elements in the 3th period have higher atomic size than those in the 2nd period, therefore, atomic radii of Si and P are higher than those of C and N respectively. Since atomic radii decrease from left to right in period due to higher nuclear charge, therefore, C has higher atomic radius than N and Si has higher atomic radius than P. thus, the overall order of increasing atomic radii is : N < C < P < Si.

(iii) Among isoelectronic ions, the size of anions increases as the nuclear charge decreases : $F^- < O^{2-} < N^{3-}$. Since S belongs to third period while F, O, N all belong to the second period, therefore ionic radius of S^{2-} is bigger than those of F^-, O^{2-} and N^{3-} ions. Thus, the overall order of increasing ionic radii is : $F^- < O^{2-} < N^{3-} < S^{2-}$.

Objective Questions

1. According to modern periodic law the properties of elements repeat at regular intervals when the elements are arranged in order of :
(a) decreasing atomic number
(b) increasing atomic weight
(c) increasing atomic number
(d) decreasing atomic weights

2. If the aufau principle has not been followed, Ca ($Z = 20$) would have been placed in the:
(a) s-block (b) p-block
(c) d-block (d) f-block

3. Which of the following is the incorrect match ?
(a) $[Ar]3d^5\,4s^1 \rightarrow$ 4th period, 6th group
(b) $[Kr]\,4d^{10} \rightarrow$ 5th period, 12th group
(c) $[Rn]6d^2 7s^2 \rightarrow$ 7th period, 3th group
(d) $[Xe]\,4f^{14}\,5d^2\,5s^2 \rightarrow$ 6th period, 5th group

4. Which of the following sequence represents atomic number of only representative elements
(a) 55, 12, 48, 53 (b) 13, 33, 54, 83
(c) 3, 33, 53, 87 (d) 22, 33, 55, 66

5. Which of the following is not representative element :
(a) Tellurium (b) Tantalum
(c) Thallium (d) Astatine

6. Choose the correct order of ionic radius for the following species.
(a) $Cl^- > I^- > Te^{2-} > Ar^+$
(b) $Te^{2-} > I^- > Cl^- > Ar^+$
(c) $I^- > Te^{2-} > Cl^- > Ar^+$
(d) $I^- > Cl^- > Ar^+ > Te^{2-}$

7. Choose the correct order of radius for the following species.
(a) $Na^+ < Na < Na^-$
(b) $Na^- > Na^+ > Na$
(c) $Na < Na^- < Na^+$
(d) $Na > Na^+ > Na^-$

8. Element Hg has two oxidation states Hg^{+1} & Hg^{+2}. the right order of radii of these ions.
(a) $Hg^{+1} > Hg^{+2}$ (b) $Hg^{+2} > Hg^{+1}$
(c) $Hg^{+1} = Hg^{+2}$ (d) $Hg^{+2} \geq Hg^{+1}$

9. Highest size will be of
(a) Br^- (b) I
(c) I^- (d) I^+

10. If the ionic radii of K^+ and F^- are nearly the same (i.e., 1.34 Å), then the atomic radii of K and F respectively are :
(a) 1.34Å, 1.34 Å (b) 0.72 Å, 1.96 Å
(c) 1.96 Å, 0.72 Å (d) 1.96 Å, 1.32 Å

11. Ionization enthalpy of an atom is equal to :
(a) Electron gain enthalpy of the cation
(b) Electronegativity of the ion
(c) Ionization enthalpy of the cation
(d) None of these

12. The second ionization potential of element is invariable higher than first ionization potential because :
(a) The size of cation is smaller than its atom
(b) it is easier to remove electron from cation
(c) Ionization is an endothermic process
(d) None of these

13. The ionization energy will be higher when the electron is removed from :
(a) s-orbital (b) p-orbital
(c) d-orbital (d) f-orbital

14. Alkaline earth metals always form dipositive ions due to
(a) $IE_2 - IE_1 > 10$ eV (b) $IE_2 - IE_1 = 17$ eV
(c) $IE_2 - IE_1 < 10$ eV (d) None of these

15. Amongst the following elements, the highest ionization energy is :
(a) $[Ne]\,3s^2\,3p^1$ (b) $[Ne]\,3s^2\,3p^3$
(c) $[Ne]\,3s^2\,3p^2$ (d) $[Ar]\,3d^{10}\,4s^2\,4p^3$

16. The amount of energy released on the addition of an electron in outermost shell of an atom is called :
(a) Ionisation enthalpy
(b) Hydration enthalpy
(c) Electronegativity
(d) Electron gain enthalpy

17. Second electron gain enthalpy :
(a) is always negative
(b) is always positive
(c) can be positive or negative
(d) is always zero

18. The electron affinity of the members of oxygen family of the periodic table, follows the sequence
(a) $O > S > Se$ (b) $S > O > Se$
(c) $O < S > Se$ (d) $Se > O > S$

19. The process requires absorption of energy is
(a) $F \rightarrow F^-$ (b) $Cl \rightarrow Cl^-$
(c) $O^- \rightarrow O^{2-}$ (d) $H \rightarrow H^-$

20. Of the following elements, which possesses the

highest electron affinity?
(a) As (b) O
(c) S (d) Se

21. Which of the following species has the highest electronegativity ?
(a) C(sp hybridized) (b) N (sp^2 hybrdized)
(c) N (sp hybridized) (d) C (sp^3 hybridized)

22. In the compound M – O – H, the M – O bond will be broken if :
(a) Δ (E.N.) of M and O < Δ (E.N.) of O and H
(b) Δ (E.N.) of M and O = Δ (E.N.) of O and H
(c) Δ (E.N.) of M and O > Δ (E.N.) of O and H
(d) Cannot be predicated according Δ (E.N.) data

23. The outermost electronic configuration of most electronegative element is:
(a) $ns^2\ np$ (b) $ns^2\ np^4$
(c) $ns^2\ np^5$ (d) $ns^2\ np^6$

24. In the following which configuration of element has maximum electronegativity.
(a) $1s^2, 2s^2\ 2p^5$ (b) $1s^2, 2s^2\ 2p^6$
(c) $1s^2, 2s^2\ 2p^4$ (d) $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^3$

25. On the Pauling's electronegativity scale, which element is next to F .
(a) Cl (b) O
(c) Br (d) Ne

Answer Key

1. (a) 2. (c) 3. (d)
4. (b) 5. (b) 6. (b)
7. (a) 8. (a) 9. (c)
10. (c) 11. (a) 12. (a)
13. (a) 14. (c) 15. (b)
16. (d) 17. (b) 18. (c)
19. (c) 20. (c) 21. (c)
22. (c) 23. (c) 24. (a)
25. (b)

Examplar Questions

1. Consider the isoelectronic species, Na^+, Mg^{2+}, F^- and O^{2-}. The correct order of increasing length of their radii is _________.
(i) $F^- < O^{2-} < Mg^{2+} < Na^+$
(ii) $Mg^{2+} < Na^+ < F^- < O^{2-}$
(iii) $O^{2-} < F^- < Na^+ < Mg^{2+}$
(iv) $O^{2-} < F^- < Mg^{2+} < Na^+$

2. Which of the following is not an actinoid?
(i) Curium ($Z = 96$)
(ii) Californium ($Z = 98$)
(iii) Uranium ($Z = 92$)
(iv) Terbium ($Z = 65$)

3. The order of screening effect of electrons of s, p, d and f orbitals of a given shell of an atom on its outer shell electrons is:
(i) $s > p > d > f$
(ii) $f > d > p > s$
(iii) $p < d < s > f$
(iv) $f > p > s > d$

4. The first ionisation enthalpies of Na, Mg, Al and Si are in the order:
(i) Na < Mg > Al < Si
(ii) Na > Mg > Al > Si
(iii) Na < Mg < Al < Si
(iv) Na > Mg > Al < Si

5. The electronic configuration of gadolinium (Atomic number 64) is
(i) $[Xe]\,4f^3\,5d^5\,6s^2$
(ii) $[Xe]\,4f^7\,5d^2\,6s^1$
(iii) $[Xe]\,4f^7\,5d^1\,6s^2$
(iv) $[Xe]\,4f^8\,5d^6\,6s^2$

6. The statement that is **not** correct for periodic classification of elements is:
(i) The properties of elements are periodic function of their atomic numbers.
(ii) Non metallic elements are less in number than metallic elements.
(iii) For transition elements, the $3d$-orbitals are filled with electrons after $3p$-orbitals and before $4s$-orbitals.
(iv) The first ionisation enthalpies of elements generally increase with increase in atomic number as we go along a period.

7. Among halogens, the correct order of amount of energy released in electron gain (electron gain enthalpy) is:
(i) F > Cl > Br > I
(ii) F < Cl < Br < I
(iii) F < Cl > Br > I
(iv) F < Cl < Br < I

8. The period number in the long form of the periodic table is equal to
(i) magnetic quantum number of any element of the period.
(ii) atomic number of any element of the period.
(iii) maximum Principal quantum number of any element of the period.
(iv) maximum Azimuthal quantum number of any element of the period.

9. The elements in which electrons are progressively filled in $4f$-orbital are called
(i) actinoids
(ii) transition elements
(iii) lanthanoids
(iv) halogens

10. Which of the following is the correct order of size of the given species:
(i) $I > I^- > I^+$
(ii) $I^+ > I^- > I$
(iii) $I > I^+ > I^-$
(iv) $I^- > I > I^+$

11. The formation of the oxide ion, O^{2-} (g), from oxygen atom requires first an exothermic and then an endothermic step as shown below:

$$O(g) + e^- \longrightarrow O^-(g);\ \Delta H^\ominus = -141\,kJ\,mol^{-1}$$
$$O^-(g) + e^- \longrightarrow O^{2-}(g);\ \Delta H^\ominus = +780\,kJ\,mol^{-1}$$

Thus process of formation of O^{2-} in gas phase is unfavourable even though O^{2-} is isoelectronic with neon. It is due to the fact that,
(i) oxygen is more electronegative.

(ii) addition of electron in oxygen results in larger size of the ion.
(iii) electron repulsion outweighs the stability gained by achieving noble gas configuration.
(iv) O^- ion has comparatively smaller size than oxygen atom.

12. Comprehension given below is followed by some multiple choice questions. Each question has one correct option. Choose the correct option.

In the modern periodic table, elements are arranged in order of increasing atomic numbers which is related to the electronic configuration. Depending upon the type of orbitals receiving the last electron, the elements in the periodic table have been divided into four blocks, viz, *s*, *p*, *d* and *f*. The modern periodic table consists of 7 periods and 18 groups. Each period begins with the filling of a new energy shell. In accordance with the Arfbau principle, the seven periods (1 to 7) have 2, 8, 8, 18, 18, 32 and 32 elements respectively. The seventh period is still incomplete. To avoid the periodic table being too long, the two series of *f*-block elements, called lanthanoids and actinoids are placed at the bottom of the main body of the periodic table.

(a) The element with atomic number 57 belongs to
(i) *s*-block
(ii) *p*-block
(iii) *d*-block
(iv) *f*-block

(b) The last element of the *p*-block in 6th period is represented by the outermost electronic configuration.
(i) $7s^2\,7p^6$
(ii) $5f^{14}\,6d^{10}\,7s^2\,7p^0$
(i) $4f^{14}\,5d^{10}\,6s^2\,6p^6$
(iv) $4f^{14}\,5d^{10}\,6s^2\,6p^4$

(c) Which of the elements whose atomic numbers are given below, cannot be accommodated in the present set up of the long form of the periodic table?
(i) 107
(ii) 118
(iii) 126
(iv) 102

(d) The electronic configuration of the element which is just above the element with atomic number 43 in the same group is ________.
(i) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^2$
(ii) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^3\,4p^6$
(ii) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6\,4s^2$
(iv) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^7\,4s^2$

(e) The elements with atomic numbers 35, 53 and 85 are all ________.
(i) noble gases
(ii) halogens
(iii) heavy metals
(iv) light metals

13. Electronic configurations of four elements A, B, C and D are given below :
(A) $1s^2 2s^2 2p^6$
(B) $1s^2 2s^2 2p^4$
(C) $1s^2 2s^2 2p^6 3s^1$
(D) $1s^2 2s^2 2p^5$

Which of the following is the correct order of increasing tendency to gain electron :
(i) A < C < B < D
(ii) A < B < C < D
(iii) D < B < C < A
(iv) D < A < B < C

Examplar Solutions

1. (ii)
2. (iv)
3. (i)
4. (i)
5. (iii)
6. (iii)
7. (iii)
8. (iii)
9. (iii)
10. (iv)
11. (iii)
12.(a) (iii),
(b) (iii),
(c) (iii),
(d) (i),
(e) (ii)
13. (i)

JEE and NEET Previous Year

Jee Previous Year

Q.1. In general, the properties that decrease and increase down a group in the periodic table, respectively are **[2019 Mains]**

(a) electronegativity and atomic radius
(b) electronegativity and electron gain enthalpy
(c) electron gain enthalphy and electronegativity
(d) atomic radius and electronegativity

Q.2. The option(s) with only amphoteric oxides is(are) **[2017 Adv.]**

(a) NO, B_2O_3, PbO, SnO_2
(b) Cr_2O_3, CrO, SnO, PbO
(c) Cr_2O_3, BeO, SnO, SnO_2
(d) ZnO, Al_2O_3, PbO, PbO_2

Q.3. The ionic radii (in Å) of N^{3-}, O^{2-} and F^- respectively are **[2015 Mains]**

(a) 1.36, 1.40 and 1.71
(b) 1.36, 1.71 and 1.40
(c) 1.71, 1.40 and 1.36
(d) 1.71, 1.36 and 1.40

Q.4. Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy? **[2015 Mains]**

(a) $CaSO_4$ (b) $BeSO_4$
(c) $BaSO_4$ (d) $SrSO_4$

Q.5. Which among the following is the most reactive? **[2015 Mains]**

(a) Cl_2 (b) Br_2
(c) I_2 (d) ICI

Assertion and Reason
Read the following questions and answer as per the direction given below:

(a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I.
(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.
(c) Statement I is true; Statement II is false
(d) Statement I is false; Statement II is true.

Q.6. Statement I Nitrogen and oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen.
Statement II The reaction between nitrogen and oxygen requires high temperature. **[2015 Mains]**

Q.7. Which one has the highest boiling point? **[2014 Mains]**

(a) He (b) Ne
(c) Kr (d) Xe

Q.8. Which of the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se and Ar? **[2013 Mains]**

(a) $Ca < S < Ba < Se < Ar$
(b) $S < Se < Ca < Ba < Ar$
(c) $Ba < Ca < Se < S < Ar$
(d) $Ca < Ba < S < Se < Ar$

Q.9. Identify the least stable ion amongst the following. **[2002 Mains]**

(a) Li^+ (b) Be^-
(c) B^- (d) C^-

Q.10. The set representing the correct order of first ionization potential is **[2001]**

(a) $K > Na > Li$
(b) $Be > Mg > Ca$
(c) $B > C > N$
(d) $Ge > Si > C$

NEET Previous Year

Q.11. Which of the following orders of ionic radii is correctly represented ? **[2014]**

(a) $H^- > H^+ > H$ (b) $Na^+ > F^- > O^{2-}$
(c) $F^- > O^{2-} > Na^+$ (d) $Al^{3+} > Mg^{2+} > N^{3-}$

Q.12. Identify the wrong statement in the following. **[2012]**

(a) Amongst isoelectronic species, smaller the positive charge on the cation, smaller is the ionic radius
(b) Amongst isoelectronic species, grater the negative charge on the anion, larger is the ionic radius
(c) Atomic radius of the elements increases as one moves down the first group of the periodic table
(d) Atomic radius of the elements decreases as one moves across from left to right in the 2nd period of the periodic table

Q.13. The correct order of the decreasing ionic radii among the following isoelectronic species is **[2010]**

(a) $Ca^{2+} > K^+ > S^{2-} > Cl^-$
(b) $Cl^- > S^{2-} > Ca^{2+} > K^+$
(c) $S^{2-} > Cl^- > K^+ > Ca^{2+}$
(d) $K^+ > Ca^{2+} > Cl^- > S^{2-}$

Q.14. Amongst the elements with following electronic configurations, which one may have the highest ionisation energy? **[2009]**
(a) $[Ne]3s^23p^3$ (b) $[Ne]3s^23p^2$
(c) $[Ne]3d^{10}4s^24p^3$ (d) $[Ne]3s^23p^1$

Q.15. Which one of the elements with the following outer orbital configurations may exhibit the largest number of oxidation states? **[2009]**
(a) $3d^3, 4s^2$ (b) $3d^5, 4s^1$
(c) $3d^5, 4s^2$ (d) $3d^2, 4s^2$

Q.16. Identify the correct order of the size of the following. **[2007]**
(a) $Ca^{2+} < K^+ < Ar < S^2 < Cl^-$
(b) $Ca^{2+} < K^+ < Ar < Cl^- < S^{2-}$
(c) $Ar < Ca^{2+} < K^+ < Cl^- < S^{2-}$
(d) $Ca^{2+} < Ar < K^+ < Cl^- < S^{2-}$

Q.17. Which one of the following orders is not in accordance with the property sated against it? **[2006]**
(a) $F_2 > CI_2 > Br_2 > I_2$ Oxidising power
(b) HI > HBr > HCl > HF Acidic property in water
(c) $F_2 > CI_2 > Br_2 > I_2$ Electronegativity
(d) $F_2 > CI_2 > Br_2 > I_2$ Bond dissociation energy

Q.18. Ionic radii are **[2004]**

(a) Inversely proportional to effective nuclear charge
(b) inversely proportional to square of effective nuclear charge
(c) directly proportional to effective nuclear charge
(d) directly proportional to square of effective nuclear charge

Q.19. The ions O^{2-}, F^-, Na^+Mg^{2+} and Al^{3+} are isoelectronic. Their ionic radii show **[2003]**
(a) an increase from O^{2-} to F^- and then decrease from Na^+ to Al^{3+}
(b) a decrease from O^{2-} to F^- then increase from Na^+ to Al^{3+}
(c) a significant increase from O^{2-} to Al^{3+}
(d) a significant decrease from O^{2-} to Al^{3+}

Q.20. which of the following order is wrong? **[2002]**
(a) $NH_3 < PH_3 < AsH_3$ - Acidic
(b) Li < Be < B < C- 1st Ionisation potential
(c) $Al_2O_3 < MgO < Na_2O < K_2O$ - basic
(d) $Li^+ < Na^+ < K^+ < Cs^+$ - Ionic radius

Q.21. Which one of the following arrangements does not truly represent the property indicated against it? **[2000]**
(a) $Br_2 < Cl_2 < F_2$ Oxidising power
(b) $Br_2 < Cl_2 < F_2$ Electronegativity
(c) $Br_2 < F_2 < Cl_2$ Electron affinity
(d) $Br_2 < Cl_2 < F_2$ Bond energy

Answer Key

1. (a)
2. (a,b)
3. (c)
4. (b)
5. (d)
6. (a)
7. (d)
8. (c)
9. (b)
10. (b)
11. ()
12. (a)
13. (c)
14. (a)
15. (c)
16. (b)
17. (d)
18. (a)
19. (d)
20. (a)
21. (d)

4 CHEMICAL BONDING

CHEMICAL BOND

Chemical Bond is a force of attraction which takes place between atom ions and molecules.
Various chemical bonds can be categorized into two types :

1. Bonds which constitute molecules or formula units. These are :

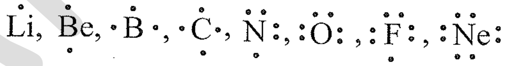
- **(i)** Ionic bonds
- **(ii)** Covalent bonds
- **(iii)** Co-ordinate or dative bonds.

2. Bonds which hold various particles in solid or liquid state of the substances.
These are also called Interparticle forces. These are :

- **(i)** Metallic bonds
- **(ii)** Dipole-dipole forces
- **(iii)** Vander Wall forces
- **(iv)** Hydrogen bonds.

(I) CLASSICAL APPROACH KOSSEL-LEWIS APPROACH (ELECTRONIC THEORY OF VALENCY)

Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds.
In the case of sodium and chlorine, this can happen by the transfer of an electron from sodium to chlorine thereby giving the Na^+ and Cl^- ions.
In the case of other molecules like Cl_2, H_2, F_2, etc., the bond is formed by the sharing of a pair of electrons between the atoms. In the process each atom attains a **stable outer octet of electrons**.
<u>**LEWIS SYMBOLS:**</u> G.N. Lewis, an American chemist introduced simple notations to represent valence electrons in an atom. These notations are called **Lewis symbols**. For example, the Lewis symbols for the elements of second period are as under:



$$\dot{\text{Li}},\ \overset{\cdot}{\underset{\cdot}{\text{Be}}},\ \cdot\dot{\text{B}}\cdot,\ \cdot\overset{\cdot}{\underset{\cdot}{\text{C}}}\cdot,\ \overset{\cdot}{\underset{\cdot}{\text{N}}}:,\ :\ddot{\text{O}}:,\ :\overset{\cdot\cdot}{\underset{\cdot}{\text{F}}}:,\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Ne}}}:$$

SIGNIFICANCE OF LEWIS SYMBOLS :
The number of dots around the symbol represents the number of valence electrons.
This number of valence electrons helps to calculate the common or **group valence** of the element.
The group valence of the elements is generally either equal to the number of dots in Lewis symbols or 8 minus the number of dots or valence electrons.

OCTET RULE

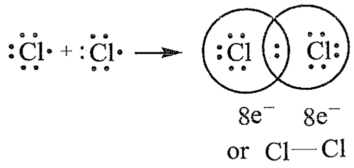
Kössel and Lewis in 1916 developed an important theory of chemical combination between atoms known as **electronic theory of chemical bonding.**
According to this, **atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells. This is known as octet rule**

COVALENT BOND

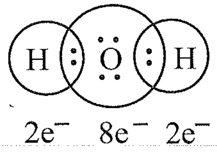
The bond formed by the sharing of valence electrons in between two atoms to have an octet in their valence shells is called **covalent bond**

The Lewis-Langmuir theory can be understood by considering the formation of the chlorine molecule, Cl_2.

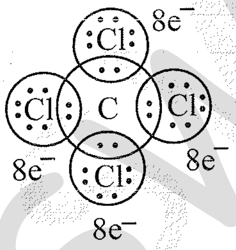
SINGLE BOND



Covalent bond between two Cl atoms

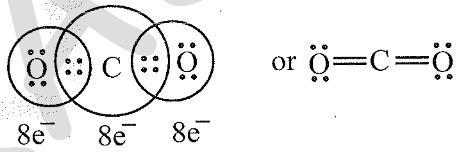


H atoms attain a duplet of electrons and O, the octet

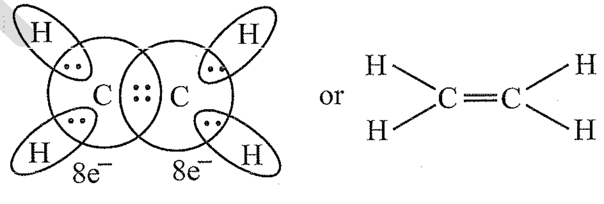


Each of four Cl atoms along with the C atom attains octet of electrons

DOUBLE BOND

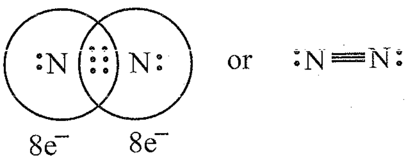


Double bonds in CO_2 molecule

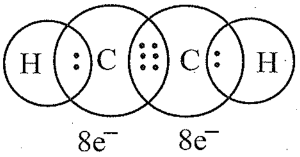


C_2H_4 molecule

TRIPLE BOND



N_2 molecule

 or $H-C\equiv C-H$

C_2H_2 molecule

Limitation of the Octet Rule:

The octet rule, though useful is not universal. It is quit useful for understanding the structure of most of the organic compounds.

There are three types of exception to the octet rule.

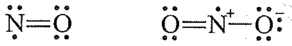
1. The Incomplete Octet of the central atom:

In some compounds the number of electrons surrounding the central atom is less than eight.

Eg: $Li:Cl$ $H:Be:H$ $Cl:\overset{Cl}{\ddot{B}}:Cl$

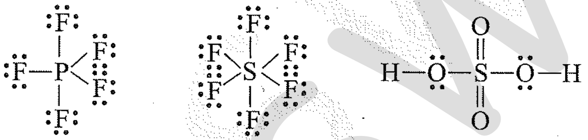
2. Odd Electron Molecules:

In molecules with an odd number of electrons like nitric oxide NO and nitrogen dioxide NO_2.



3. The Expanded Octet:

Element in and beyond the third period of the periodic table have apart from 3s and 3p orbital. Bd orbitals also available for bonding in which the number of electrons more than eight.



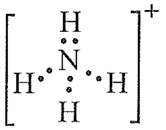
Other Drawbacks:

- It is clear that octet rule is based upon the chemical inertness of noble gases. Xe, Kr also combine with oxygen and flurine to form a number of compounds like XeF_2, KrF_2, $XeOF_2$ etc.
- This theory does not account for the shape of molecules.
- It does nor explain the relative stability of the molecules being totally silent about the energy of a molecule.

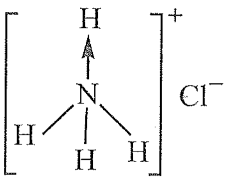
DATIVE BOND

It is a special case of covalent bond. It is formed by mutual sharing of electrons between the two atoms but the shared pair of electrons is contributed only by one of the two atoms. The other atom simply participate in sharing the atom which donates an electron pair for sharing is called donor and it must have already completed its octet.

Examples :

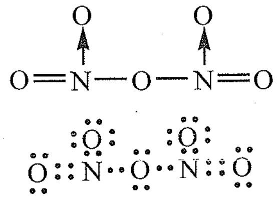


1. NH_4^+

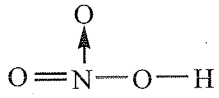


Bonds in Ammonium chloride are covalent bond, co-ordinate bond and ionic bond.

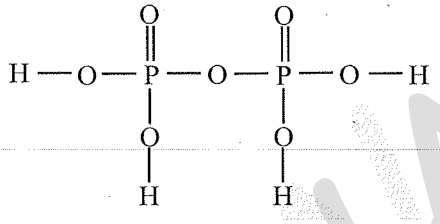
2. N_2O_5



3. HNO_3



4. $H_4P_2O_7$



ELECTROVALNT BOND

The electrostatic force of attraction holding the oppositely charged ions is called electrovalent bond or ionic bond.

It was proposed by Kossel.

Necessary conditions for stable ionic bond:

1. **IONISATION ENERGY** of cation forming element should be low.
2. **ELECTRON AFFINITY** of anion forming element should be high.
3. Greater **electronegativity** difference.
4. **Lattice energy** should be high.

FORMAL CHARGE

Lewis dot structures in general do not represent the actual shapes of the molecules. In case of polyatomic ion, the net charge μ possessed by the ion as a whole and not by a particular atom.

$$\left[\begin{array}{l}\text{Formal charge}\\ \text{of an atom in}\\ \text{a Lewis structure}\end{array}\right]=\left[\begin{array}{l}\text{Total No. of valence}\\ \text{electron in free atom}\end{array}\right]-\left[\begin{array}{l}\text{Total No. of}\\ \text{bon-bonding}\\ \text{e}^-\text{(loanpair)}\end{array}\right]-y_2\left[\begin{array}{l}\text{Total number of}\\ \text{bonding (shared e}^-\text{)}\end{array}\right]$$

Generaly the lowest energy structure in the one with the smallest formed charges on the atoms. The formal charge is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighbouring atom.

LATTICE ENTHLPY (LE)

The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions.

For example, the lattice enthalpy of $NaCl$ is $788\,kJ\,mol^{-1}$. This means that $788\,kJ$ of energy is required to separate one mole of solid $NaCl$ into one mole of $Na^+(g)$ and one mole of $Cl^-(g)$ to an infinite distance.

Lattice energy depends on :

1. **Size of the ions** (smaller)
2. **Magnitude of charge on them.** (higher)

CHARACTERISTICS OF IONIC COMPOUNDS

1. They have **high melting and boiling points** due to strong attractive forces between the ions.
2. Due to fixed positions occupied by the ions in solid state, they do not conduct electricity. However, they become **good conductors in their molten state or in their dissolved state.**
3. **They are soluble in polar solvent with high dielectric constant such as water.**
   On dissolution in water ionic compounds undergo hydration and energy released in this process is called **hydration energy.**

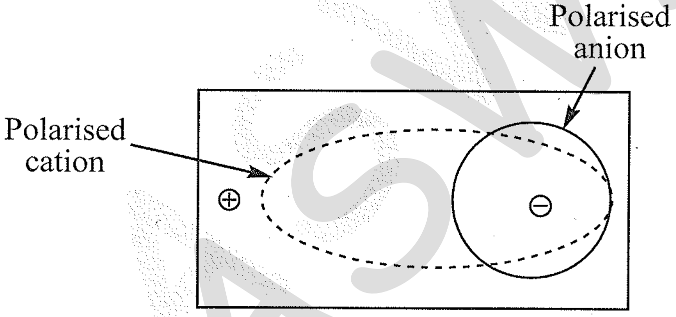
FAJAN'S RULES

NO BOND IS 100% IONIC IN NATURE

(a) In the ionic bond, the cation tend to polarize the electron cloud of the anion by pulling electron density towards itself. This causes development of covalent character in ionic bond because the electron density gets localized in between the nuclei.

(b) The tendency of cation to bring about the polarization of anion is expressed as its **polarizing power.**

(c) The ability of anion to undergo polarization is called its **polarisability.**
The polarizing power of cation and polarisability of anion are decided on the basis of Fajan Rules as given below :



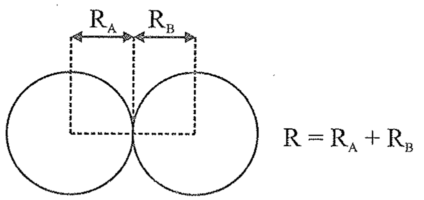
IONIC POTENTIAL. It is a measure of the polarizing power of a cation and is defined as the ratio of charge to the radius of the cation.

Ionic potential = $\Psi = \dfrac{\text{Charge on cation}}{\text{Radius of cation}}$

Large ionic potentials are associated with strong polarizing effects *i.e.,* increased covalency.

BOND PARAMETERS

1. **BOND LENGTH :** Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule.

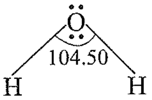


2. **BOND ENTHALPY (Bond Energy) :** The amount of energy required to break one mole of bonds of a particular type so as to separate them into gaseous atoms is called bond dissociation enthalpy or simply bond enthalpy.

$$H_2 \longrightarrow H(g) + H(g) \qquad \Delta H^\circ = 435.8 \text{KJ mol}^{-1}$$

3. **BOND ANGLE :** Angle between two adjacent bonds at an atom in a molecule made up of three or more

atoms is known as the bond angle.



4. **BOND ORDER :** In the Lewis description of covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule.

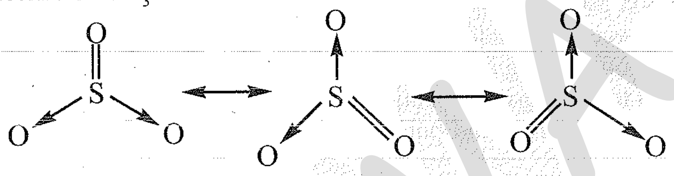
$\text{B.O.} = \frac{1}{2}(N_b - N_a)$ where N_b = NO. of bonding orbitals and N_a = No. of antibonding orbital

RESONANCE

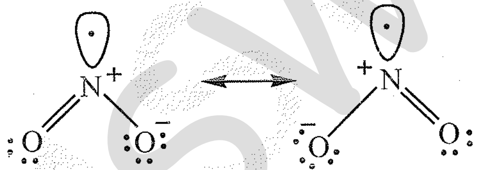
When a molecule is represented by more than one electronic arrangement, none of which is able to explain the observed characteristic of the molecule. Then, the actual molecular structure is intermediate of various electronic arrangements and is known as **Resonance Hybrid.**

The various electronic arrangements are called **resonating structure** or **cannoning structure** or **contributing structures.**

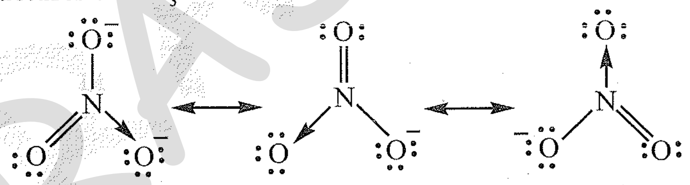
(i) Resonance structure of SO_3



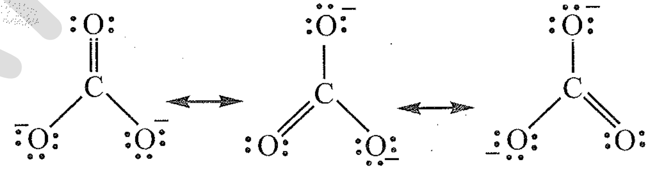
(ii) Resonance structures of NO_2



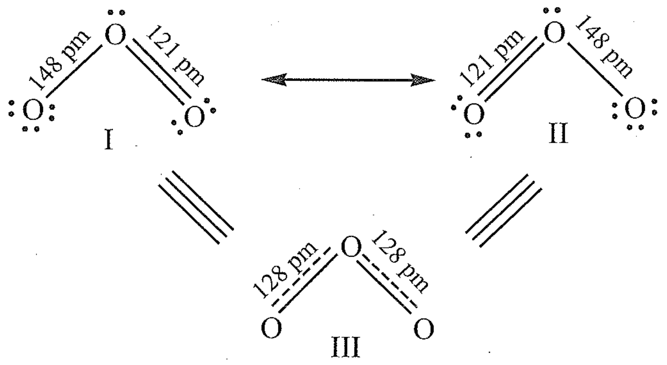
(iii) Resonance structures of NO_3^- ion



(iv) Resonance structures of CO_3^{2-} ion



(v) Resonance structures of ozone



DIPOLE MOMENT (μ)

It is defined as the product of the magnitude of charge on any of the atom and the distance between the atoms. It is represented by μ.

It is a vector quantity .

Mathematically $\mu = q \times d$

Where $q =$ charge on any of the atom

$d =$ distance between the positive and negative centre

Units of dipole moment are : DEBYE (denoted by D);

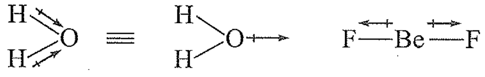
$1D = 10^{-18}$ esu-cm.

$1D = 3.33564 \times 10^{-30}$ Cm

where 'C' is coulomb and 'm' is meter.

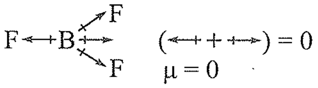
POLAR AND NON-POLAR MOLECULES

1. Molecules with $\mu = 0$ are **non-polar** while those with $\mu \neq 0$ are **polar.**
2. Higher the dipole moment of the molecule, greater is its polarity. For example, H_2O (μ=1.84 D) is more polar than HCl (μ=1.03D) .
3. In diatomic molecule, the dipole moment of the bond is same as the dipole moment of the molecule.
4. In polyatomic molecule, the dipole moment, μ of molecules is the resultant of various bond moments. For example in H_2O molecule, which has a bent structure, the two $O-H$ bonds are oriented at an angle of 104.50 . Net dipole moment of $6.17 \times 10^{-30}\ Cm$ ($1D = 3.33564 \times 10^{-30}\ Cm$) is the resultant of the dipole moments of two $O-H$ bonds.



(a) Bond dipole

(b) Resultant Dipole moment



Net Dipole moment, $\mu = 1.85D$

$= 1.85 \times 3.33564 \times 10^{-30}\ Cm = 6.17 \times 10^{-30}\ Cm$

THE VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

This theory provides a simple procedure to predict the shapes of covalent molecules.
Sidgwick and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms.
It was further developed and redefined by Nyholm and Gillespie (1957).

The Main Postulates of VSEPR Theory Are As Follows:

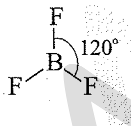
1. The shape of a molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) around the central atom.
2. Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
3. These pairs of electrons tend to occupy such positions in space that minimize repulsion and thus maximise distance between them.
4. The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
5. A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
6. Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

The Repulsive Interaction of Electron Pairs Decreases in the Order:

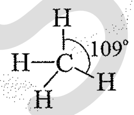
Lone pair – Lone pair > Lone pair – Bond pair > Bond pair – Bond pair

1. Molecules in which the central molecules in which the central atom has one or more lone pairs.
2. AB_2, AB_3, AB_4, AB_5 and AB_6 the arrangement of electron pairs and the B, atoms arround the central atom A are:- linear, trigonal planar, ttrahedral, trigonal – bipyramidal and octahedral.

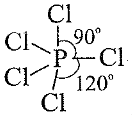
BF_3—(AB_3) CH_4—(AB_4) and PCl_5—(AB_5)



BF_3



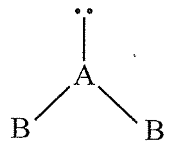
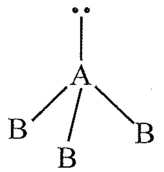
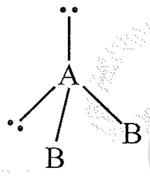
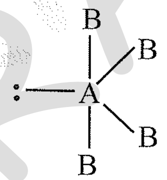
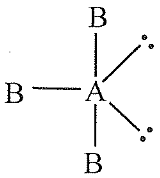
CH_4

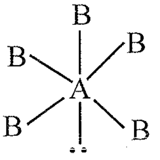
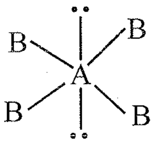


PCl_5

The shapes of molecules in which central atom has no lone pair.

SHAPE (GEOMETRY) OF SOME SIMPLE MOLECULES/IONS WITH CENTRAL IONS HAVING ONE OR MORE LONE PAIRS OF ELECTRONS (E)

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons pairs	Shape	Examples	Reason for the shape acquired
AB_2E	2	1	 Trigonal planar	Bent	SO_3, O_2	Theoretically the shape should have been triangular planar but actually it is found to be bent or v-shaped. The reason being the lone pair-bond pair repulsion is much more as compared to the bond pair-bond pair repulsion. So the angle is reduced to 119.5° from 120°.
AB_3E	3	1	 Tetrahedral	Trogonal pyramidal	NH_3	Had there been a bp in place of lp the shape would have been tetrahedral but one lone pair is present and due to the repulsion between lp-bp (which is more than bp-bp repulsion) the angle between bond pairs is reduced to 107° from 109.5°.
AB_2E_2	2	2	 Tetrahedral	Bent	H_2O	The shape should have been tetrahedral if there were all bp but two lp are present so the shape is distorted tetrahedral or angular. The reason is lp-lp repulsion is more than lp-bp repulsion which is more than bp-bp repulsion. Thus, the angle is reduced to 104.5° from 109.5°.
AB_4E	4	1	 Trigonal bi-pyramidal	See saw	SF_4	The lp is in an equatorial position, and there are two lp-bp repulsions. Hence, arrangement is more stable. The shape shown in fig. is described as a distorted tetrahedron, a folded square or (More stable) a see-saw.
AB_3E_2	3	2	 Trigonal bi-pyramidal	T-shape	ClF_3	The lp are at equatorial position so there are less lp-bp repulsions as compared to others in which the lp are at axial positions. So T-shaped structure is most stable.

AB_5E	5	1	 Octahedral	Square pyrimad	BrF_5	
AB_4E_2	4	2	 Octahedral	Square planar	XeF_4	

VALENCE BOND THEORY

Valence bond theory was introduced by Heitler and London (1927) and developed further by Pauling and others. A discussion of the valence bond theory is based on the knowledge of **atomic orbitals, electronic configurations of elements, the overlap criteria of atomic orbitals, the hybridization of atomic orbitals and the principles of variation and superposition.**

OVERLAPPING OF ATOMIC ORBITALS

When two atoms come close to each other, there is overlapping of atomic orbitals. This overlap may be positive, negative or zero depending upon the properties of overlapping of atomic orbitals. The various arrangements of *s* and *p* orbitals resulting in positive, negative and zero overlap .

Types of Overlapping and Nature of Covalent Bonds

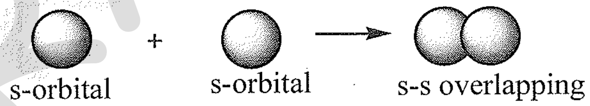
The covalent bond may be classified into two types depending upon the types of overlapping:

(i) Sigma (σ) bond

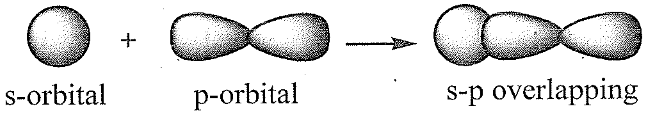
(ii) pi (π) bond

(i) **Sigma (σ) bond :** This type of covalent bond is formed by the end to end (hand-on) overlap of bonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

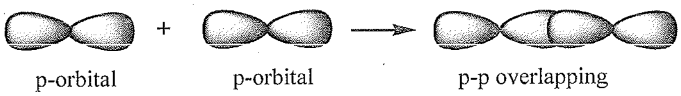
- ***s-s* overlapping :** In this case, there is overlap of two half filled *s*-orbitals along the internuclear axis as shown below :



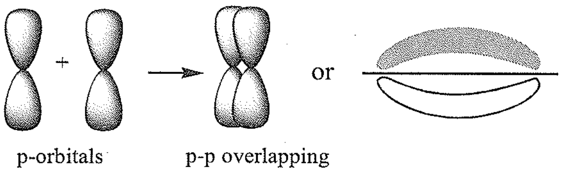
- ***s-p* overlapping :** This type of overlap occurs between half filled *s* -orbitals of one atom and half filled *p* -orbitals of another atom.



- ***p–p* overlapping :** This type of overlap takes place between half filled *p* -orbitals of the two approaching atoms.



(ii) **pi (π) bond :** In the formation of pi bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.



DIFFERENCES BETWEEN SIGMA AND PI BOND

S.No.	Sigma (σ) bond	Pi (π) bond
1	It is formed due to axial overlap of the two orbitals.	This bond is formed by this lateral (side ways) overlap of two p-orbitals.
2	There can be only one sigma bond between atoms.	There can be more than one π-bond between the two atoms.
3	The electron density is maximum and cylindrically symmetrical about the bond axis.	The electron density is high along a direction at right angle to the bond axis.
4	The bonding is relatively strong.	The bonding due to a π-bond is weak.
5	Free rotation of atoms about sigma bond is possible.	Free rotation about a pi bond is not possible.
6	It can be formed in dependently, i.e. there can be a sigma bond without having a π-bond in any molecule.	The π-bond is formed only after sigma bond has been formed.

HYBRIDISATION

Pauling introduced the concept of hybridisation. According to him the **atomic orbitals combine to form new set of equivalent orbitals known as hybrid orbitals**. Unlike pure 2orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as **hybridization** which can be **defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape.**

Salient Features of Hybridisation

The main features of hybridisation are as under :

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridization indicates the geometry of the molecules.

Important Condition for Hybridisation.

1. The orbitals present in the valence shell of the atom are hybridised.
2. The orbitals undergoing hybridisation should have almost equal energy.
3. Promotion of electron is not essential condition prior to hybridisation.
4. It is not necessary that any half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

Types of Hybridisation

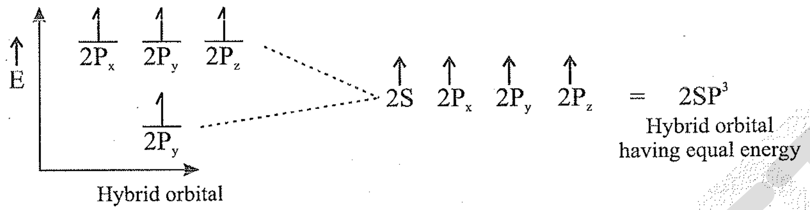
1. SP^3 Hybridisation:

when one of the 'S' orbital combines with '3' P-orbital of same shell result to form SP^3 hybrid orbital.

$$\underbrace{2S + 2P_x + 2P_y + 2P_z}_{\text{Atomic orbital}} = \underbrace{2SP^3}_{\text{Hybrid orbital}}$$

- All the four SP^3 hybrid orbital are completely equalent and symetrical.
- These orbital are directed towards corner of regular tetrahedron.
- Angle between each hybrid orbital is always 109.5° or 109.5° 28'

Graphical Explanation:



Number of atomic orbital = Number of Hybrid orbital
Total number of atomic orbital = 4
Energy of all the mixed orbital is identical
$4\ E\ 2SP^3 = E\ 2S + E\ 2P^3$

$$E\ 2SP^3 = \frac{E\ 2S + E\ 2P^3}{4}$$

Order of energy for SP^3 hybridisation and size.
$2P > 2SP^3 > 2S$

Type	No. of B.P.	No. of e^- pair	No. of L.P.	Bond Angle	Geometry	Eg
AB_4	4	4	0	109.5°	tetrahedral	CH_4
AB_3L	3	4	1	107°	pyramidal	NH_3
AB_2L_2	2	4	2	105°	V-shaped	H_2S

Note:

An SP^3 Hybridisation electronegativity power of SP^3 hybrid lobes than SP^2 and SP.

Bond angle $= \cos\theta = \left(-\frac{1}{m}\right)$

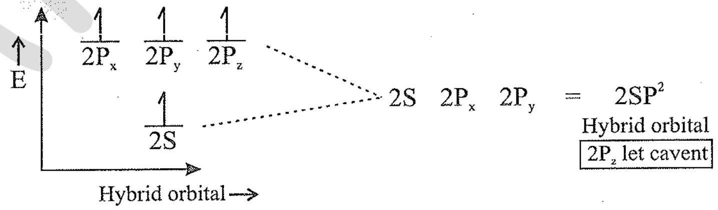
Where m = participation of 'P' orbital.

2. SP^2 Hybridisation:

When one of the 'S' orbital combines with any two of the 'P' orbital to form SP^2 hybridisation.

- In SP^2 hybridisation one of the P orbital remain left.
- The total No. of hybrid orbital in SP^2 hybridisation is 3.

Graphical Explanation:



- Total No. of atomic orbital = Total No. of hybrid orbital = 3
- Energy of all the hybrid orbital are equalent.

  $3E\ 2SP^2 = E\ (2S) + E\ 2P^2$

  $$E\ 2SP^2 = \frac{E\ (2S) + E\ (2P^2)}{3}$$

- Order of energy and its size

  $2P > 2SP^2 > 2S$

- **Bond Angle:**

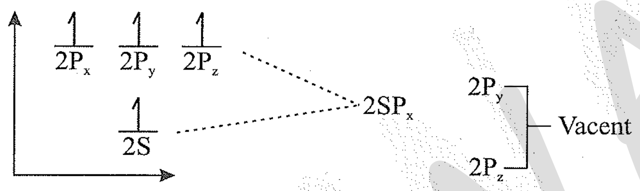
$\cos\theta = -\frac{1}{m} \quad \theta = 120^\circ$

Type	No. of Bond Pair	No. of e^- Pair	NO. of lone pair	B Angle	Geometry	Example
AB_3	3	3	0	120°	trangular planner	C_2H_4, Co_3^{2-}, BH_3
AB_2L	2	2	1	less than 125°	V-shaped	So_2, No_2, $SnCl_2$

3. SP-Hybridisation

- When one of the 'S' orbitalcombines with only any one of the 'P' orbital result to form SP Hybrid orbital and known as 'SP' hybridisation.
- In SP hybridisation, there are only two SP hybrid lobe which are completely equalent and symitrical.
- Energy of 'SP' hybrid orbital is more than 'S' orbital but less than 'P' orbital.

Graphical Explanation:



- No. of atomic orbital = No. of hybrid orbital = 2
- Energy of all hybrid orbital is identical.

$2E\ 2SP = E\ 2S + E\ 2P_x$

$E\ 2SP = \frac{E\ 2S + E\ 2P_x}{2}$

Order of energy and size

$2P > 2SP > 2S$

- Bond Angle:

$\cos\theta = \left(-\frac{1}{m}\right) = 180^\circ$

Concept of Bond length, Bond strength, Reactivity between SP^2, SP^3 and SP Hybridisation:

Order of Rigidity = Single Bond < Double Bond < Triple Bond

Order of Bond Strength = $C-C \quad C=C \quad C\equiv C$

Reactivity order = $C\equiv C > C=C > C-C$

Order of Bond length = $C-C > C=C > C\equiv C$

$1.5\,\text{Å} \quad 1.34\,\text{Å} \quad 1.20\,\text{Å}$

Note:

- Spherical nature increases ∝ % of S character.
- Electronegativity Increases ∝ % of 'S' character.
- Acidic order also increases ∝ % of 'S' character.
- Reactivity increases ∝ % of 'S' character.

Hybridisation of elemental involving d-Orbital:

sp^3d:

- When one of the 'S' orbital combines with all the three 'P' orbital and only one 'd' orbital result to form SP^3d hybrid orbital.
- The energy of all these atomic orbital should be identical.

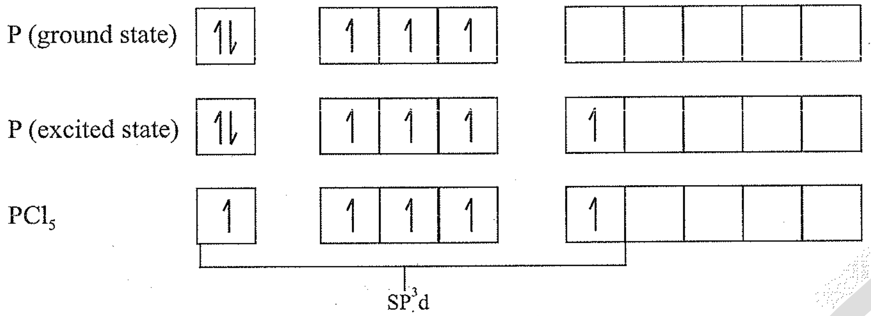
$3S + 3P_x + 3P_y + 3P_z + 3d_{z^2} = 5\ SP^3d$

- Among the five 'd' orbital only d_{z^2} atomic orbital has only two lobe.
- It shows trigonal bipyramidal geometry

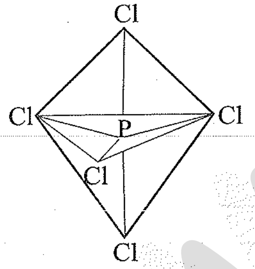
- It's bond angle is 120°, 90°.

Formation of PCl_5:

The ground state and excited state outer electronic configuration of phosphorus (z = 15)



SP^{3}d hybrid orbitals filled by electron pairs donated by five Cl atom.



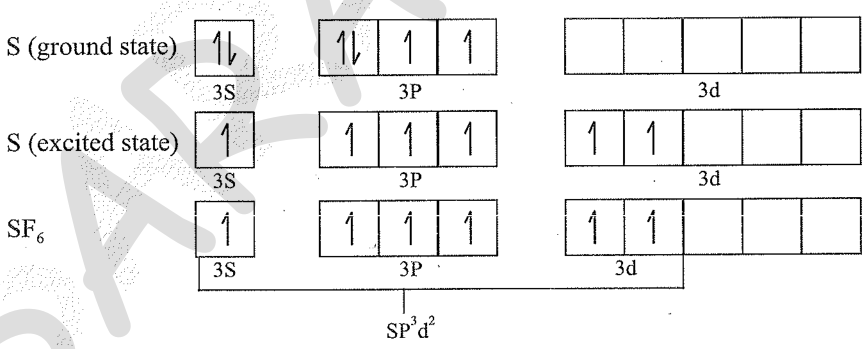
(Trigonal bipyramidal geometry)

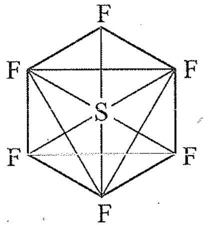
SP^3d^2:

- When one of 'S' orbital at least 3S, combines with all the three 'P' orbital (at least 3P) and also combine with two of the 'd' orbital to form 6SP^{3}d^2 hybrid orbital.
- Among the fire d orbital in SP3d2 hybridisation only d_{z^2} and $d_{x^2y^2}$ atomic orbital takes part in hybridisation to explain the real geometry of molecule.

Formation of SF_6 (SP^3d^2-Hybridisation):

In SF_6 the central sulphur atom has ground state outer electronic configuration $3S^2 3P^4$.





Octahedral geometry of SF_6 molecule

Shapes of Molecule	Hybridisation	Atomic Orbital	Example
Square Planner	dsp^2	d+S+P(2)	$[P+(Cl)_4^-]^{2-}$
Trigonal bipyramidal	SP^3d	S+P(3)+d	PF_5, PCl_5
Square pyramidal	SP^3d^2	S+P(3)+d(2)	BrF_5
Octahedral	SP^3d^2, d^2SP^3	S+P(3)+d(2), d(2)+S+P(3)	SF_6, $[CrF_6]^{3-}$

MOLECULAR ORBITAL THEORY

Molecular orbital (MO) theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features of this theory are :

(i) The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.

(ii) The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.

(iii) While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus, an atomic orbital is monocentric while a molecular orbital is polycentric.

(iv) The number of molecular orbital formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as **bonding molecular orbital** while the other is called **antibonding molecular orbital.**

(v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.

(vi) Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital.

(vii) The molecular orbitals like atomic orbital are filled accordance with the Pauli's exclusion principle and Hund's rule.

Types of Molecular Orbitals

Molecular orbitals of diatomic molecules are designated as σ (sigma), π (pi), *d* (delta), etc. In this nomenclature, the **sigma** (s) **molecular orbitals are symmetrical around the bond-axis while pi** (p) **molecular orbitals are not symmetrical.**

For example, the linear combination of 1s orbitals centered on two nuclei produces two molecular orbitals which are symmetrical around the bond-axis. Such molecular orbitals are of the s type and are designated as $\sigma 1s$ and $\sigma^* 1s$.

If internuclear axis is taken to be in the z-direction, it can be seen that a linear combination of $2p_z$ **orbitals of two atoms also produces two sigma molecular orbitals designated as** $\sigma 2p_Z$ **and** $\sigma^* 2p_Z$

QUESTIONS

NCERT EXERCISE & EXAMPLES

Formation of a Chemical Bond

1. Explain the formation of a chemical bond.

2. Write the favourable factors for the formation of ionic bond.

3. Arrange the bonds in order of increasing ionic character in the molecules : LiF, K_2O, N_2, SO_2 and ClF_3.

Polar Covalent Bond

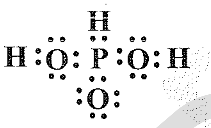
4. Explain with the help of a suitable example polar covalent bond.

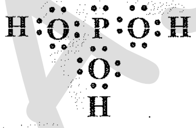
Lewis Structures

5. Write the Lewis dot structure of CO molecule.

6. Write the Lewis structure of the nitrite ion, NO_2^-.

7. H_3PO_3 can be represented by structures 1 and 2 shown below. Can these two structures taken as the canonical forms of the resonance hybrid representing H_3PO_3? If not, give reasons for the same.


(1)


(2)

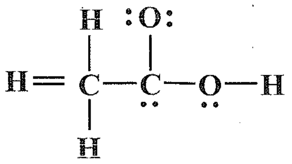
8. Write Lewis dot symbols for atoms of the following elements : Mg, Na, B, O, N, Br.

9. Write Lewis symbols for the following atoms and ions : S and S^{2-}, Al and Al^{3+}; H and H^-.

10. Draw the Lewis structures for the following molecules and ions : $H_2S, SiCl_4, BeF_2, CO_3^{2-}, HCOOH$

11. Use Lewis symbols to show electron transfer between the following atoms to form cations and anions : (a) K and S (b) Ca and O (c) Al and N.

12. The skeletal structure of CH_3COOH as shown below is correct but some of the bonds are shown incorrectly. Write the correct Lewis structure for acetic acid



Octet Rule

13. Define octet rule. Write its significance and limitations.

Resonance

14. Explain the important aspects of resonance with reference to the CO_3^{2-} ion.

15. Write the resonance structures for SO_3, NO_2 and NO_3^-.

Hybridisation

16. Describe the hybridisation in case of PCl_5. Why are the axial bonds longer as compared to equatorial bonds ?

17. Which hybrid orbitals are used by carbon atoms the following molecules ?
(a) CH_3-CH_3
(b) $CH_3-CH=CH_2$
(c) CH_3-CH_2-OH
(d) CH_3CHO
(e) CH_3COOH

18. Describe the change in hybridisation (if any) of the Al atom in the following reaction :
$$AlCl_3 + Cl^- \longrightarrow AlCl_4^-$$

19. Is there any change in the hybridisation of B and N atoms as a result of the following reactions ?
$$BF_3 + NH_3 \longrightarrow F_3B.NH_3$$

Sigma and π Bonds

20. What is the total number of sigma and π bonds the following molecules ? (a) C_2H_2 (b) C_2H_4 ?

21. Considering X-axis as the internuclear axis which out of the following will not form a sigma bond and why?
(a) 1s and 1s (b) 1s and $2p_x$
(c) $2p_x$ and $2p_y$ (d) 1s and 2s.

Valence Bond Theory

22. Explain the formation of H_2 molecule on the

basis of Valence bond theory.

VSEPR Theory

23. Discuss the shape of the following molecules using VSEPR model :
$\mathbf{BeCl_2, BCl_3, SiCl_4, AsF_5, H_2S, PH_3}$

24. Although geometries of NH_3 and H_2O molecules are distorted tetrahedral, bond angle in water is less than that of NH_3. Discuss.

25. Apart from tetrahedral geometry, another possible geometry for CH_4 is square planer with the four H atoms at the corners of the square and the C atom at the centre. Explain why CH_4 is not square planar.

26. What do you understand by bond pairs and lone pairs of electrons ? Illustrate by giving one example of each type.

Molecular Orbital Theory

27. How do you express bond strength in terms of bond order ?

28. Write the important conditions required for the near combination of atomic orbitals to form molecular orbitals.

29. Use molecular orbital theory to explain why Be_2 molecule does not exist.

30. Compare the relative stability of the following species and indicate their magnetic properties : O_2, O_2^+, O_2^- (superoxide) and O_2^{2-} (peroxide) ?

31. Write the significance of plus and a minus sign shown in representing the orbitals .

32. What is meant by the term bond order ? Calculate the bond order of : $\mathbf{N_2, O_2, O_2^+}$ and $\mathbf{O_2^-}$.

Bond Characterstics

33. Define the bond length.

Dipole Moment

34. Although both CO_2 and H_2O are triatomic molecules, the shape of H_2O molecule is bent while that of CO_2 is linear. Explain this on the basis of dipole moment.

35. Write the significance/applications of dipole moment.

36. Explain why BeH_2 molecules has a zero dipole moment although the Be–H bonds are polar.

Hydrogen Bond

37. Define hydrogen bond. Is it weaker or stronger than the van der Waals forces ?

SOLUTIONS

NCERT EXERCISE & EXAMPLES

Sol.1 Atoms of same or different elements combine resulting in the formation of a chemical bond between them. This formation of a chemical bond can be explained on the basis of various theories put forward from time to time. The atoms of different elements combine with each other in order to complete their respective octets or duplet to attain stable inert gas configuration. This they do by either transference of electrons or by sharing of electrons. Another way to explain the formation of a chemical bond is it results in lowering of energy of the system and constituents (atoms) attain greater stability.

Sol.2 Formation of an ionic bond would primarily depend upon.

- **(i)** The case of formation of the positive and negative ions from the respective neutral atoms.
- **(ii)** The arrangement of the positive and negative ions in the solid, *i.e.,* of the lattice of the crystalline compound. These in turn depend upon the following.
- **(i)** **Low Ionization Enthalpy.** The atom going to lose electrons to form a positive ion (cation) must lose them readily, *i.e.*, the element must have low ionisation enthalpy.

$$M(g) \longrightarrow M^{+}(g) + e^{-}$$

[Ionisation enthalpy]

M must have low ionization enthalpy as mostly active metals like Na, Mg, Ca have.

- **(ii)** **High electron gain enthalpy.** The atom going to accept electrons must be able to retain it, i.e., it must have high negative value of electron gain enthalpy.

$X(g) + e \longrightarrow X^{-}(g)$ [Electron gain enthalpy]

- **(iii)** **Enthalpy of lattice formation should be high.** The energy released when the requisite numbers of positive and negative ions combine to form one mole of the ionic compound is called lattice energy or enthalpy.

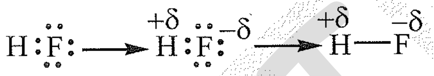
The higher the value of lattice energy of the resulting ionic compound, the greater will be the stability of the compound and hence greater will be the case of formation.

$$M^{+}(g) + X^{-}(g) \longrightarrow \underset{1\,\text{Mole}}{MX(g)} \text{ (Lattice enthalpy)}$$

Sol.3 More the difference of electronegativity, more the ionic character of the molecules

$N_2 < SO_2 < ClF_3 < K_2O < LiF$.

Sol.4 **Polar covalent bond.** Here the atoms in a covalently bonded molecule have unequal electronegativities. For example in HF, the electron pair is attracted more towards F atom due to its higher electronegativity. HF may be written as :



where $+\delta$ refers to small amount of positive charge and $-\delta$ refers to small amount of negative charge.

Sol.5 **Step 1.**

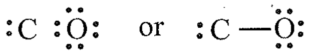
Count the total number of valence electrons of carbon and oxygen atoms. The outer (valence) shell configurations of carbon and oxygen atoms are : $2s^2 2p^2$ and $2s^2 2p^4$, respectively. The valence electrons available are $4 + 6 = 10$.

Step 2.

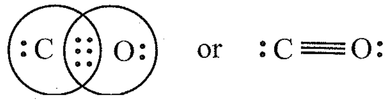
The skeletal structure of CO is written as : $C\ O$

Step 3.

Draw a single bond (one shared electron pair) between C and O and complete the octet on O, the remaining two electrons are the lone pair on C.



This does not complete the octet on carbon and hence we have to resort to multiple bonding (in this case a triple bond) between C and O atoms. This satisfies the octet rule condition for both atoms.



Sol.6 **Step 1.** Count the total number of valence electrons of the nitrogen atom, the oxygen atoms and the additional one negative charge (equal to one electron).

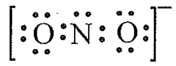
$$N\left(2s^2 2p^3\right), O\left(2s^2 2p^4\right)$$

$5 + (2 \times 6) + 1 = 18$ electrons

Step 2. The skeletal structure of NO_2^- is written as :

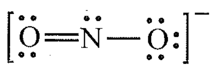
$$O \quad N \quad O$$

Step 3. Draw a single bond (one shared electron pair) between the nitrogen and each of the oxygen atoms. This, however, does not complete the octet on nitrogen if the remaining two electrons constitute lone pair on it.

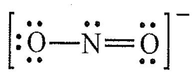


Hence we have to resort to multiple bonding between nitrogen and one of the oxygen atoms (in this case a double bond). This leads to the following Lewis dot structures.

or



or



Sol.7 No, these (1) and (2) structures cannot be taken as canonical forms of H_3PO_3 because the positions of atoms have been changed.

Sol.8 $\cdot\text{Mg}\cdot$, $\dot{\text{Na}}$, $\cdot\dot{\text{B}}\cdot$, $:\ddot{\text{O}}:$, $:\dot{\underset{\cdot}{\text{N}}}\cdot$, $:\ddot{\underset{\cdot\cdot}{\text{Br}}}\cdot$

Sol.9 ∵ ${}_{16}S = 2, 8, 6$ ∴ Lewis symbol = $:\ddot{\underset{\cdot\cdot}{S}}:$,

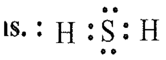
S^{2-} ions = $\left[:\ddot{\underset{\cdot\cdot}{S}}:\right]^{2-}$

${}_{13}Al = 2, 8, 3$ ∴ Lewis symbol = $\cdot\dot{Al}\cdot$,

Al^{3+} ion = $[Al]^{3+}$

${}_1H = 1$ ∴ Lewis symbol = $H^{\bullet}$, H^- ion = $\dot{H}\cdot$

Sol.10



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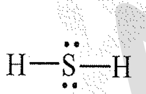

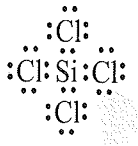

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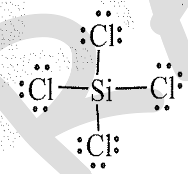

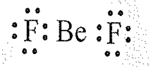

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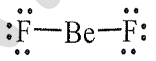

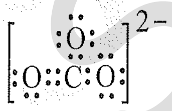

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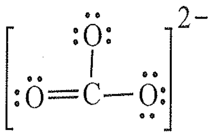

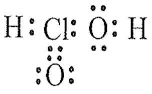

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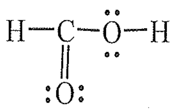
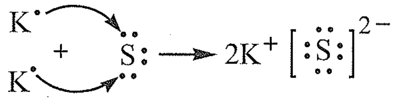


Sol.11 **(a)** K and S

$K^{\cdot} \longrightarrow K^+ + e^-$

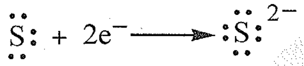
2,8,8,1 → 2,8,8

or



$K^{\cdot} \longrightarrow K^+ + e^-$

2, 8, 8, 1 → 2, 8, 8

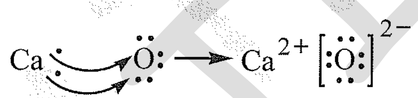


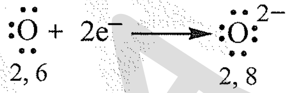
(b) *Ca* and *O*

$Ca: \longrightarrow Ca^{2+} + 2e^-$

2, 8, 8, 2 → 2, 8, 8

or

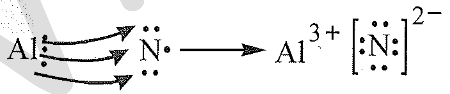


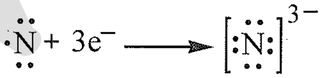


(c) *Al* and *N*

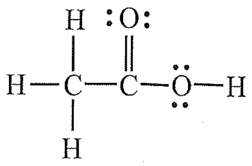
$Al\vdots \longrightarrow Al^{3+} + 3e^-$

or

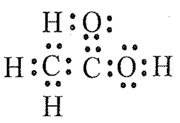




Sol.12 The correct Lewis structure for acetic acid (CH_3COOH) is :



Or



Sol.13 According to this rule : Atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet (acquiring eight electrons) in their valence shells.

Significance : Acquiring 8 electrons (octet formation) in the valence shells of atoms leads to stable electronic configuration because all noble gases (except *He*) have 8 electrons in their valence shells and they generally do not react chemically.

Neon = $Ne = 10 = 2,8$

Argon = $Ar = 18 = 2,8,8$

Krypton = $Kr = 36 = 2,8,18,8$

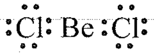
Xenon = $Xe = 54 = 2,8,18,18,8$

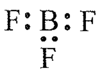
Radon = $Rn = 86 = 2,8,18,32,18,8$.

All other elements of the periodic table possess less than 8 electrons in their valence shells and hence are chemically reactive. Thus atoms of elements combine to acquire 8 electrons in their valence shells to acquire the inertness or stability of the noble gas near to them.

Limitations : (i) Formations of compounds involving hydrogen. Hydrogen atom has only one electron in its valence shell, it needs one more electron to acquire the nearest noble gas configuration of Helium. Hence hydrogen needs to complete its duplet (acquiring 2 electrons in its valence shell) rather than octet.

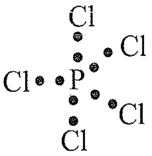
(ii) Formation of compounds like (incomplete Octet) $BeCl_2, BF_3, AlCl_3$. In each of these examples central atom *Be* in $BeCl_2$, *B* in BF_3 and *Al* in $AlCl_3$ has less than 8 electrons i.e., these compounds are electron deficient compounds


[Be has only 4 electrons around it]


and


[*B* and *Al* have only 6 electrons around it]
Thus octet rule is violated.

(iii)
Formation of compounds like (Extended Octet)
PCl_5,$SF_6$$IF_7$. In all these compounds, the central atom has more than 8 electrons.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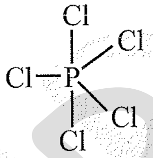
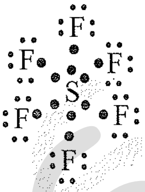
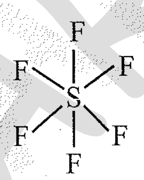
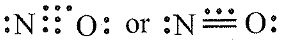

[P has 10 electrons]

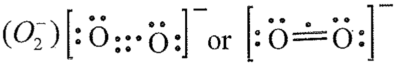

or

[S has12 electrons]

I has 14 electrons around it in IF_7.

(iv) Formation of compounds on noble gases. Noble gases on whom octet rule is based have already 8 electrons in their valence shells and should not form compounds. Recently *Xe* has been found to form compounds like XeF_2, XeF_4, XeF_6 etc.

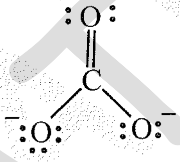
(v) Odd electron bonds/Odd electron molecules. There are certain molecules and ions like *NO*, and O_2 in which the bonded atoms contain odd number of electrons between them.

1. Nitric oxide [NO] 

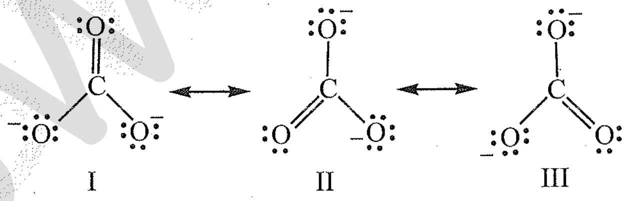
2. Superoxide ion (O_2^-) 

(vi) It does not explain the shape of the molecules and their relative stability.

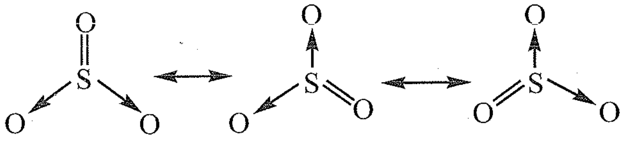
Sol.14 The single Lewis structure based on the presence of two single bonds and one double bond between carbon and oxygen atoms is inadequate to represent the molecule accurately as it represents unequal bonds.



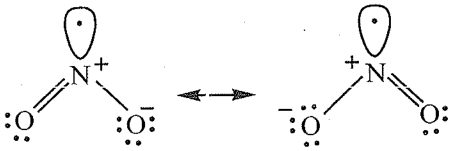
According to the experimental findings, all carbon to oxygen bonds in CO_3^{2-} are equivalent. Therefore the carbonate ion is best described as a resonance hybrid of the canonical forms I, II, and III shown below :



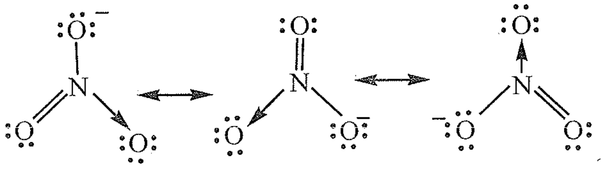
Sol.15 Resonance structure of SO_3



Resonance structures of NO_2



Resonance structures of NO_3^- ion



Sol.16 The $P-Cl$ equatorial bond length is 2.04 Å whereas $P-Cl$ axial bond length is 2.19 Å. The reason for the longer axial bond length is that the three $P-Cl$ equatorial bonds are repelled only by two electron pairs, but the

two axial $P-Cl$ bonds are repelled by three electron pairs. Thus the repulsion exerted on the axial bond pairs is more and hence bond length is longer.

Sol.17 **(a)** In CH_3-CH_3 carbon uses sp^3 hybrid orbitals.

(b) In $CH_3-CH=CH_2$; carbon used sp^2 and sp^3 hybrid orbitals.

(c) In CH_3-CH_2-OH; carbon uses sp^3 hybrid orbitals.

(d) In CH_3-CHO carbon uses sp^2 and sp^3 hybrid orbitals.

(e) In CH_3COOH carbon uses sp^2 and sp^3 hybrid orbitals.

Sol.18 There is change taking place in the hybridisation when $AlCl_3$ change to $AlCl_4^-$. $AlCl_3$ is sp^2 hybridised and $AlCl_4^-$ is sp^3 hybridised.

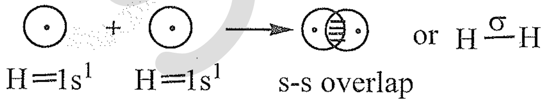
Sol.19 In BF_3, B is sp^2 hybridised and in NH_3, N is sp^3 hybridised. After the reaction the hybridisation of B changes to sp^3 but that of N remains unchanged.

Sol.20 **(a)** There are total three sigma bonds [one $C-C$ sigma and two $C-H$ sigma] and two π bonds [between the two C atoms] in C_2H_2.

(b) There are total five sigma bonds [one $C-C$ sigma and four $C-H$ sigma] and only one π bond [between the two C atoms] in C_2H_4.

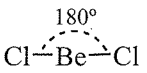
Sol.21 Since x-axis is being considered as the internuclear axis and y-axis is perpendicular to x-axis, therefore $2p_x$ and $2p_y$ atomic orbitals can overlap only side-wise (lying on y-axis). Since overlapping of p-orbitals side-wise results in the formation of pi (π) bond, therefore $2p_x$ and $2p_y$ will not form a sigma bond.

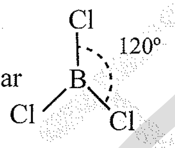
Sol.22 In H_2 molecule 1s atomic orbitals of both the hydrogen atoms overlap end on ($s-s$ overlap) resulting in the formation of a sigma bond, between them.

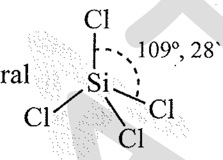


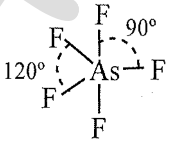
Sol.23 According to VSEPR theory : If the central atom is linked to different atoms or is surrounded by bond pairs as well as lone pairs of electrons, the repulsions between them are different. As a result the molecule has an irregular or distorted geometry. The order of repulsions between electron pairs is as follows :

Lone pair-lone pair repulsions > lone pair-bond pair repulsions > bond pair-bond pair repulsions. The exact shape of the molecule depends upon the total number of electron pairs present around the central atom.

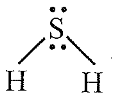
BeCl₂ : Linear  [No lone pairs of electron on Be]

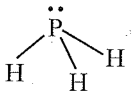
BCl₃ : Trigonal planar  [No lone pairs of electron on B]

SiCl₄ : Tetrahedral  [No lone pairs of electron on Si]

AsF₅ : Trigonal bipyramid  [No lone pairs of electron on As]

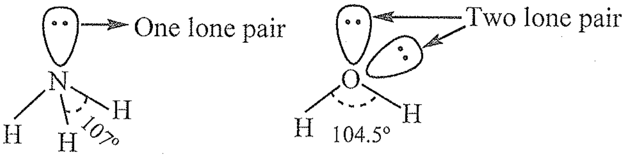
Shape of H₂S. The shape would have been tetrahedral if there were all bond pairs. But two lone pairs of electrons are present on sulphur and so the shape is distorted tetrahedral or angular.

H₂S : Bent 

PH₃ is  distorted trigonal bipyramid/Pyramidal

had there been a bond pair of electrons in place of lone pair, the shape would have been tetrahedral but one lone pair causes repulsion and the angle between the bond pairs is reduced.

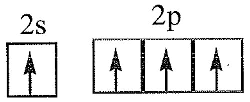
Sol.24 Both NH_3 and H_2O involve sp^3 hybridization and so their expected shape should be tetrahedral. But whereas in NH_3, there is one lone pair of electrons on N, there are two lone pairs of electrons present on oxygen in H_2O. According to VSEPR theory lone pair-lone pair repulsions are more in H_2O than lone pair-bond pair repulsions in NH_3.



Two lone pairs repel the bonded pairs of electrons more than one lone pair and therefore the bond angle between bond pair shrinks from 107° in case of NH_3 to 104.5° in H_2O.

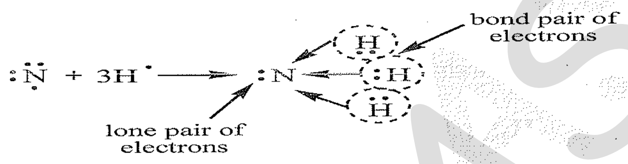
Sol.25 $C = 6 = 1s^2, 2s^2 2p_x^1 2p_y^1$ ground state

$= 1s^2, 2s^1 2p_x^1 2p_y^1 2p_z^1$ Excited state

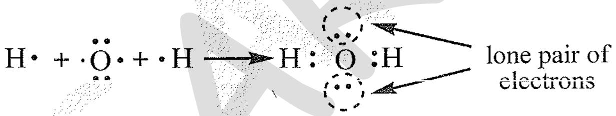


C can undergo only sp^3 hybridization which leads to tetrahedral geometry with $4H$ atoms at the corners of tetrahedron and C in the centre. Only those molecules can give rise to square planar arrangement in which the central atom can undergo dsp^2 hybridization which is not possible with C as it does not have d orbital with it.

Sol.26 The electrons which are present between the two atoms and shared by them are called bonded pairs of electrons. For example H_2 molecule has only one bond pair of electrons.



Whereas NH_3 molecule has both lone pairs (as shown above) and three bond pair of electrons. H_2O has two lone pairs of electrons. Lone pair electrons are those which are not shared by another atom.



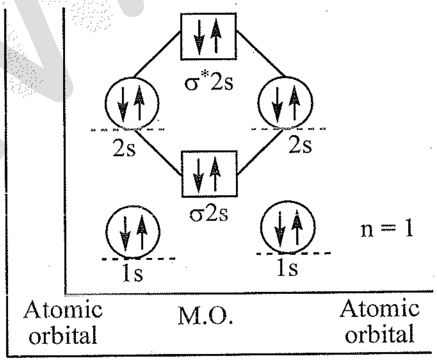
Sol.27 Bond strength ∝ Bond order.

Sol.28 The linear combination of atomic orbitals to form molecular orbitals takes place only if the following constraints are satisfied.

1. **The combining atomic orbitals must have the same or nearly the same energy.** This means that $1s$ orbital can combine another $1s$ but not with $2s$ orbital because the energy of $2s$ orbital is appreciably higher than that of $1s$ orbital. This is not true the atoms are very different.
2. **The combining atomic orbitals must have the same symmetry about the molecular axis.** By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having same or nearly the same energy will not combine if they do not have the same symmetry. For example, $2p_z$ orbital of atom can combine with $2p_z$ orbital of the other atom but not with $2p_x$ or $2p_y$ orbitals because of their different symmetries.
3. **The combining atomic orbitals must overlap to the maximum extent.** Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

Sol.29 The electronic configuration of $Be = 4 = 1s^2, 2s^2$. Be_2 molecule is not formed because bond order in this case = 0
The molecular orbital (hypothetical) is
$KK(\sigma 2s)^2 (\sigma^* 2s)^2$

Bond order $= \frac{2-2}{2} = 0$



Sol.30 Molecular orbitals of O_2, O_2^+, O_2^- and O_2^{2-} are as following

$O_2: \sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 <$
$(\pi 2p_x^2 = \pi 2p_y^2)(\pi^* 2p_x^1 = \pi^* 2p_y^1)$

Bond order $= \frac{1}{2}[10-6] = \frac{4}{2} = 2$; It has two unpaired electrons in each of $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ molecular orbitals. It is paramagnetic

$O_2^+ = \sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 <$
$(\pi 2p_x^2 = \pi 2p_y^2)(\pi^* 2p_x^1)$

Bond order $= \frac{1}{2}[10-5] = \frac{5}{2} = 2\frac{1}{2}$

There is one unpaired electron in $\pi^*_{2p_x}$ M.O.
∴ It is also paramagnetic.
But it is less paramagnetic than O_2 as O_2 has 2 unpaired electrons.

$O_2^- = \sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 <$

$(\pi 2p_x^2 = \pi 2p_y^2)(\pi^* 2p_x^2 = \pi^* 2p_y^1)$

Bond order $= \frac{1}{2}[10-7] = \frac{3}{2} = 1\frac{1}{2}$

There is one unpaired electron present in $(\pi^*_{2p_y})^2$ M.O.

$\therefore$ O_2^- is also paramagnetic like O_2^+, but less paramagnetic than O_2.

$$O_2^- = \sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 <$$
$$(\pi 2p_x^2 = \pi 2p_y^2)(\pi^* 2p_x^1 = \pi^* 2p_y^2)$$

Bond order $= \frac{1}{2}[10-8] = \frac{2}{2} = 1$

There is no unpaired electron present in O_2^{2-}.

$\therefore$ O_2^{2-} is diamagnetic

Thus O_2^{2-} is more paramagnetic than O_2^+ or O_2, whereas O_2^{2-} is diamagnetic.

The stability of these species varies directly as bond order.

$\therefore$ Stability increases from O_2^{2-} to O_2^+ as follows :

Bond	O_2^{2-}	$<$	O_2	$<$	O_2^-	$<$	O_2^+
Order	1		1.5		2		2.5

Sol.31 Crests of the electron wave are usually given a '+' sign and the trough a '–' sign. Thus bonding M.O. is formed by the combination of '+' with '+' and '–' with '–' part of the electron wave whereas antibonding M.O.s are formed by the overlap of '+' with '–' part. These '+' or '–' signs have nothing to do with the electrical charges on the orbitals.

Sol.32

Bond order of N_2 $= \frac{1}{2}[N_b - N_a] = \frac{10-4}{2} = \frac{6}{2} = 3$.

Bond order of O_2 : $= \frac{1}{2}[N_b - N_a] = \frac{10-6}{2} = \frac{4}{2} = 2$.

Bond order of O_2^+ $= \frac{1}{2}[N_b - N_a]$

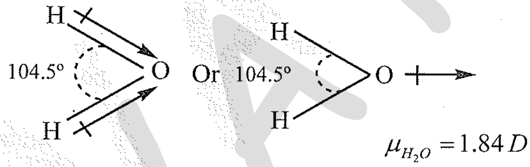
$= \frac{10-5}{2} = \frac{5}{2} = 2\frac{1}{2}$.

Bond order of O_2^- $= \frac{1}{2}[N_b - N_a]$

$= \frac{10-7}{2} = \frac{3}{2} = 1\frac{1}{2} .= 1.5$

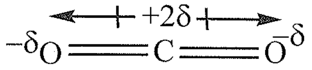
Sol.33 The average distance between the centres of the nuclei of the two bonded atoms is called its bond length.

Sol.34 Both CO_2 and H_2O are triatomic molecules but CO_2 molecule is linear whereas H_2O molecule is having a bent structure. H_2O molecule has dipole moment of 1.84 D. There are two $O-H$ bonds in H_2O molecule and both the bonds are polar. Since H_2O molecule has a net dipole moment, hence the two $O-H$ dipoles are not in a straight line opposing each other (as they would cancel out in that case). This immediately rules out the linear structure $(H-O-H)$ for water, the two $O-H$ bonds cannot lie along the same line in the same direction also. Therefore, the two $O-H$ bonds in H_2O molecule must be inclined to each other at certain angle. Thus H_2O molecule has an angular or bent structure.



$\mu_{H_2O} = 1.84\,D$

CO_2 has two $C=O$ polar bonds. No doubt these polar bonds possess the same value of dipole moment, but the overall dipole moment of molecule is found out to be zero. The explanation for this is individual dipole moments in this molecule are of equal magnitude but their directions are opposite to each other and hence cancel out. This shows that CO_2 molecule is Linear



Sol.35 Applications of Dipole moment :

(1) In determining the polarity of bonds : As $\mu = e \times d$, obviously greater is the magnitude of dipole moment, higher will be the polarity of the bond. This is applicable to molecule containing only one bond like HCl, HBr etc. In non-polar molecules like H_2, O_2, N_2 the dipole moment is zero. It is because there is no charge separations in these molecule $[e=0]$. Thus dipole moment can also be used to distinguish between polar and non-polar molecules.

(2) In the calculation of percentage ionic character.

Take the example of HCl. Its $\mu = 1.03\,D$

If HCl is 100% ionic, each end would carry charge = one unit

i.e., 4.8×10^{-10} *e.s.u.*

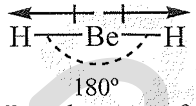
d (bond length) in $H-Cl = 1.275\,\text{Å}$

$\therefore$ for 100% ionic character, dipole moment will be

$$\mu_{ionic} = e \times d = 4.8\times10^{-10}\ e.s.u.\times1.275\times10^{-8}\ cm$$
$$= 6.12\times10^{-18}\ e.s.u.\ cm = 6.12\ D$$
$$\therefore \%\ \text{ionic character} = \frac{\mu\ observed}{\mu\ ionic}\times100$$
$$= \frac{1.03}{6.12}\times100 = 16.83$$

(3) **In determining the symmetry (or shape) of the molecules.** Dipole moment is an important property in determining the shape of molecules containing 3 or more atoms. For instant if any molecule possesses two or more polar bonds, it will not be symmetric if it possesses some net molecular dipole moment as in case of water (H_2O) $\mu = 1.84\,D$ and ammonia $(\mu_{NH_3} = 1.49\,D)$ But if a molecule contains a number of similar atoms linked to a central atom the overall dipole moment of the molecule is found out to be zero, this will imply that the molecule is symmetrical as is the case of CO_2, BF_3, CH_4, CCl_4 etc.

Sol.36 Due to *sp* hybridization shown by Be in BeH_2, the molecule BeH_2 is linear. Though the individual $Be-H$ bonds are polar (due to difference of electronegativity) yet BeH_2 has a dipole moment of zero as dipole moment is a vector quantity (it has both magnitude and direction). The individual polar character of $Be-H$ bond cancel out as the dipoles are equal and opposite as shown below :



Resultant μ = 0

Sol.37 When a molecule containing a H atom is linked to a highly electronegative atom (like N, O, F), this atom attracts the shared pair of electrons more and so this end of the molecule becomes slightly negative while the other end (i.e., H-end) becomes slightly positive. The negative pole of one molecule attracts the positive pole of the other molecule and so on and as a result, a weaker bond is formed between them. This bond is called hydrogen bond. It is represented by dotted lines as shown in the next page :

$$----\overset{+\delta}{H}—\overset{-\delta}{X}----\overset{+\delta}{H}—\overset{-\delta}{X}----\overset{+\delta}{H}—\overset{-\delta}{X}$$

As a result of Hydrogen bonding, μ H-atom links the two electronegative atoms simultaneously, one by a covalent bond and the other by a hydrogen bond. Hence it is said to form a HYDROGEN BRIDGE.

Hydrogen bond is a weak bond, but it is stronger than van der Waals forces.

QUESTION ALIKE

Based on Lewis Structure

1. Write the Lewis dot structure of CO molecule.
2. Write the Lewis structure of the nitrite ion, NO_2^-.
3. Explain the structure of CO_3^{2-} ion in terms of resonance.
4. Explain the structure of CO_2 molecule.
5. Draw the Lewis dot structure of HCN molecule.
6. Draw the Lewis dot structure of CO_3^{2-} ion.
7. To draw Lewis structure of CO_2.
8. To draw the Lewis structure of CN^- ion

Based on Formal Charge (F.C.) on an atom in a molecule/ion

9. Calculate formal charge on each O-atom of O_3 molecule.
10. Calculate the formal charge on
    (i) S in HSO_4^- ion **(ii)** Cl in $HClO_4$
11. Write the formal charges on atoms in
    (i) carbonate ion Co_3^{2-}
    (ii) nitrite ion No_2^-

Based on Calculation of Total Number of Electron Pairs, Bond Pairs and Lone Pairs and Predicting the Shapes of the Molecules and Ions.

12. On the basis of VSEPR theory, predict the shapes of the following :
    (i) ClF_3 **(ii)** BrF_5
    (iii) NH_2^- **(iv)** H_3O^+

Based on Applications of Dipole Moment

13. Calculate the percent ionic character of HCl. Given that the observed dipole moment is 1.03 D and bond length of HCl is 1.275 Å.
14. The dipole moment LiH is 1.964 × 1029C m and the interatomic distance between Li and H in the molecule is 1.596 Å. Calculate the percent ionic character of the molecule.
15. Calculate the fractional charge on each atom in HBr molecule. Given that
    Dipole moment of HBr = 0.78 D
    Bond distance of HBr = 1.41 Å
    Electronic chargae, e = 4.8 × 10-10 esu.

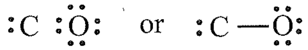
QUESTION ALIKE SOLUTIONS

Sol.1

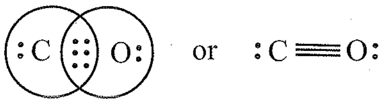
Step 1. Count the total number of valence electrons of carbon and oxygen atoms. The outer (valence) shell configurations of carbon and oxygen atoms are : $2s^2 2p^2$ and $2s^2 2p^4$, respectively. The valence electrons available are $4+6=10$.

Step 2. The skeletal structure of CO is written as : $C\ O$

Step 3. Draw a single bond (one shared electron pair) between C and O and complete the octet on O, the remaining two electrons are the lone pair on C.



This does not complete the octet on carbon and hence we have to resort to multiple bonding (in this case a triple bond) between C and O atoms. This satisfies the octet rule condition for both atoms.



Sol.2

Step 1. Count the total number of valence electrons of the nitrogen atom, the oxygen atoms and the additional one negative charge (equal to one electron).

$N(2s^2 2p^3), O(2s^2 2p^4)$

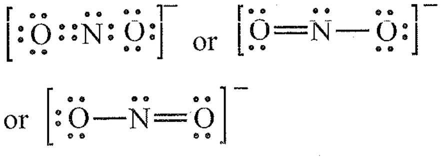
$5+(2\times 6)+1=18$ electrons

Step 2. The skeletal structure of NO_2^- is written as :

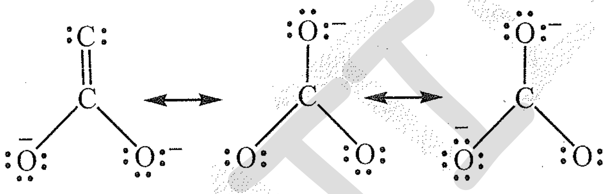
$O \quad N \quad O$

Step 3. Draw a single bond (one shared electron pair) between the nitrogen and each of the oxygen atoms. This, however, does not complete the octet on nitrogen if the remaining two electrons constitute lone pair on it.

Hence we have to resort to multiple bonding between nitrogen and one of the oxygen atoms (in this case a double bond). This leads to the following Lewis dot structures.

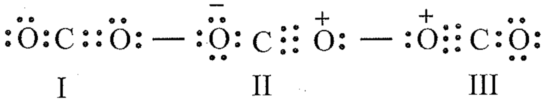


Sol.3 The single Lewis structure based on the presence of two single bonds and one double bond between carbon and oxygen atoms is inadequate to represent the molecule accurately as it represents unequal bonds. According to the experimental findings, all carbon to oxygen bonds in CO_3^{2-} are equivalent. Therefore the carbonate ion is best described as a resonance hybrid of the canonical forms I, II and III shown below.



Resonance in CO_3^{2-},
I II and III represent the three canonical forms.

Sol.4 The experimentally determined carbon and oxygen bond length in CO_2 is $115\,pm$. The length of a normal carbon and oxygen double bond $(C=O)$ and carbon to oxygen triple bond $(C\equiv O)$ are $121\,pm$ and $110\,pm$ respectively. The carbon-oxygen bond lengths in CO_2 $(115\,pm)$ lie between the values for $C=O$ and $C\equiv O$. Obviously, a single Lewis structures cannot depict this position and it becomes necessary to write more than one Lewis structures and to consider that the structures of CO_2 is best described as a hybrid of the canonical or resonance forms I, II and III.



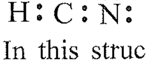
Resonance in CO_2 molecule, I, II and III represent the three canonical forms.

Sol.5

Step 1. Total number of valence electron in HCN
$=1+4+5+=10$
$({}_1H=1, {}_6C=2,4, {}_7N=2,5)$

Step 2. Skeletal structure is
H C N (C is least electronegative)

Step 3. Putting one shared pair of electrons between H and C and one between C and N, and the remaining as lone pairs, we have



In this structure, duplet of H is complete but octets of C and N are not complete. Hence, multiple bonding is required between C and N. Octets of C and N will be complete, if there is triple bond between C and N. Thus, we have,

$\mathrm{H:C\,\vdots\vdots\,\ddot{N}}$ or $\mathrm{H-C\equiv\ddot{N}}$

Sol.6

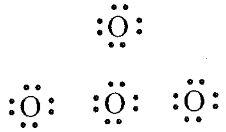
Step 1. Total number of valence electrons of $CO_3 = 4 + 3\times 6 = 22$ $\left({}_6C = 2,4,\ {}_8O = 2,6\right)$

Step 2. Total number of electrons to be distributed in $CO_3^{2-} = 22 + 2$ (for two units – ve charge) $= 24$

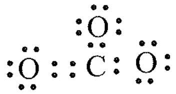
Step 3. The skeletal structure of CO_3 is

  O
O C O

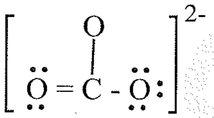
Step 4. Putting one shared pair of electrons between each C and O and completing the octets of oxygen, we have



In this structure, octet of C is not complete. Hence, multiple bonding is required between C and one of the O – atoms. Drawing a double bond C and one O-atom serves the purpose.



or



Alternatively, the structure may be obtained through the following steps :

Step 1. Calculate the total number of valence electrons (A) after subtracting for the cation or adding for the anion.

Step 2. Calculate the number of electrons (N) for complete octet of all the atoms.

Step 3. Calculate the number of electrons (S) present as shared pairs by subtracting A from N, i.e., S = N – A.

Step 4. Draw the skeletal structure and represent the shared pairs.

Step 5. Complete the structure by representing the unshared electrons (U = A – S).

Sol.7

Step 1. $A = 1\times 4$ (for C) $+ 2\times 6$ (for O)
$= 4 + 12 = 16$ electrons.

Step 2. $N = 1\times 8$ (for C) $+ 2\times 8$ (for O)
$= 8 + 16 = 24$ electrons.

Step 3. $S = N - A = 24 - 16 = 8$ electrons (shared).

Step 4. Drawing skeletal structure with shared pairs
O::O C::O

Step 5. $U = A - S = 16 - 8 = 8$.
∴ Complete Lewis structure will be
$:\ddot{O}=C=\ddot{O}:$

Sol.8

Step 1. $A = 1\times 4$ (for C) $+ 1\times 5$ (for N) $+ 1$ (for negative charge) $= 10$ electrons.

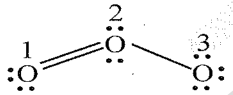
Step 2. $N = 1\times 8$ (for C) $+ 1\times 8$ (for N) $= 16$ electrons.

Step 3. $S = N - A = 16 - 10 = 6$ electrons (shared).

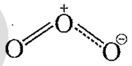
Step 4. Drawing skeletal structure with shared pairs.

Step 5. $U = A - S = 10 - 6 = 4$
∴ Complete Lewis structure will be
$:C\,\vdots\vdots\,N:^{-}$

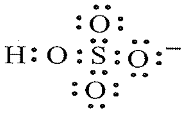
Sol.9 Lewis structure of O_3 is as follows :



The atomic have numbered as 1, 2 and 3.
Formal charge on end and O-atom numbered 1
$= 6 - 4 - \frac{1}{2}(4) = 0$
Formal charge on central O-atom numbered 2
$= 6 - 2 - \frac{1}{2}(6) = +1$
Formal charge on end O-atom numbered 3
$= 6 - 6 - \frac{1}{2}(2) = -1$
Hence, we represent O_3 alongwith formal charges as follows:

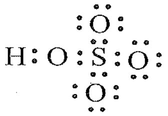


Sol.10 **(i)** Lewis structure of HSO_4^- ion is



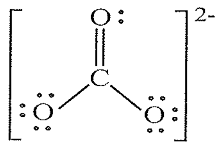
Applying the formula for calculation of formal charge,
Formal charge on S atm
$= 6 - 0 - \frac{1}{2}(8) = 6 - 4 = +2$

(ii) Lewis structure of $HClO_4$ is



Formal charge on $Cl = 7 - 0 - \frac{1}{2}(8) = +3$

Sol.11 **(i)** Lewis structure of CO_3^{2-} ion is



Formal charge on C atom

$= 4 - 0 - \frac{1}{2}(8) = 0$

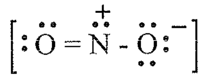
Formal charge on double bonded O atom

$= 6 - 4 - \frac{1}{2}(4) = 0$

Formal charge on single bonded O atom

$= 6 - 6 - \frac{1}{2}(2) = -1$

(ii) Lewis structure of NO_2^- is



$\left[:\ddot{O} = \overset{+}{\ddot{N}} - \underset{..}{\ddot{O}}:^{-}\right]$

Formula charge on N atom

$= 5 - 2 - \frac{1}{2}(6) = 0$

Formal charge on double bonded O atom

$= 6 - 4 - \frac{1}{2}(4) = 0$

Formal charge on single bonded O atom

$= 6 - 6 - \frac{1}{2}(2) = -1$

Sol.12 **(i) Shape of** ClF_3

No. of valence electrons of the central Cl atom $= 7$

No. of atoms linked to it by single bonds $= 3$

$\therefore$ Total no. of electron pairs around Cl

$= \frac{7+3}{2} = 5$

No. of bond pairs = No. of atoms linked to $Cl = 3$

$\therefore$ No. of lone pairs $= 5 - 3 = 2$

Thus, the molecule is the type of AB_3L_2

Hence, it is T-shaped.

(ii) Shape of BrF_5

No. of valence electrons of central Br atom $= 7$

No. of atoms linked to it by single bonds $= 5$

$\therefore$ Total no. of electron pairs around $Br = \frac{7+5}{2} = 6$

No. of bond pairs = No. of atoms linked to $Br = 5$

$\therefore$ No. of lone pairs $= 6 - 5 = 1$

Thus, the molecule is of the type AB_5L. Hence, it has square pyramidal shape.

(iii) Shape of NH_2^-

No. of valence electrons of central N atom $= 5 + 1$ (due to one unit –ve charge) $= 6$

No. of atoms linked to it $= 2$

$\therefore$ Total no. of electron pairs around

$N = \frac{6+2}{2} = 4$

No. of bond pairs $= 2$

$\therefore$ No. of lone pairs $= 4 - 2 = 2$

Thus, the ion of the type AB_2I_2. Hence, it has a bent shape (V-shape).

(iv) Shape of H_3O^+ **ion**

No. of valence electrons of central 'O' atom $= 6 - 1$ (due to one unit +ve charge) $= 5$

No. of atoms linked to 'O' atom $= 3$

$\therefore$ Total no. of electron pairs around 'O'

$= \frac{5+3}{2} = 4$

No. of bond pairs $= 3$

$\therefore$ No. of bond pairs $= 4 - 3 = 1$

Thus, the ion is of the type AB_3L. Hence, its shape is trigonal pyramidal.

Sol.13 If HCl were 100% ionic, each end would carry charge equal to one unit, viz, 4.8×10^{-10} esu. As bond length of HCl is 1.275 Å, its dipole moment for 100% ionic character would be

^{m}Ionic = q × d = 4.8 10^{-10} esu

1.275 × 10^{-8} cm

= 6.12 × 10^{-18} esu cm = 6.12 D

^{m}observed = 1.03 D (Given)

$\therefore$ % ionic character $= \frac{^{\mu}observed}{^{\mu}ionic} \times 100$

$= \frac{1.03}{6.12} \times 100 = 16.83\%$

Sol.14 If the molecule were 100% ionic,

^{m}Ionic = q × d

= (1.602×10^{-19}C) (1.596×10^{10} m)

= 2.557 × 10^{29} C m

^{m}observed = 1.96 ×1029 C m (Given)

$\therefore$ % ionic character $= \frac{^{\mu}observed}{^{\mu}ionic} \times 100$

$= \frac{1.96\ 1029\ Cm}{2.557 \times 10^{-29}\ Cm} \times 100 = 76.81\%$

Sol.15 Suppose partial charge on H = +q. Then partial charge on Br = -q

Dipole moment (m) = q × d

or $= \frac{\mu}{d} = \frac{0.78 \times 10^{-18}\ esu\,cm}{1.41 \times 10^{-8}\ cm}$

= 0.55 × 10^{-10} esu.

Fractionl charge $(\delta) = \frac{q}{e} = \frac{0.55 \times 10^{-10}\ esu}{4.8 \times 10^{-10}\ esu}$

$= 0.11$

$\therefore\ \delta_H + = 0.11, \delta_{Br} - = -0.11$.

Objective Questions

1. Which is the best description of a covalent bond?
   (a) Electrons are simultaneously attracted by more than one nucleus.
   (b) Filled orbitals of two or more atoms overlap one another
   (c) Unocuppied orbitals of two or more atoms overlap one another
   (d) Oppositely charged ions attract one another

2. Chemical bond implies
   (a) repulsion
   (b) attraction
   (c) attraction and repulsion
   (d) none of these

3. Which of the following statements is true about hybridization
   (a) only those atomic orbitals can be hybridized which do not differ much in shape.
   (b) Only those atomic orbitals can be hybridized which do not differ much in energy
   (c) Only those atomic orbitals can be hybridized which do not differ much in size
   (d) Only those atomic orbitals can be hybridized which do not differ much in overlap integrals.

4. For exhibiting tetravalency, carbon atoms have to be excited. Now, which of the following statements is true ?
   (a) Excitation occurs before bonding
   (b) Bonding occur before excitation
   (c) both bonding excitation occur simultaneously
   (d) Two bonds are formed first, then excitation occurs followed by formation of another two bonds

5. In $2sp^2$ orbital, character of $2p_x$ orbital will be
   (a) always 33.33% (b) always 0%
   (c) always 66.66% (d) either 33.33% or 0%

6. In $2sp^3$ orbital
   (a) characters of $2p_x$, $2p_y$ and $2p_z$ orbitals are equal to each other but less than that of 2s-orbital
   (b) characters of $2p_x$, $2p_y$ and $2p_z$ orbitals are equal to each other but more than that of 2s
   (c) characters of 2s, sp_x, $2p_y$ and $2p_z$ orbitals are equal to each other
   (d) characters of $2p_x$, $2p_y$ and $2p_z$ are not equal to each other

7. Which of the following statements is not correct regarding bonding molecular orbitals ?
   (a) Bonding molecule orbitals posses less energy than the atomic orbitals from which they are formed
   (b) Bonding molecular orbitals have low electron density between the two nuclei
   (c) Electron in bonding molecular contributes to the attraction between atoms
   (d) They are formed when the lobes of the combing atomic orbitals have the same sign

8. Which of the following statement(s) is true :
   (a) Higher the bond order lesser the bond length
   (b) Higher the bond order greater the bond length
   (c) Higher the bond order lesser the bond energy
   (d) Higher the bond order lesser the number of bonds

9. The compound in which the mentioned bond angle in parenthesis is found to be greater than expected not due to back bonding is :
   (a) $H_3SiNCS(\angle Si-N-C)$
   (b) BI_3 $(\angle I-B-I)$
   (c) $MeNCS(\angle CNC)$
   (d) None of these

10. Both $N(SiH_3)_3$ and $NH(SiH_3)_2$ compounds have trigonal planar skeleton. Incorrect statement about both compounds is :
    (a) $\mathrm{Si\hat{N}Si}$ bond angle in $NH(SiH_3)_2$ > $\mathrm{Si\hat{N}Si}$ bond angle in $N(SiH_3)_3$
    (b) N–Si bond length in $NH(SiH_3)_2$ > N–Si bond length in $N(SiH_3)_3$
    (c) N–Si bond length in $NH(SiH_3)_2$ < N – Si bond length in $N(SiH_3)_3$
    (d) Back bonding strength in $NH(SiH_3)_2$ > Back bonding strength in $N(SiH_3)_3$

11. If the measured dipole moment for the molecule is zero then for which of given formula the shape of the molecule cannot predicted.
    (a) AX_3 (b) AX_4
    (c) AX_5 (d) None of these

12. Which of the following statements is correct ?
    (a) Noble gases are insoluble in water
    (b) The solubility of noble gases in water in fairly high due to London dispersion force.
    (c) The solubility of noble gases increases with the decrease in size of the noble gas atom.
    (d) The solubility of noble gases in water in fairly high due to dipole-induced dipole

interaction.

13. Which of the following statements is correct for covalent bond
(a) Electrons are shared between two atoms
(b) It may be polar or non-polar
(c) Direction is non-polar
(d) Valency electrons are attracted

14. The bond between two identical non-metal atoms has a pair of electrons.
(a) Unequally shared between the two
(b) Transferred fully from one atom to another
(c) With identical spins
(d) Equally shared between them

15. Which of the following element does not show inert pair effect ?
(a) Tl (b) Pb
(c) Bi (d) Sn

16. Which of the following compound is not a strong oxidizing agent ?
(a) PbO_2 (b) $PbCl_4$
(c) Pb_3O_4 (d) CCl_4

17. Which of the following is a covalent compound
(a) Al_2O_3 (b) AlF_3
(c) $AlCl_3$ (d) $Al_2(SO_4)_3$

18. Solid NaCl is a bad conductor of electricity because :
(a) in solid NaCl there are no ions
(b) Solid NaCl is covalent
(c) in solid NaCl there is no mobility of ions
(d) in solid NaCl there are no electrons

19. Amongst LiCl, $BeCl_2$, $MgCl_2$ and RbCl the compounds with greatest and least ionic character, respectively are:
(a) LiCl and RbCl
(b) RbCl and $BeCl_2$
(c) RbCl and $MgCl_2$
(d) $MgCl_2$ and $BeCl_2$

20. The compound with the highest degree of covalency is :
(a) NaCl (b) $MgCl_2$
(c) AgCl (d) CsCl

21. Which of the following substances has the highest melting point ?
(a) NaCl (b) KCl
(c) MgO (d) BaO

22. The melting point of RbBr is 682°C while that of NaF is 988°C. the principal reason for this fact is :
(a) the molar mass of NaF is smaller than that of RbBr
(b) the bond in RbBr has more covalent character than the bond in NaF
(c) the difference in electronegativity between Rb and Br is smaller than the difference between Na and F
(d) the internuclear distance, $r_c + r_a$ is greater for RbBr than for NaF

23. Sodium bicarbonate has :
(a) Ionic bond (b) Covalent bond
(c) Hydrogen bond (d) All of these

24. Among the carbonates of alkali metals which one has highest thermal stability ?
(a) Cs_2CO_3 (b) Rb_2CO_3
(c) K_2CO_3 (d) Na_2CO_3

25. The fluoride which is most soluble in water is :
(a) CaF_2 (b) BaF_2
(c) SrF_2 (d) BeF_2

Answer Key

1. (a) 2. (b) 3. (b)
4. (c) 5. (d) 6. (b)
7. (b) 8. (a) 9. (d)
10. (b) 11. (d) 12. (a)
13. (a,b) 14. (d) 15. (d)
16. (d) 17. (c) 18. (c)
19. (b) 20. (c) 21. (c)
22. (d) 23. (d) 24. (a)
25. (d)

Examplar Questions

1. Isostructural species are those which have the same shape and hybridisation. Among the given species identify the isostructural pairs.

(i) [NF_3 and BF_3]
(ii) [BF_4^- and NH_4^+]
(iii) [BCl_3 and $BrCl_3$]
(iv) [NH_3 and NO_3^-]

2. Polarity in a molecule and hence the dipole moment depends primarily on electronegativity of the constituent atoms and shape of a molecule. Which of the following has the highest dipole moment?

(i) CO_2
(ii) HI
(iii) H_2O
(iv) SO_2

3. The types of hybrid orbitals of nitrogen in $NO^+{}_2$, NO_3^- and NH_4^+ respectively are expected to be

(i) sp, sp^3 and sp^2
(ii) sp, sp^2 and sp^3
(iii) sp^2, sp and sp^3
(iv) sp^2, sp^3 and sp

4. Hydrogen bonds are formed in many compounds e.g., H_2O, HF, NH_3 . The boiling point of such compounds depends to a large extent on the strength of hydrogen bond and the number of hydrogen bonds. The correct decreasing order of the boiling points of above compounds is :

(i) $HF > H_2O > NH_3$
(ii) $H_2O > HF > NH_3$
(iii) $NH_3 > HF > H_2O$
(iv) $NH_3 > H_2O > HF$

5. In PO_4^{3-} ion the formal charge on the oxygen atom of P–O bond is

(i) + 1
(ii) – 1
(iii) – 0.75
(iv) + 0.75

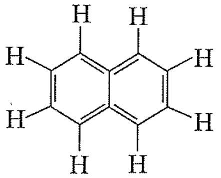
6. In NO_3^- ion, the number of bond pairs and lone pairs of electrons on nitrogen atom are

(i) 2, 2
(ii) 3, 1
(iii) 1, 3
(iv) 4, 0

7. Which of the following species has tetrahedral geometry?

(i) BH_4^-
(ii) NH_2^-
(iii) $CO^2{}_3{}^-$
(iv) H_3O^+

8. Numb of π bonds and σ bonds in the following structure is–



(i) 6, 19
(ii) 4, 20
(iii) 5, 19
(iv) 5, 20

9. Which molecule/ion out of the following does **not** contain unpaired electrons?

(i) N_2^+
(ii) O_2
(iii) O_2^{2-}
(iv) B_2

10. In which of the following molecule/ion all the bonds are **not** equal?

(i) XeF_4
(ii) BF_4^-
(iii) C_2H_4
(iv) SiF_4

11. In which of the following substances will hydrogen bond be strongest?

(i) HCl (ii) H_2O

(iii) HI (iv) H_2S

12. If the electronic configuration of an element is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^2\,4s^2$, the four electrons involved in chemical bond formation will be_____.

(i) $3p^6$ (ii) $3p^6, 4s^2$

(iii) $3p^6, 3d^2$ (iv) $3d^2, 4s^2$

13. Which of the following angle corresponds to sp^2 hybridisation?

(i) 90° (ii) 120°

(iii) 180° (iv) 109°

The electronic configurations of three elements, A, B and C are given below.
Answer the questions 14 to 17 on the basis of these configurations.

A	$1s^2$	$2s^2$	$2p^6$	-	-
B	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^3$
C	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^5$

14. Stable form of **A** may be represented by the formula :

(i) A (ii) A_2

(iii) A_3 (iv) A_4

15. Stable form of **C** may be represented by the formula :

(i) C (ii) C_2

(iii) C_3 (iv) C_4

16. The molecular formula of the compound formed from B and C will be

(i) BC (ii) B_2C

(iii) BC_2 (iv) BC_3

17. The bond between B and C will be

(i) Ionic (ii) Covalent

(iii) Hydrogen (iv) Coordinate

18. Which of the following order of energies of molecular orbitals of N_2 is correct?

(i) $(\pi 2p_y) < (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$

(ii) $(\pi 2p_y) > (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$

(iii) $(\pi 2p_y) < (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$

(iv) $(\pi 2p_y) > (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$

19. Which of the following statement is **not** correct from the view point of molecular orbital theory?

(i) Be_2 is not a stable molecule.

(ii) He_2 is not stable but $He^{+}{}_{2}$ is expected to exist.

(iii) Bond strength of N_2 is maximum amongst the homonuclear diatomic molecules belonging to the second period.

(iv) The order of energies of molecular orbitals in N_2 molecule is

$$\sigma 2s < \sigma^* 2s < \sigma 2p_z < (2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

20. Which of the following options represents the correct bond order :

(i) $O_2^- > O_2 > O^{+}{}_{2}$ (ii) $O_2^- < O_2 < O_2^+$

(iii) $O_2^- > O_2 < O_2^+$ (iv) $O_2^- < O_2 > O^{+}{}_{2}$

21. The electronic configuration of the outer most shell of the most electronegative element is

(i) $2s^2 2p^5$ (ii) $3s^2 3p^5$

(iii) $4s^2 4p^5$ (iv) $5s^2 5p^5$

22. Amongst the following elements whose electronic configurations are given below, the one having the highest ionisation enthalpy is

(i) $[Ne]3s^2 3p^1$ (ii) $[Ne]3s^2 3p^3$

(iii) $[Ne]3s^2 3p^2$ (iv) $[Ar]3d^{10} 4s^2 4p^3$

Examplar Solutions

1. (ii)
2. (iii)
3. (ii)
4. (ii)
5. (ii)
6. (iv)
7. (i)
8. (iii)
9. (iii)
10. (iii)
11. (ii)
12. (iv)
13. (ii)
14. (i)
15. (ii)
16. (iv)
17. (ii)
18. (i)
19. (iv)
20. (ii)
21. (i)
22. (ii)

JEE and NEET Previous Year

Jee Previous Year

Q.1. Which one of the following among each pair will release maximum energy on gaining one electron (A = F, Cl), (B = S, Se), (C = Li, Na) **[2020 Mains]**

(a) (A) = Cl, (B) = S, (C) = Li
(b) (A) = S, (B) = Cl, (C) = Li
(c) (A) = Li, (B) = Cl, (C) = S
(d) (A) = Cl, (B) = Li, (C) = S

Q.2. According to molecular orbital theory, which of the following is true with respect to Li_2^+ and Li_2^-? **[2019 Mains]**

(a) Both are unstable
(b) Li_2^+ is unstable and Li_2^- is stable
(c) Both are stable
(d) Li_2^+ is stable and Li_2^- is unstable

Q.3. The compound that does not produce nitrogen gas by the thermal decomposition is **[2018 Mains]**

(a) $(NH_4)_2Cr_2O_7$ (b) NH_4NO_2
(c) $(NH_4)_2SO_4$ (d) $Ba(N_3)_2$

Q.4. Which of the following species is not paramagnetic? **[2017 Mains]**

(a) NO (b) CO
(c) O_2 (d) B_2

Q.5. The sum of the number of lone pairs of electrons on each central atom in the following species is $[TeBr_6]^{2-}, [BrF_2]^+, SNF_3$ and $[XeF_3]^-$

(Atomic number : N = 7, F= 9, S= 16, Br= 35, Te = 52, Xe = 54) **[2017 Adv.]**

Q.6. Among the number of diamagnetic species is $H_2, He_2^+, Li_2, Be_2, B_2, C_2, N_2, O_2^-$ and F_2, the number of diamagnetic species is
(Atomic numbers : H= 1, He = 2, Li = 3, Be = 4, B= 5, C = 6, N = 7, O = 8, F = 9) (2017 Adv.)

Q.7. Dipole moment is shown by **[2017 Mains]**

(a) 1, 4 dichlorobenzene
(b) *cis*-1, 2- dichloroethene
(c) *trans*-1, 2 dichloroethene
(d) *trans*-1, 2-dichloro – 2 pentene

Q.8. The group having isoelectronic species is **[2017 Mains]**

(a) O^{2-}, F^-, Na^+, Mg^{2+}
(b) O^-, F^-, Na, Mg^+
(c) O^{2-}, F^-, Na, Mg^{2+}
(d) O^-, F^-, Na^+, Mg^{2+}

Q.9. According to molecular orbital theory, which of the following statement is (are) correct? **[2016 Adv.]**

(a) C_2^{2-} is expected to be diamagnetic
(b) O_2^{2+} is expected to have a longer bond length than O_2
(c) N_2^+ and N_2^- have the same bond order
(d) He_2^+ has the same energy as two isolated He atoms

Q.10. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is **[2015 Mains]**

(a) ion-ion interaction
(b) ion-dipole interaction
(c) London force
(d) hydrogen bond

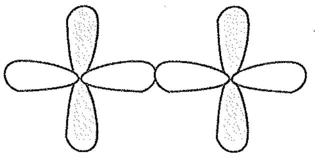
Q.11. Among the triatomic molecules/ions $BeCl_2, N_3^-, N_2O, NO_2^+, O_3, SCl_2, ICl_2^-, I_3^-$ and XeF_2, the total number of linear molecules(s) ion(s) where the hybridization of the central atom does not have contribution from the *d*-orbital(s) is [atomic number of S=16, Cl=17, I= 53 and Xe =54] **[2015 adv.]**

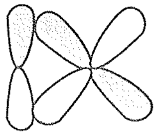
Q.12. The correct statement of the molecule CsI_3 is **[2014 Mains]**

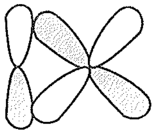
(a) it is a covalent molecule
(b) it contains Cs^+ and I_3^- ions
(c) it contains Cs^{3+} and I^- ions
(d) it contains Cs^+, I^- and lattice I_2 molecule

Q.13. Match of orbital overlap figures shown in Column I with the description given inColumn II and select the correct answer using the codes given below the Columns. **[2014 Adv.]**

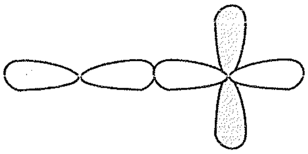
Column I Column II

A.  1. *p-d*π antibonding

B.  2. *d-d*σ bonding

C.


3. p-$d\pi$ bonding

D.


4. d-$d\sigma$ antibonding

Codes

	A	B	C	D
(a)	4	3	2	1
(b)	1	2	3	4
(c)	2	3	1	4
(d)	4	1	2	3

Q.14. Hydrogen bonding plays a central role in which of the following phenomena? **[2014 Adv.]**
(a) Ice floats in water
(b) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions
(c) Formic acid is more acidic than acetic acid
(d) Dimerisation of acetic acid in benzene

Q.15. A list of species having the formula XZ_4 is given below **[2014 adv.]**

$XeF_4, SF_4, SiF_4, BF_4^-, BrF_4^-, [Cu(NH_3)_4]^{2+}, [FeCl_4]^{2-},$

$[CoCl_4]^{2-}$ and $[PtCl_4]^{2-}$

Difining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is

Q.16. Which one of the following molecules is expected to exhibit diamagnetic behavior? **[2013 Adv.]**
(a) C_2 (b) N_2
(c) O_2 (d) S_2

Q.17. In which of the following pairs of molecules/ions both the species are not likely to exist? **[2013 Mains]**
(a) H_2^+, He_2^{2-} (b) H_2^-, He_2^{2-}
(c) H_2^{2+}, He_2 (d) H_2^-, He_2^{2+}

Q.18. Stability of the species Li_2, Li_2^- and Li_2^+ increases in the order of **[2013 Mains]**
(a) $Li_2 < Li_2^+ < Li_2^-$ (b) $Li_2^- < Li_2^+ < Li_2$
(c) $Li_2 < Li_2^- < Li_2^+$ (d) $Li_2^- < Li_2 < Li_2^+$

Q.19. The total number of lone-pair of electrons in melamine is **[2013 Adv.]**

Q.20. The species having pyramidal shape is **[2010 Mains]**
(a) SO_3 (b) BrF_3
(c) SiO_3^{2-} (d) OSF_2

Q.21. Based VSEPR theory, the number of 90° F — Br — F angles in BrF_5 is **[2010 Mains]**

Q.22. Assuming that hund's rule is violated the bond order and magnetic nature of the diatomic molecule B_2 is **[2010 Mains]**
(a) 1 and diamagnetic
(b) 0 and diamagnetic
(c) 1 and paramagnetic
(d) 0 and paramagnetic

Q.23. Match each of the diatomic molecules in Column I with its property/properties in Column II. **[2009 Mains]**

	Column I		Column II
A.	B_2	p.	Paramagnetic
B.	N_2	q.	Undergoes oxidation
C.	O_2^-	r.	Undergoes reduction
D.	O_2	s.	Bond order ≥ 2
		t.	Mixing of '*s*' and '*p*' orbitals

Codes

	A	B	C	D
(a)	q, r, s	p, r, t, s	q, r, t	p, q, t
(b)	p, q, r, t	q, r, s, t	p, q, r, t	p, r, s t
(c)	q, r, s, t	p, q, r	r, s, t	p, q, r, t
(d)	p, q, s, t	p, q, s	p, t	q, r, t

Q.24. Hyperconugation involves overlap of which of the following orbitals? **[2008 Mains]**
(a) $\sigma - \sigma$ (b) $\sigma - p$
(c) $p - p$ (d) $\pi - \pi$

Q.25. The species havingbond order paramagnetic compound is **[2007 Mains]**
(a) NO^- (b) NO^+
(c) CN^- (d) N_2

Q.26. Among the following, the paramagnetic compound is **[2007 Mains]**
(a) Na_2O_2 (b) O_3
(c) N_2O (d) KO_2

Q.27. Match the reactions in Column I with nature of the reactions/type of the products in Column II. **[2007 Mains]**

	Column I	Column II
A.	$O_2^- \rightarrow O_2 + O_2^{2-}$	1. Redox reaction
B.	$CrO_4^{2-} + H^+ \rightarrow$	2. One of the products has Trigonal planar sturcture
C.	$MnO_4^- + NO_2^- + H^+ \rightarrow$	3. Dimeric bridged Tetrahedral metal ion
D.	$NO_3^- + H_2SO_4 + Fe^{2+} \rightarrow$	4. Disproportionation

Codes

	A	B	C	D
(a)	2	1,4	3	4

(b) 1,4 3 1,2 1
(c) 2 3 1 4
(d) 3 4 2,3 1

Q.28. Which of the following contains maximum number of lone pairs on the central atom? **[2005 Mains]**
(a) ClO_3^-
(b) XeF_4
(c) SF_4
(d) I_3^-

Q.29. Number of lone pair(s) in $XeOF_4$ is/are **[2004 Mains]**
(a) 0
(b) 1
(c) 2
(d) 3

Q.30. According to Mo theory, **[2004 Mains]**
(a) O_2^+ is paramagnetic and bond order greater than O_2
(b) O_2^+ is paramagnetic and bond order less than O_2
(c) O_2^+ is diamagnetic and bond order is less than O_2
(d) O_2^+ is diamagnetic and bond order is more than O_2

Q.31. Which of the the following are isoelectronic and isostructural ?

$NO_3^-, CO_3^{2-}, ClO_3^-, SO_3$ **[2003 Mains]**
(a) NO_3^-, CO_3^{2-}
(b) SO_3, NO_3^-
(c) ClO_3^-, CO_3^{2-}
(d) ClO_3^{2-}, SO_3

Q.32. Among the following, molecule with the highest dipole moment is **[2003 Mains]**
(a) CH_3Cl
(b) CH_2Cl_2
(c) $CHCl_3$
(d) CCl_4

Q.33. Which of the following molecular species has unpaired electron(s) ? **[2002 Mains]**
(a) N_2
(b) F_2
(c) O_2^-
(d) O_2^{2-}

Q.34. The nodal plan in the π–bond of ethane is located in **[2002 Mains]**
(a) the molecular plane
(b) a plane parallel to the molecular plane
(c) a plane perpendicular to the molecular plane which bisects the carbon-carbon σ-bond at right angle
(d) a plane perpendicular to the molecular plane which contains the carbon-carbon σ-bond

Q.35. Specify the coordination geometry around and hybridisation of N and B atoms in a 1 : 1 complex of BF_3 and NH_3. **[2002 Mains]**
(a) N : tetrahedral, sp^3 ; B : tetrahedral, sp^3
(b) N : pyramidal,, sp^3 ; B : pyramidal, sp^3
(c) N : pyramidal,, sp^3 ; B : planar, sp^3
(d) N : pyramidal,, sp^3; B : tetrahedral, sp^3

Q.36. The correct order of hybridization of the central atom in the following species $NH_3, (PtCl_4]^{2-}, PCl_5$ and BCl_3 is **[2001]**
(a) dsp^2, dsp^3, sp^2 and sp^3
(b) sp^3, dsp^2, sp^3d and sp^2
(c) dsp^2, sp^2, sp^3 and dsp^3
(d) dsp^2, sp^3, sp^2 and dsp^3

Q.37. Amongst H_2O, H_2S, H_2Se and H_2Te the one with the highest boiling point is **[2000]**
(a) H_2O because of hydrogen bonding
(b) H_2Te because of higher molecular weight
(c) H_2S because of hydrogen bonding
(d) H_2Se because of lower molecular weight

Q.38. Molecular shape of SF_4, CF_4 and XeF_4 are **[2000]**
(a) the same, with 2, 0 and 1 lone pair of electrons respectively
(b) the same, with 1, 1 and 1 lone pair of electrons respectively
(c) different, with 0, 1 and 2 lone pair of electrons respectively
(d) different, with 1, 0 and 2 lone pair of electrons respectively

NEET Previous Year

Q.39. In the structure of ClF_3, the number of lone pair of electron on central atom 'Cl' is **[2018]**
(a) One
(b) Two
(c) Three
(d) Four

Q.40. Consider the following species:
CN^+, CN^-, NO and CN
Which one of these will have the highest bond order? **[2018]**
(a) NO
(b) CN^-
(c) CN
(d) CN^+

Q.41. Which of the following molecules has the maximum dipole moment? **[2014]**
(a) CO_2
(b) CH_4
(c) NH_3
(d) NF_3

Q.42. Which one of the following molecules contain no π–bond? **[2014]**
(a) CO_2
(b) H_2O
(c) SO_2
(d) NO_2

Q.43. Which of the following is a polar molecule? **[2013]**
(a) BF_3
(b) SF_4
(c) SiF_4
(d) XeF_4

Q.44. Bond order of 1.5 is shown by **[2013]**

(a) O_2^+ (b) O_2^-

(c) O_2^{2-} (d) O_2

Q.45. Which of the following species contains three bond pairs and one lone pair around the central atom? **[2013]**

(a) H_2O (b) BF_3

(c) NH_2^- (d) PCl_3

Q.46. The pair of species with the same bond order is **[2013]**

(a) O_2^{2-} , B_2 (b) O_2^+, NO^+

(c) NO, CO (d) N_2, O_2

Q.47. Which of the two ions from the list given below, have the geometry that is explained by the same hybridization of orbitals, NO_2^- , NO_3^- , NH_2^-, NH_4^+, SCN^- ? **[2011]**

(a) NH_4^+, and NO_3^- (b) SCN^- and NH_2^-

(c) NO_2^- and NH_2^- (d) NO_2^- and NO_3^-

Q.48. Which of te following is least likely to behave as Lewis base? **[2011]**

(a) NH_3 (b) BF_3

(c) OH^- (d) H_2O

Q.49. Which of the following has the minimum bond length? **[2011]**

(a) O_2^- (b) O_2^{2-}

(c) O_2 (d) O_2^+

Q.50. Which one of the following species does not exist under normal conditions? **[2010]**

(a) Be_2^+ (b) Be_2

(c) B_2 (d) Li_2

Q.51. The correct order of increasing bond angles in the following species is **[2010]**

(a) $Cl_2O < ClO_2 < ClO_2^-$

(b) $ClO_2 < Cl_2O < ClO_2^-$

(c) $Cl_2O < ClO_2^- < ClO_2$

(d) $ClO_2^- < Cl_2O < ClO_2$

Q.52. What is the dominant intermolecular force on bond that must be overcome in converting liquid CH_3OH to a gas? **[2009]**

(a) Hydrogen bonding

(b) Dipole-dipole interaction

(c) Covalent bonds

(d) London or dispersion force

Q.53. In which of the following molecules/ions BF_3, NO_2^- , NH_2^- and H_2O, the central atom is sp^2 hybridised? **[2009]**

(a) NO_2^- and NH_2^- (b) NH_2^- and H_2O

(c) NO_2^- and H_2O (d) BF_2 and NO_2^-

Q.54. According to molecular orbital theory which of the following lists rank the nitrogen species in terms of increasing bond order? **[2009]**

(a) $N_2^- < N_2 < N_2^{2-}$ (b) $N_2^{2-} < N_2^- < N_2$

(c) $N_2 < N_2^{2-} < N_2^-$ (d) $N_2^- < N_2^{2-} < N_2$

Q.55. Four diatomic species are listed below in different sequences. Which of these presents the correct order of their increasing bond order? **[2009]**

(a) $O_2^- < NO < C_2^{2-} < He_2^+$

(b) $NO < C_2^{2-} < O_2^- < He_2^+$

(c) $C_2^{2-} < He_2^+ < NO < O_2^-$

(d) $He_2^+ < O_2^- < NO < C_2^{2-}$

Q.56. The correct order of increasing bond angles in the following triatomic species is **[2008]**

(a) $NO_2^- < NO_2^+ < NO_2$

(b) $NO_2^- < NO_2 < NO_2^+$

(c) $NO_2^+ < NO_2 < NO_2^-$

(d) $NO_2^+ < NO_2^- < NO_2$

Q.57. The angular shape of ozone molecule (O_3) consists of **[2008]**

(a) 1 sigma and 2 pi-bonds

(b) 2 sigma and 2 pi-bonds

(c) 1 sigma and 1 pi-bonds

(d) 2 sigma and 1 pi-bonds

Q.58. The correct order of C—O bond length among CO, CO_3^{2-} , CO_2 is **[2007]**

(a) $CO_2 < CO_3^{2-} < CO$

(b) $CO < CO_3^{2-} < CO_2$

(c) $CO_3^{2-} < CO_2 < CO$

(d) $CO < CO_2 < CO_3^{2-}$

Q.59. Which of the following is not a correct statement? **[2006]**

(a) The electron deficient molecules can act as lewis acids

(b) The canonical structures have no real existence

(c) Every AB_5 molecule does infact have square pyramid structure

(d) Multiple bonds are always shorter than corresponding single bond

Q.60. The electronegativity difference between N and F is greater than that between N and Y yet the dipole moment of NH_3 (1.5 D) is larger than that of NF_3 (0.2 D). This is because **[2006]**

(a) in NH_3 as well as in NF_3 , the atomic dipole and bond dipole are in the same direction

(b) in NH_3 the atomic dipole and bond dipole are in the same direction whereas in NF_3 these are in opposite directions.

(c) in NH_3 as well as NF_3, the atomic dipole and bond dipole are in opposite directions
(d) in NH_3 the atomic dipole and bond dipole are in the opposite directions whereas in NF_3, these are in the same directions.

Q.61. Which of the following is not isostructural with $SiCl_4$? **[2006]**
(a) SCl_4 (b) SO_4^{2-}
(c) PO_4^{3-} (d) NH_4^+

Q.62. Which of the following species has linear shape? **[2006]**
(a) NO_2^- (b) SO_2
(c) NO_2^+ (d) O_3

Q.63. Which of the following would have a permanent dipole moment? **[2006]**
(a) BF_3 (b) SiF_4
(c) SF_4 (d) XeF_4

Q.64. In BrF_3 molecule, the lone pairs occupy equatorial positions to minimise **[2004]**
(a) lone pair-bond pair repulsion
(b) bond pair-bond pair repulsion
(c) lone pair-lone pair repulsion and lone pair-bond pair repulsion
(d) lone pair-lone pair repulsion

Q.65. H_2O is dipolar, whereas BeF_2 is not. It is because **[2004]**
(a) the electronegativity of F is greater than that of O
(b) H_2O involves hydrogen bonding whereas BeF_2 is a discrete molecule
(c) H_2O is linear and BeF_2 is angular
(d) H_2O is angular and BeF_2 is linear

Q.66. In regular octahedral molecule, MX_6 the number of X—M—X bond at 180^0 is **[2004]**
(a) 3 (b) 2
(c) 6 (d) 4

Q.67. Strongest hydrogen bonding is shown is **[2004]**
(a) H_2O (b) NH_3
(c) HF (d) H_2S

Q.68. Which of the following statement is not correct for sigma and pi-bonds from between two carbon atoms? **[2003]**
(a) Free rotation of atoms about a sigma bond is allowed but not in case of a pi-bond
(b) Sigma bond determines the direction between carbon atoms but a pi-bond has no primary effect in this regard
(c) Sigma bond is stronger than a pi-bond
(d) Bond energies of sigma and pi-bonds are of the oredr5 of 264 K.J/mol and 347 kJ/mol, respectively

Q.69. Which of the following has $p\pi-d\pi$ - bonding **[2002]**
(a) NO_3^- (b) SO_3^{2-}
(c) BO_3^{3-} (d) CO_3^{2-}

Q.70. In which of the following , bond angle is maximum? **[2001]**
(a) NH_3 (b) NH_4^+
(c) PCl_3 (d) SCl_2

Q.71. The relationship between the dissociation energy of N_2 and N_2^+ is **[2000]**
(a) dissociation energy of N_2^+ > dissociation energy of N_2
(b) dissociation energy of N_2 = dissociation energy of N_2^+
(c) dissociation energy of N_2> dissociation energy of N_2^+
(d) dissociation energy of N_2 can either the lower or higher than the dissociation energy of N_2^+

Q.72. Which one the following is planar ? **[2000]**
(a) XeF_4 (b) XeO_4
(c) XeO_3F (d) XeO_3F_2

Answer Key

1. (a)	2. (d)	3. (c)	4. (b)	5. (6)	6. ()
7. (b, d)	8. (a)	9. (a, c)	10. (b)	11. (F)	12. (b)
13. (a, b)	14. (a, b, d)	15. (4)	16. (a, b)	17. (c)	18. (b)
19. (6)	20. (d)	21. ()	22. (a)	23. ()	24. (c)
25. (a)	26. (d)	27. ()	28. ()	29. (b)	30. (a)
31. (a)	32. (a)	33. (a)	34. (a)	35. (a)	36. (b)
37. (a)	38. (a)	39. (b)	40. (b)	41. (c)	42. (b)
43. (b)	44. (b)	45. (d)	46. (a)	47. (d)	48. (b)
49. (d)	50. (b)	51. (d)	52. (a)	53. (d)	54. (b)
55. (d)	56. (b)	57. (d)	58. (d)	59. (c)	60. (b)
61. (a)	62. (c)	63. (c)	64. (d)	65. (d)	66. (a)
67. (c)	68. (d)	69. (b)	70. (b)	71. (c)	72. (a)

6 THERMODYNAMICS

Study of energy transformation is known as Thermodynamics. In other words the branch of science which deals with the study of different forms of energy and the quantitative relationships between them is known as thermodynamics.

IMPORTANCE OF THERMODYNAMICS

The importance of thermodynamics lies in the follows facts :

(i) **It helps us to predict whether any given chemical reaction will occur under the given set of conditions.**

(ii) It helps in predicting the extent of reaction before the equilibrium is attained.

LIMITATIONS OF THERMODYNAMICS

The limitations of thermodynamics are as follows :

(i) It does not tell anything about the rate at which the process takes place.

(ii) It does not tell anything about the mechanism of the process (i.e., the path followed by the process).

(iii) It does not deals with individual atom or molecules.

TYPES OF SYSTEM

Further the systems are classified according to the movements of matter and energy in or out of the system.

1. Open system **2.** Closed system **3.** Isolated system

1. **OPEN SYSTEM:** In an open system, there is exchange of energy and matter between system and surroundings
   e.g. The presence of reactants in an open beaker is an example of an open system.
2. **CLOSED SYSTEM:** In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings.
   The presence of reactants in a closed vessel made of conducting material
   e.g.,copper or steel is an example of a closed system.
3. **ISOLATED SYSTEM:** In an isolated system, there is no exchange of energy or matter between the system and the surroundings.
   e.g. The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.
4. **MACROSCOPIC SYSTEM:** A system containing a large no. of chemical species (atoms, ions or molecules) is called macroscopic system.

MACROSCOPIC PROPERTIES

The properties of the system which arise from the collective behaviour of large no. of species are called macroscopic properties. E.g. pressure, temperature, volume, viscosity etc.

Macroscopic properties like pressure and temperature do not change with time for a system in equilibrium state.

These are further classified into two types as follows :

(1) Extensive properties.

(A) **These are those properties which depend upon the quantity of the matter contained in the system.**

(2) Intensive properties.

(A) **These are those properties which depend only upon the nature of the substance and are independent of the amount of the substance present in the system.**

STATE OF A SYSTEM

The state of the system is specified by state functions or state variables.
The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties.
The state of a gas by quoting its pressure (*p*), volume (*V*), temperature (*T*), amount (*n*) etc.

STATE VARIABLES

If any of these properties of the system changes, the system is said to be in different state, i.e., the state of the system changes. That is why these properties of a system are called state variables.
e.g.Variables like *p*, *V*, *T* are called state variables or state functions because their values depend only on the state of the system and not on how it is reached.

STATE FUNCTIONS

The thermodynamics parameters which depend only upon\ the initial and final state of the system and are independent of the manner as to how the change is brought about are called state functions.
e.g.Examples, of physical quantities which are state function include pressure, volume, temperature, internal energy, enthalpy, entropy, free energy etc.

THERMODYNAMIC PROCESS

The operation which brings about the changes in the state of the system is termed as thermodynamic process.

1. **Isothermal process :** It is the process which is carried out at constant temp. **($\Delta T = 0$).**
2. **Adiabatic process :** It is the process in which no heat exchange occurs between the system and the surroundings **($q = 0$).**

DIFFERENCES BETWEEN REVERSIBLE AND IRREVERSIBLE PROCESS

S.No.	Reversible Process	Irreversible Process
1	The process is carried out infinitesimally slowly, i.e., difference between the driving force and the opposing force is very-very small.	This process is not carried out infinitesimally slowly but is carried out rapidly, i.e., the difference between the driving force and the opposing force is quite large.
2	At any stage during the process, equilibrium is not disturbed.	Equilibrium may exist only after the completion of the process.
3	It takes infinite time for completion	It takes finite time for completion
4	It is only imaginary and cannot be achieved in actual practice.	These process actually occur in nature.
5	Work obtained in this process is maximum.	Work obtained in this process is not maximum.

THERMODYNAMIC QUANTITIES

1. INTERNAL ENERGY
2. ENTHALPY
3. ENTROPY
4. GIBB 'S FREE ENERGY

INTERNAL ENERGY

1. The energy thus stored within a substance (or a system) is called its internal energy.

   OR

   A quantity which represents the total energy of the system.
2. **It is denoted by U or E**
3. It may be chemical, electrical, mechanical or any other type of energy you may think of, the sum of all these is the energy of the system.
4. It is the sum of different types of energies associated with atoms and molecules such as electronic energy (E_e), nuclear energy (E_n), chemical bond energy (E_c), potential energy (E_p) and kinetic energy (E_k) which is further the sum of translational energy (E_t), vibrational energy (E_v) and rotational energy (E_r).

   $U \text{ or } E = E_e + E_n + E_c + E_p + E_k$
5. **Internal energy change.** It is not possible to find its absolute value but change of internal energy when the reactants change into products or when a system changes from initial state to the final state is easily measurable and is represented by $\Delta U \text{ or } \Delta E$ .If the internal energy of a system in the initial state is U_1 and in the final state, it is U_2, then the change of internal energy (ΔU) may be given by

   $\Delta U = U_2 - U_1$

   Similarly, in a chemical reaction, if U_R is the internal energy of the reactants and U_p is the internal energy of the products, then energy change accompanying the process would be

   $\Delta U = U_p - U_R$

FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is simply the law of conservation of energy which states that
Energy can neither be created nor destroyed although it may be converted from one form to another.

or

The total energy of the universe (i.e., the system and the surroundings) remains constant, although it may undergo transformation from one form to the other.

or

FORMULAE BASED ON FIRST LAW OF THERMODYNAMICS

1. **ISOTHERMAL PROCESS:**

   $\Delta T = 0; \Delta U = 0$

   $\therefore q = -W$

   Work done by the system at the expence of heat absorbed
2. **ADIABATIC PROCESS:**

   $q = 0$

   $\Delta U = W$

   Work done by the system at the expence of internal energy
3. **CYCLIC PROCESS:**

   $\because \Delta U = 0$

   $\therefore q = -W$
4. **ISOCHORIC PROCESS:**

   $\Delta V = 0$

   $P \times \Delta V = 0$

   $q_v = \Delta U$
5. ISOBARIC PROCESS

   $\Delta P = 0$

   $q_p = \Delta H$

HEAT

heat is another mode of energy exchanged between the system and the surroundings as a result of the difference of temperature between them.

It is usually represented by the letter '*q*'.

Note: Heat given to the system (q = +ve)
Heat given by the system (q = −ve)

Units of '*q*'. Heat is usually measured in terms of 'calories'. **A calorie is defined as the quantity of heat required to raise the temperature of one gram of water through 1°C (in the vicinity of 15°C)**

In the **S.I. system**, heat is expressed in terms of **joules**. The two types of units are related to each other as under :

1 calorie = 4.184 joules

which means the same thing as

1 joule = 0.2390 calories

ENTHALPY

A useful new state function. We know that the heat absorbed at constant volume is equal to change in the internal energy i.e., $\Delta U = q_v$. But most of chemical reactions are carried out not at constant volume, but in flasks or test tubes under constant atmospheric pressure. We need to define another state function which may be suitable under these conditions.

We may write equation as :

$$\Delta V = q_p + w$$

$$\because\ w = -p\Delta V$$

$$\Delta U = q_p - p\Delta V \text{ at constant pressure,}$$

where q_p is heat absorbed by the system and $-p\Delta V$ represent expansion work done by the system.

Let us represent the initial state by subscript 1 and final state by 2

We can rewrite the above equation as

$$U_2 - U_1 = q_p - p(V_2 - V_1)$$

On rearranging, we get

$$q_p = (U_2 + pV_2) - (U_1 + pV_1) \qquad ....(6.6)$$

Now we can define another thermodynamic function, the enthalpy H [Greek word *enthalpien*, to warm or heat content] as :

$$H = U + pV \qquad ....(6.7)$$

so, equation (6.6) becomes

$$q_p = H_2 - H_1 = \Delta H$$

Although q is a path dependent function, H is a state function because it depends on U, p and V, all of which are state functions. Therefore, ΔH is independent of path. Hence, q_p is also independent of path. For finite changes at constant pressure, we can write equation 6.7 as

$$\Delta H = \Delta U + \Delta pV$$

Since p is constant, we can write

$$\Delta H = \Delta U + p\Delta V \qquad ...(6.8)$$

RELATIONSHIP BETWEEN HEAT OF REACTION AT CONSTANT PRESSURE AND THAT AT CONSTANT VOLUME

Let us consider a reaction involving gases. If V_A is the total volume of the gaseous reactants, V_B is the total volume of the gaseous products, n_A is the number of moles of gaseous reactants and n_B is the number of moles of gaseous products, all at constant pressure and temperature, then using the ideal gas law, we write,

$$pV_A = n_A RT \text{ and } pV_B = n_B RT$$

Thus, $pV_B - pV_A = n_B RT - n_A RT = (n_B - n_A)RT$

or $p(V_B - V_A) = (n_B - n_A)RT$

or $p\Delta V = \Delta n_g RT \qquad ....(6.9)$

Here, Δng refers to the number of moles of gaseous products minus the number of moles of gaseous reactants.

Substituting the value of $p\Delta V$ from equation 6.9 in equation 6.8, we get

$$\Delta H = \Delta U + \Delta n_g RT \qquad ....(6.10)$$

The equation 6.10 is useful for calculating ΔH from ΔU and *vice versa.*

HEAT CAPACITY, SPECIFIC HEAT CAPACITY AND MOLAR HEAT CAPACITY

The heat capacity of a system is defined as the amount of heat required to raise the temperature of the system through 1°C.

Thus, if q is the amount of heat supplied to a system and as a result, if the temperature of the system rises from T_1 and T_2, then the heat capacity (C) of the system is given by

$$C = \frac{q}{T_2 - T_1 =} = \frac{q}{\Delta T} \qquad \ldots\text{(i)}$$

If δq is small amount of heat absorbed by a system which raises the temperature of the system by a small amount dT (say from T to $T + dT$), then the heat capacity of the system will be given by

$$C = \frac{\delta q}{dT} \qquad \ldots\text{(ii)}$$

Types of heat capacities or molar heat capacities

Since 'q' is not a state function and depends upon the path followed, therefore C is also not a sate function. Hence, to know the value of C, the conditions such as constant volume or constant pressure have to be specified which define the path.

Thus, there are two types of hat capacities, which are

- **(i)** Heat capacity at constant volume (represented by C_v).
- **(ii)** Heat capacity at constant pressure (represented by C_p).

The heat supplied to a system to raise its temperature through 1°C keeping the volume of the system constant is called that capacity at constant volume. Similarly,

the heat supplied to a system to raise its temperature through 1°C keeping the external pressure constant is called heat capacity at constant pressure.

RELATIONSHIP BETWEEN C_p AND C_v FOR AN IDEAL GAS

At constant volume, the heat capacity, C is denoted by C_V and at constant pressure, this is denoted by C_p.

Let us find the relationship between the two.

We can write equation for heat, q

at constant volume as $q_v = C_V\ q_V = C_V\Delta T = \Delta U$

at constant pressure as $q_p = C_p\Delta T = \Delta H$

The difference between C_p and C_V can be derived for an ideal gas as:

For a mole of an ideal gas, $\Delta H = \Delta U + \Delta(pV)$

$$= \Delta U + \Delta(RT)$$

$$= \Delta U + R\Delta T$$

$$\Delta H = \Delta U + R\Delta T$$

On putting the values of ΔH and ΔU, we have

$$C_p\Delta T = C_V\Delta T + R\Delta T$$

$$C_p = C_v + R$$

$$\boxed{\mathrm{C_p - C_v = R}}$$

For n moles of the gas

$$\boxed{\mathrm{C_p - C_v = nR}}$$

MEASUREMENT OF ΔU AND ΔH : CALORIMETRY

1. Energy changes associated with chemical or physical processes can be measured by an experimental technique called **calorimetry.**
2. In calorimetry, the process is carried out in a vessel called calorimeter, which is immersed in a known volume of a liquid. Knowing the heat capacity of the liquid in which calorimeter is immersed and the heat capacity of calorimeter, it is possible to determine the heat evolved in the process by measuring temperature changes.
3. Measurements are made under two different conditions:
   (i) at constant volume, (q_v) or (ΔU)
   (ii) at constant pressure, (q_p) or (ΔH)

(A) ΔU MEASUREMENTS.

For chemical reactions, heat absorbed at constant volume, is measured in a **bomb calorimeter**

HEAT OF REACTION

OR

ENTHALPY OF REACTION

OR

ENTHALPY CHANGE OF REACTION

In a chemical reaction, reactants are converted into products and is represented by,

Reactants $\longrightarrow$ Products

The enthalpy change accompanying a reaction is called the reaction enthalpy.

The enthalpy change of a chemical reaction, is given by the symbol $\Delta_r H$

Let us consider the following two examples :

$CH_4(g)+2O_2(g)\longrightarrow CO_2(g)+2H_2O(g)$, $\Delta H=-890.4\,kJ\,mol^{-1}$

Enthalpy of reaction,

ΔH = Sum of enthalpies of products – Sum of enthalpies of reactants.

LATEST IUPAC SYMBOLS FOR ENTHALPY CHANGES

ENTHALPY OF REACTION IS REPRESENTED BY $\Delta_r H$
ENTHALPY OF COMBUSTION IS REPRESENTED BY $\Delta_c H$
ENTHALPY OF FORMATION IS REPRESENTED BY $\Delta_f H$
ENTHALPY OF VAPORIZATION IS REPRESENTED BY $\Delta_{vap} H$

The standard state values are represented by putting the superscript $\ominus$ or o on H,
i.e., $\Delta_f H^{\ominus}$ or $\Delta_r H^{\circ}, \Delta_c H^{\ominus}$ or $\Delta_c H^{\circ}, \Delta_f H^{\ominus}$ or $\Delta_f H^{\circ}$ etc.

A few important heats of reactions are as follows :

1. **ENTHALPY OF COMBUSTION :**
   The enthalpy of combustion of a substance is defined as the heat change (usually the heat evolved) when 1 mole of substance is completely burnt or oxidized in oxygen
   e.g., $CH_4(g)+2O_2(g)\longrightarrow CO_2(g)+2H_2O(g)$, $\Delta_c H=-890.4\,kJ\,mol^{1}$
   Standard enthalpy of combustion is the amount of heat evolved when one mole of the substance under standard conditions (298 K, 1 bar pressure) is completely burnt to form the products also under standard conditions. It is represented by $\Delta_c H^{\circ}$.
2. **ENTHALPY OF FORMATION :**
   The enthalpy of formation of a substance is defined as the heat change, i.e., heat evolved or absorbed

when 1 mole of the substance is formed from its elements under given conditions of temperature and pressure. It is usually represented by $\Delta_f H$.

3. **STANDARD ENTHALPY OF FORMATION:**
The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. Its symbol is $\Delta_f H^0$.

4. **ENTHALPY OF SOLUTION :**
Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent.
The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible.
The dissolution of an ionic compound in water takes place in the following two steps :

Step 1. Dissociation of the ionic solid into free ions. The energy required for this process is called lattice energy or lattice enthalpy.

Step 2. Hydration of the ions (or in general, called salvation of the ions, if solvent other than water is used). The energy released in this process is called hydration energy or enthalpy hydration.

$$\begin{tikzcd}
AB\,(s) \arrow[rr, "\Delta_{sol}H"] \arrow[dr, "\text{Step 1}", "\Delta_{lattice}H"'] & & A^+\,(aq) + B^-\,(aq) \\
& A^+\,(g) + B^-\,(g) \arrow[ur, "\text{Step 2}", "\Delta_{hyd}H"'] &
\end{tikzcd}$$

Thus, $\Delta_{sol}H = \Delta_{lattice}H + \Delta_{hyd}H$

LATTICE ENTHALPY AND ITS CALCULATION (BORN-HABER CYCLE)

Lattice enthalpy of an ionic compound is the enthalpy change that occurs when one mole of the ionic compound dissociates into ions in the gaseous state.

5. **ENTHALPY OF ATOMIZATION :**
When one mole of a given substance dissociates into gaseous atoms, the enthalpy change accompanying the process is called enthalpy of atomization.
It is represented by the symbol $\Delta_a H^\circ$. For example,

$$H_2(g) \longrightarrow 2H(g),\ \Delta_a H^\circ = 435.0\,kJ\,mol^{-1}$$

$$CH_4(g) \longrightarrow C(g) + 4H(g),\ \Delta_a H^\circ = 1665\,kJ\,mol^{-1}$$

$$Na(s) \longrightarrow Na(g),\ \Delta_a H^\circ = 108.4\,kJ\,mol^{-1}$$

6. **ENTHALPY OF IONIZATION :**
When a covalent compound on dissolution in water splits to produce ions in the solution, the enthalpy of change accompanying the process is called enthalpy of ionization.

7. **ENTHALPY OF FORMATION OF IONS :**
When an ionic solid is dissolved in water, free ions are produced in the aqueous solution. For the calculation of enthalpy of formation of an ion in the aqueous solution, enthalpy of formation of H^+ ion in the aqueous solution is taken as zero.

8. **ENTHALPY OF HYDRATION :**
The amount of enthalpy change (i.e., the heat evolved or absorbed) when one mole of the anhydrous salt combines with the required number of moles of water so as to change into the hydrated salt, is called the enthalpy of hydration or heat of hydration.

9. **ENTHALPY OF HYDROGENATION :**
The amount of enthalpy change that takes pale when one mole of an unsaturated organic compound is completely hydrogenated is called enthalpy of hydrogenation.

10. **ENTHALPY OF ALLOTROPIC TRANSFORMATION :**

The enthalpy change that takes place when one mole of one form of an allotropic modification changes to another is called enthalpy of allotropic transformation.

11. ENTHALPY CHANGES DURING PHASE TRANSITION :

1. ENTHALPY OF FUSION :

Enthalpy of fusion is the enthalpy change accompanying the transformation of one mole of a solid substance into its liquid state at its melting point. It is also called molar enthalpy of fusion.

12. ENTHALPY OF VAPORIZATION :

It is the amount of heat required to convert one mole of a liquid into its vapour state at its boiling point. It is called molar enthalpy of vaporization.

13. ENTHALPY OF SUBLIMATION :

Sublimation is a process in which a solid on heating changes directly into gaseous state below its melting point.

Enthalpy of sublimation of a substance is the enthalpy change accompanying the conversion of 1 mole of a solid directly into vapour phase at a given temperature below its melting point.

BOND ENTHALPY OR BOND ENERGY

We know that energy is evolved when a bond is formed and energy is required for the dissociation of a bond. Hence, bond energy is defined as follows :

Bond energy is the amount of energy released when one mole of bonds are formed from the isolated atoms in the gaseous state or the amount of energy required to dissociate one mole of bonds present between the atoms in the gaseous molecules. It is represented by $\Delta_b H$ *or* $\Delta_{bond} H$.

For diatomic molecules like $H_2, O_2, N_2, Cl_2, HCl, HF$ etc., the bond energies are equal to their dissociation energies. These may also be called as their enthalpies of atomization.

For polyatomic molecules, the bond energy of a particular bond is not the same when present in different types of compounds (e.g., bond energy of C – Cl is not same in $CH_3Cl, CH_2Cl, CHCl_3, CCl_4$). In fact, bond energy of a particular type of bond is not same even in the same compound (e.g., in CH_4, the bond energy for first, second, third and fourth C – H bonds are not equal; their values being + 427 + 439 + 452 and + 347 kJ mol^{-1} respectively). Their total sum gives the enthalpy of atomization of $CH_4(g)$. Thus,

$$\Delta_a H^\circ (CH_4, g)$$

$$= 427 + 439 + 452 + 347 = 1667 \text{ kJ } mol^{-1}$$

BOND ENTHALPIES

Formulas and Units :

(i) $\Delta_r H = \sum \Delta_f H(\text{Products}) - \sum \Delta_f H(\text{Reactants})$

(ii) $\Delta_r H = \sum$ Bond Energies or Enthalpies of Reactants – $\sum$ Bond Energies or enthalpies of Products

$= \sum B.E.(\text{Reactants}) - \sum B.E.(\text{Products})$ **(Note carefully)**

Limitations of the First Law of Thermodynamics-introduction of the Second Law of Thermodynamics

It provides no information concerning the spontaneity or feasibility of the process, ie., whether the process is possible or not.

ENTROPY

This is another thermodynamic function used to express the extent of disorder in a system. It is usually represented by 'S' and is defined as follows :

Entropy is a measure of randomness or disorder of the system

The greater the randomness, the higher is the entropy. Evidently, for a given substance, the crystalline solid state has the lowest entropy, the gaseous state has the highest entropy and the liquid state has the entropy in-between the two. Like internal energy and enthalpy, it is a state function. The change in its value during a process, called the entropy

change (represented by ΔS) is given by
$\Delta S = S_2 - S_1 = \sum S_{products} - \sum S_{reactants}$.

II LAW OF THERMODYNAMICS

The entropy of the universe always increase in the course of every spontaneous change.

Combined statement of I And II law of thermodynamics : The energy of the universe is conserved whereas the entropy of the universe increases in any natural process.

ENTROPY CHANGES DURING PHASE TRANSFORMATIONS

(1) **entropy of fusion.**
(2) **Entropy of vaporization.**
(3) **Entropy of sublimation.**

QUESTIONS

NCERT EXERCISE & EXAMPLES

Internal Energy

1. Express the change in internal energy of a system when

(i) No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have ?

(ii) No work is done on the system, but q amount of heat is taken out from the system and given to the surroundings. What type of wall does the system have ?

(iii) w amount of work is done by the system and q amount of heat is supplied to the system. What type of system would it be ?

2. Two litres of an ideal gas at a pressure of 10 atm expands isothermally into a vacuum until its total volume is 10 litres. How much heat is absorbed and how much work is done in the expansion ?

3. Consider the same expansion, but this time against a constant external pressure of 1 atm.

4. Consider the same expansion, to a final volume of 10 litres conducted reversibly.

5. If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1 bar and 100°C is 41 kJ mol^{-1}. Calculate the internal energy change, when

(i) 1 mol of water is vapourised at 1 bar pressure and 100°C.

(ii) 1 mol of water is converted into ice.

6. A swimmer coming out from a pool is covered with a film of water weighing about 18 g. How much heat must be supplied to evaporate this water at 298 K ? Calculate the internal energy of vapourisation at 100°C.

$\Delta_{vap}H^{\ominus}$ for water at 373 K = 40.66 kJ mol^{-1}

Internal Energy

7. 1 g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation

$$\textbf{C (graphite)} + O_2(g) \rightarrow CO_2(g)$$

During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7 kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm ?

Entropy

8. Predict in which of the following, entropy increases/decreases :

(i) A liquid crystallizes into a solid.

(ii) Temperature of a crystalline solid is raised from 0 K to 115 K.

(iii) $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

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

9. For oxidation of iron,

$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

Entropy change is -549.4 JK^{-1} mol^{-1} at 298 K. Inspite of negative entropy change of this reaction, why is the reaction spontaneous ?

($\Delta_f H^{\ominus}$ for this reactions -1648×10^3 J mol^{-1})

Hess Law

10. The combustion of one mole of benzene takes place at 298 K and 1 atm. After combustion, $CO_2(g)$ and $H_2O(l)$ are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation, $\Delta_f H^{\ominus}$ of benzene. Standard enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are -393.5 kJ mol^{-1} and -285.83 kJ mol^{-1} respectively.

Gibb's Free Energy

11. Calculate $\Delta_r G^{\ominus}$ for conversion of oxygen to ozone, $3/2\ O_2(g) \rightarrow O_3(g)$ at 298 K. If K_p for this conversion is 2.47×10^{-29}.

12. Find out the value of equilibrium constant for the following reaction at 298 K.

$$2NH_3(g) + CO_2(g) \rightleftharpoons NH_2CONH_2(aq) + H_2O(l)$$

Standard Gibbs energy change, $\Delta_r G^{\ominus}$ at the given temperature is -13.6 kJ mol^{-1}.

13. At 60°C, dinitrogen tetroxide is fifty percent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

SOLUTIONS

NCERT EXERCISE & EXAMPLES

Sol.1 (i) $\Delta U = w_{ad}$, wall is adiabatic

(ii) $\Delta U = -q$, thermally conducting walls

(iii) $\Delta U = q - w$, closed system.

Sol.2 We have $q = -w = p_{ex}(10 - 2) = 0\,(8) = 0$

No work is done; no heat is absorbed.

Sol.3 We have $q = -w = p_{ex}(8) = 8$ litre-atm

Sol.4 We have $q = -w = 2.303 \times 10 \log 10/2$

$= 16.1$ litre-atm

Sol.5 (i) The change $H_2O(l) \rightarrow H_2O(g)$

$\Delta H = \Delta U + \Delta n_g RT$, substituting the values, we get

$\Delta U = 41.00\ kJ\ mol^{-1} - 1 \times 8.3\ J\ mol^{-1}\ K^{-1} \times 373\ K$

$= 41.00\ kJ\ mol^{-1} - 3.096\ kJ\ mol^{-1}$

$= 37.904\ kJ\ mol^{-1}$

(ii) The change $H_2O(l) \rightarrow H_2O(s)$

There is negligible change in volume,

So, we can put $p\Delta V = \Delta n_g RT = 0$ in this case,

$\Delta H = \Delta U$

So, $\Delta U = 41.00\ kJ\ mol^{-1}$

Sol.6 We can represent the process of evapouration as

$18\ g\ H_2O(l) \xrightarrow{\text{Vapouration}} 18\ g\ H_2O(g)$

No. of moles in 18 g $H_2O(l)$ is

$$= \frac{18g}{18\ g\ mol^{-1}} = 1\ mol$$

$\Delta_{vap}U = \Delta_{vap}H^\ominus - p\Delta V$

$= \Delta_{vap}H^\ominus - \Delta n_g RT$

(assuming steam behaving as an ideal gas),

$\Delta_{vap}H^\ominus - \Delta n_g RT = 40.66\ kJ\ mol^{-1}$

$-(1)\,(8.314\ JK^{-1}\ mol^{-1})\,(373\ K)\,(10^{-3}\ kJ\ J^{-1})$

$\Delta_{vap}U^\ominus = 40.66\ kJ\ mol^{-1} - 3.10\ kJ\ mol^{-1}$

$= 37.56\ kJ\ mol^{-1}$

Sol.7 Suppose q is the quantity of heat from the reaction mixture and C_v is the heat capacity of the calorimeter, then the quantity of heat absorbed by the calorimeter.

$q = C_v \times \Delta T$

Quantity of heat from the reaction will have the same magnitude but opposite sign because the heat lost by the system (reaction mixture) is equal to the heat gained by the calorimeter.

$q = -C_v \times \Delta T$

$= -20.7\ kJ/K \times (299 - 298)\ K$

$= -20.7\ kJ$

(Here, negative sign indicates the exothermic nature of the reaction)

Thus, ΔU for the combustion of the 1g of graphite

$= -20.7\ kJ\ K^{-1}$

For combustion of 1 mol of graphite,

$$= \frac{12.0\,g\,mol^{-1} \times (-20.7\,kJ)}{1g}$$

$= -2.48 \times 10^2\ kJ\ mol^{-1}$

Sol.8 (i) After freezing, the molecules attain an ordered state and therefore, entropy decreases.

(ii) At 0 K, the constituent particles are static and entropy is minimum. If temperature is raised to 115 K

(iii) Reactant, $NaHCO_3$ is a solid and it has low entropy. Among products there are one solid and two gases. Therefore, the products represent a condition of higher entropy.

(iv) Here one molecule gives two atoms i.e., number of particles increases leading to more disordered state. Two moles of H atoms have higher entropy than one mole of dihydrogen molecule.

Sol.9 One decides the spontaneity of a reaction by considering

ΔS_{total} ($\Delta S_{sys} + \Delta S_{surr}$). For calculating ΔS_{surr}, we have to consider the heat absorbed by the surroundings which is equal to $-\Delta_r H^\ominus$. At temperature T, entropy change of the surroundings is

$$\Delta S_{surr} = -\frac{\Delta_r H^\ominus}{T} \quad \text{(at constant pressure)}$$

$$= -\frac{(-1648 \times 10^3\ J\ mol^{-1})}{298\ K}$$

$= 5530\ JK^{-1}\ mol^{-1}$

Thus, total entropy change for this reaction

$\Delta_r S_{total} = 5530\ JK^{-1}\ mol^{-1} + (-549.4\ JK^{-1}\ mol^{-1})$

$= 4980.6\ JK^{-1}\ mol^{-1}$

This shows that the above reaction is spontaneous.

Sol.10 The formation reaction of benzene is given by :

$6C\ (graphite) + 3H_2(g) \rightarrow C_6H_6(l);\ \Delta_f H^\ominus = ?$ ….(i)

The enthalpy of combustion of 1 mol of benzene is :

$C_6H_6(l) + 15/2\ O_2 \rightarrow 6CO_2(g) + 3H_2O(l);$

$\Delta_c H^\ominus = -3267.0\ kJ\ mol^{-1}$ ….(ii)

The enthalpy of combustion of 1 mol of $CO_2(g)$:
$C\ (graphite) + O_2(g) \rightarrow CO_2(g);$
$\Delta_f H^{\ominus} = -393.5\ kJ\ mol^{-1}$ ....(iii)
The enthalpy of combustion of 1 mol of $H_2O(l)$ is :
$H_2(g) + ½\ O_2(g) \rightarrow H_2O(l);$
$\Delta_f H^{\ominus} = -285.83\ kJ\ mol^{-1}$ ....(iv)
Multiplying eqn. (iii) by 6 and eqn. (iv) by 3 we get :
$6C\ (graphite) + 6O_2(g) \rightarrow 6CO_2(g);$
$\Delta_f H^{\ominus} = -2361\ kJ\ mol^{-1}$
$3H_2(g) + 3/2\ O_2(g) \rightarrow 3H_2O(l);$
$\Delta_f H^{\ominus} = -857.49\ kJ\ mol^{-1}$
Summing up the above two equations :
$6C\ (graphite) + 3H_2(g) + 15/2\ O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l);$
$\Delta_f H^{\ominus} = -3218.49\ kJ\ mol^{-1}$ ....(v)
Reversing equation (ii);
$6CO_2(g) + 3H_2O(l) \rightarrow C_6H_6(l) + 15/2\ O_2(g);$
$\Delta_f H^{\ominus} = 3267.0\ kJ\ mol^{-1}$ ....(vi)
Adding equations (v) and (vi), we get
$6C\ (graphite) + 3H_2(g) \rightarrow C_6H_6(l);$
$\Delta_f H^{\ominus} = 48.51\ kJ\ mol^{-1}$

Sol.11 We know $\Delta_r G^{\ominus} = -2.303\ RT \log K_p$ and $R = 8.314\ JK^{-1}\ mol^{-1}$
Therefore, $\Delta_r G^{\ominus} = -2.303\ (8.314\ JK^{-1}\ mol^{-1}) \times (298\ K)\ (\log 2.47 \times 10^{-29})$
$= 163000\ J\ mol^{-1}$
$= 163\ kJ\ mol^{-1}$.

Sol.12 We know,

$$\log K = \frac{-\Delta_r G^{\ominus}}{2.303\ RT}$$

$$= \frac{(-13.6 \times 10^3\ J\ mol^{-1})}{2.303\ (8.314\ JK^{-1} mol^{-1})\ (298\ K)} = 2.38$$

Hence $K = \text{antilog } 2.38 = 2.4 \times 10^2$.

Sol.13 $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
If N_2O_4 is 50% dissociated, the mole fraction of both the substances is given by

$$x_{N_2O_4} = \frac{1-0.5}{1+0.5};\quad x_{NO_2} = \frac{2\times 0.5}{1+0.5}$$

$$x_{N_2O_4} = \frac{0.5}{1.5}\times 1\ atm,\quad x_{NO_2} = \frac{1}{1.5}\times 1\ atm.$$

The equilibrium constant K_p is given by

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{1.5}{(1.5)^2(0.5)}$$

$= 1.33$ atm.
Since, $\Delta_r G^{\ominus} = -RT \ln K_p$

$\Delta_r G^{\ominus} = (8.314 JK^{-1} mol^{-1}) \times (333 K) \times (2.303 K) \times (0.1239 K)$
$= -763.8\ kJ\ mol^{-1}$.

QUESTION ALIKE

Based on Calculation of Entropy Change

1. Calculate the entropy change involved in conversion of one mole (18 g) of solid ice at 273 K to liquid water at the same temperature (latent heat of fusion = 6025 J mol^{-1})

2. Calculate the entropy change involved in the conversion of one mole of liquid water at 373 K to vapour at the same temperature (latent heat of vaporization of water $\ddot{A}_{vap}\mathbf{H}$ = 2.257 kJ/g).

Based on Calculation of Ä$_r$G° from Ä$_f$G° Values and on the Relation Ä$_r$G° = –2.303 RTlog K

3. Calculate the standard free energy change for the reactions

$$4NH_3(g)+5O_2(g)\longrightarrow 4NO(g)+6H_2O(l)$$

Given that the standard free energies of formation $(\ddot{A}_f G^\circ)$ for $NH_3(g), NO(g)$ and $H_2O(l)$ are – 16.8, + 86.7 and – 237.2 kJ mol^{-1} respectively. Predict the feasibility of the above reaction at the standard state.

4. For the equilibrium

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

at 298 K, $k_c = 1.8\times10^{-7}$. What is $\ddot{A}G^\circ$ for the reaction ? (R = 8.314 J K^{-1} mol^{-1})

5. Calculate the equilibrium constant, K of the following reaction at 400 K ?

$$2NOCl(g)\rightleftharpoons 2NO(g)+Cl_2(g)$$

Given that $\ddot{A}_r H^\circ = \mathbf{80.0\,kJ\,mol^{-1}}$

and $\ddot{A}_r S^\circ = \mathbf{120\,J\,K^{-1}\,mol^{-1}}$ **at 400 K.**

Based on II Law of Thermodynamics

6. Predict in which of the following, entropy increases/decreases :
   (i) A liquid crystallizes into a solid.
   (ii) Temperature of a crystalline solid is raised from 0 K to 115 K.
   (iii) $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$
   (iv) $H_2(g) \rightarrow 2H(g)$

7. For oxidation of iron,
$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$
Entropy change is –549.4 JK^{-1} mol^{-1} at 298 K. Inspite of negative entropy change of this reaction, why is the reaction spontaneous ? ($\Delta_f H^\ominus$ for this reactions -1648×10^3 J mol^{-1})

Based on Enthalpy

8. If water vapour is assumed to be perfect gas, molar enthalpy change at 1 bar and 100°C is 41 kJ mol^{-1}. Calculate the internal energy change when
   (i) 1 mol of water is vaporized at 1 bar pressure and 100°C.
   (ii) 1 mol of water is converted into ice.

Based on Internal Energy and First Law of Thermodynamics

9. Choose the correct answer.
A thermodynamic state function is a quantity.
   (i) used to determine heat changes
   (ii) whose value is independent of path
   (iii) used to determine pressure volume work
   (iv) whose value depends on temperature only.

10. For the process to occur under adiabatic conditions, the correct condition is :
   (i) ΔT = 0 (ii) Δp = 0
   (iii) q = 0 (iv) w = 0

11. In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process ?

12. A 5-litre cylinder contained 10 moles of oxygen gas at 27°C. Due to sudden leakage through the hole, all the gas escaped into the atmosphere and the cylinder got empty. If the atmospheric pressure is 1.0 atmosphere, calculate the work done by the gas.

Based on Specific Heat

13. Calculate the number of kJ necessary to raise the temperature of 60.0 g of aluminium from 35 to 55°C. Molar heat capacity of Al is 24 J mol^{-1} K^{-1}.

QUESTION ALIKE SOLUTIONS

Sol.1 Entropy change for ice → water is given by

$$\Delta_f S = \frac{\Delta_f H}{T_f}$$

Here, $\Delta_f H = 6025\, J\, mol^{-1}$, $T_f = 273\, K$

$$\therefore\ \Delta_f S = \frac{6025\, J\, K^{-1}\, mol^{-1}}{273\, K}$$

$= \mathbf{22.1\ J\ K^{-1}\ mol^{-1}}$

Sol.2 For the conversion of water → vapour, the entropy change is given by

$$\Delta_{vap} S = \frac{\Delta_{vap} H}{T_b}$$

Here, $\Delta_{vap} H = 2.257\, kJ / g$

$= 2.257 \times 18\, kJ / mol = 40.626\, kJ / mol$

$T_b = 373\, K$

$$\therefore\ \Delta_{vap} S = \frac{40.626\, kJ\, mol^{-1}}{373\, K}$$

$= 0.1089\, kJ\, K^{-1} mol^{-1}$ $= \mathbf{108.9\ J\ K^{-1}\ mol^{-1}}$

Sol.3 Here, we are given

$\Delta_f G^\circ (NH_3) = -16.8\, kJ\, mol^{-1}$

$\Delta_f G^\circ (NO) = +86.7\, kJ\, mol^{-1}$

$\Delta_f G^\circ (H_2O) = -237.2\, kJ\, mol^{-1}$

$$\Delta_r G^\circ = \sum \Delta_f G^\circ (\text{Products}) - \sum \Delta_f G^\circ (\text{Reactants})$$

$= \left[4 \times \Delta_f G^\circ (NO) + 6 \times \Delta_f G^\circ (H_2O)\right]$

$- \left[4 \times \Delta_f G^\circ (NH_3) + 5 \times \Delta_f G^\circ (O_2)\right]$

$= \left[4 \times (-16.8) + 5 \times 0\right]$ $= \mathbf{-1009.2\ kJ}$

Since $\Delta_f G^\circ$ is negative, the process is feasible.

Sol.4 $K_p = K_c (RT)^{\Delta n}$

Here $\Delta n = n_p - n_r = 2 - 1 = 1$,

$T = 298\, K, R = 8.314\, J\, K^{-1}\, mol^{-1}$

$\therefore\ K_p = (1.8 \times 10^{-7})(8.314 \times 298) = 4.46 \times 10^{-4}$

$\Delta_r G^\circ = -2.303\, RT \log K_p$

$= -2.303 \times 8.314 \times 298 \times \log(4.46 \times 10^{-4})$

$= 19118.6\, J\, mol^{-1}$ $= \mathbf{19.12\ kJ\ mol^{-1}}$

Sol.5 $\Delta_r G^\circ = \Delta_r H^\circ - T\, \Delta_r S^\circ$

$= 80000 J - 400 \times 120\, J = 32000\, J$

Now, $\Delta_r G^\circ = -2.303\, RT \log K$

$\therefore\ 32000 = -2.303 \times 8.314 \times 400 \times \log K$

or $\log K = -4.1782 = \bar{5}.8218$

$\therefore\ K = Anti \log \bar{5}.8218$ $= \mathbf{6.634 \times 10^{-8}}$

Sol.6
(i) After freezing, the molecules attain an ordered state and therefore, entropy decreases.
(ii) At 0 K, the constituent particles are static and entropy is minimum. If temperature is raised to 115 K
(iii) Reactant, $NaHCO_3$ is a solid and it has low entropy. Among products there are one solid and two gases. Therefore, the products represent a condition of higher entropy.
(iv) Here one molecule gives two atoms i.e., number of particles increases leading to more disordered state. Two moles of H atoms have higher entropy than one mole of di hydrogen molecule.

Sol.7 One decides the spontaneity of a reaction by considering ΔS_{total} ($\Delta S_{sys} + \Delta S_{surr}$). For calculating ΔS_{surr}, we have to consider the heat absorbed by the surroundings which is equal to $-\Delta_r H^\ominus$. At temperature T, entropy change of the surroundings is

$$\Delta S_{surr} = -\frac{\Delta_r H^\ominus}{T} \text{ (at constant pressure)}$$

$$= -\frac{(-1648 \times 10^3\ J\ mol^{-1})}{298\, K}$$

$= 5530\ JK^{-1}\ mol^{-1}$

Thus, total entropy change for this reaction

$\Delta_r S_{total} = 5530\ JK^{-1}\ mol^{-1} + (-549.4\ JK^{-1}\ mol^{-1})$

$= 4980.6\ JK^{-1}\ mol^{-1}$

This shows that the above reaction is spontaneous.

Sol.8 (i) For vaporization of water, the change is

$H_2O(\ell) \longrightarrow H_2O(g)$

$\Delta n_g = 1 - 0 = 1$

$\Delta H = \Delta U + \Delta n_g RT$

or $\Delta U = \Delta H - \Delta n_g\, RT$

$= 41.00\, kJ\, mol^{-1} - (1\, mol) \times (8.314 \times 10^{-3}\, kJ\, mol^{-1})$
$(373\, K)$

$= 41.00 - 3.10\, kJ\, mol^{-1}$

$= \mathbf{37.90\ kJ\ mol^{-1}}$

(ii) For conversion of water into ice, the change is

$H_2O(\ell) \longrightarrow H_2O(s)$

In this case, the volume change in negligible. Hence,

$\Delta H = \Delta U$

$41.00\,\mathbf{kJ\,mol^{-1}}$.

Sol.9 (ii) State function does not depend upon the path followed or is independent of the path followed.

Sol.10 (iii) No heat is allowed to enter or leave the system under adiabatic conditions.

Sol.11 $\Delta E = q + w$; where ΔE is the change of internal
Given $q = 701\,J$
Since the work is done by the system; w is $-ve$
$\therefore\ \Delta E = q + w = (701 - 394)\,J\ = 307\,J$
$\therefore$ Change in internal energy $= 307\,J$.

Sol.12 $V_{initial} = 5L$, T = 27°C
= 27 + 273 K = 300 K

$$V_{final} = \frac{nRT}{P} = \frac{10 \times 0.0821 \times 300}{1.0} = 24.63\,L$$

$$\Delta V = V_{final} - V_{initial} = 246.3 - 5 = 24.13\,L$$

$$w_{\exp} = -P\,\Delta V = -1 \times 241.3\,L \text{ atm}$$

$$= -24.13 \times 101.3\,J = -\mathbf{24443.7\,J}.$$

Sol.13 Mass of Al gives $= 60.0\,g$
ΔT = rise in temp $\Delta = (55 - 35) = 20.0°\,C$

No. of moles of $Al = \dfrac{60.0}{27}$

Molar heat capacity of $Al = 24\,J\,mol^{-1}\,K^{-1}$

Total heat required $= \dfrac{60.0}{27} \times 20.0 \times 24.0\,J$

$= 1086\,J$
$= 1.09\,kJ.$

Objective Questions

1. Thermodynamics is not concerned about
(a) energy changes involved in a chemical reaction.
(b) the extent to which a chemical reaction proceeds.
(c) the rate at which a reaction proceeds.
(d) the feasibility of a chemical reaction.

2. An ideal gas expands in volume from $1 \times 10^{-3} m^3$ to $1 \times 10^{-2} m^3$ at 300 K against a constant pressure of $1 \times 10^5 N m^{-2}$. The work done is
(a) – 900 J (b) – 900 KJ
(c) 270 KJ (d) 900 KJ

3. Which of the following statements is correct?
(a) The presence of reacting species in a covered beaker is an example of open system.
(b) There is an exchange of energy as well as matter between the system and the surroundings in a closed system.
(c) The pressure of reactants in a closed vessel made up of copper is an example of a closed system.
(d) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.

4. One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 L to 10 L. The ΔE for this process is (Given : R = 2 cal $mol^{-1}K^{-1}$)
(a) 163.7 cal (b) zero
(c) 138.1 cal (d) 9 L atm

5. Which one of the following is not applicable for a thermochemical equation?
(a) It tells about the physical state of the reactants and products.
(b) It tells whether the reaction is spontaneous.
(c) It tells whether the reaction is exothermic or endothermic.
(d) It tells about the allotropic form (if any) of the reactants.

6. When 1 mol of a gas is heated at constant volume, temperature is raised from 298 K to 308 K. Heat supplied to the gas is 500 J. Then which statement is correct?
(a) $q = w = -500J, \Delta U = 0$
(b) $q = \Delta U = 500J, w = 0$
(c) $q = w = 500J, \Delta U = 0$
(d) $\Delta U = 0, q = w = -500J$

7. Internal energy of an ideal gas depends on
(a) Volume (b) Temperature
(c) Pressure (d) None of these

8. Given that
$NH_3(g) + 3CI_2(g) \rightleftharpoons NCI_3(g) + 3HCI(g); -\Delta H_1$
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); -\Delta H_2$
$H_2(g) + CI_2(g) \rightleftharpoons 2HCI(g); \Delta H_3$
The enthalpy of formation of $NCI_3(g)$ in terms of ΔH_1, ΔH_2 and ΔH_3 is
(a) $\Delta H_1 = -\Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$
(b) $\Delta H_1 = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$
(c) $\Delta H_1 = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$
(d) None of these

9. Thermodynamically, the most stable form of carbon is
(a) diamond. (b) graphite.
(c) fullerenes. (d) coal.

10. The enthalpy of neutralization of HCI by NaOH is – 55.9 KJ mol^{-1}. If the enthalpy of neutralization of HCN by NaOH is – 12.1 KJ mol^{-1}, the enthalpy of dissociation of HCN is
(a) – 43.8 KJ (b) 43.8 KJ
(c) 68 KJ (d) – 68 KJ

11. Which of the following reactions represents $\Delta_{hyd}H$:
(a) $CuSO_4(s) \xrightarrow{H_2O} CuSO_4(aq); \Delta H = -x$ KJ
(b) $BaCI_2(s) + 2H_2O(I) \rightarrow BaCI_2.2H_2O(s)$; $\Delta H = -x$ KJ
(c) $CuSO_4(s) + 5H_2O(I) \xrightarrow{H_2O} CuSO_4.5H_2O(aq)$; $\Delta H = -z$ KJ
(d) None of these

12. The bond enthalpies of F_2, CI_2, Br_2 and I_2 are 155.4 KJ mol^{-1}, 243.6 KJ mol^{-1}, 193.2 KJ mol^{-1} and 151.2 KJ mol^{-1}, respectively. The strongest bond is
(a) F – F (b) CI – CI
(c) Br – Br (d) I – I

13. For the reaction $2CI(g) \rightarrow C\ell_2(g)$, the signs of ΔH and ΔS , respectively, are

(a) positive, negative. (b) positive, positive.
(c) negative, negative. (d) negative, positive.

14. If S° for $H_2, C\ell_2$ and HCL are 0.13 KJ $K^{-1}\ mol^{-1}$, 0.22 KJ $K^{-1}\ mol^{-1}$ and 0.19 KJ $K^{-1}\ mol^{-1}$, respectively, then the total change in standard entropy for the following reaction is

$H_2 + CI_2 \rightarrow 2HC\ell$

(a) 30 J $K^{-1}\ mol^{-1}$ (b) 40 J $K^{-1}\ mol^{-1}$
(c) 60 J $K^{-1}\ mol^{-1}$ (d) 20 J $K^{-1}\ mol^{-1}$

15. For a reversible isothermal expansion of an ideal gas
(a) $\Delta S_{sys} = \Delta S_{surr} = Positive$
(b) $\Delta S_{sys} = \Delta S_{surr}$
(c) $\Delta S_{sys} = \Delta S_{surr} = Negative$
(d) $\Delta S_{sys} = \Delta S_{surr} = 0$

16. When two gases are mixed, the entropy
(a) remains constant. (b) decreases.
(c) increases. (d) becomes zero.

17. In which reaction is ΔS positive?
(a) $H_2O(\ell) \rightarrow H_2O(S)$
(b) $3O_2(g) \rightarrow 2O_3(g)$
(c) $H_2O(\ell) \rightarrow H_2O(S)$
(d) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

18. Which of the following is true for an endergonic reaction?
(a) $\Delta G > 0$
(b) $\Delta H > 0$
(c) $\Delta H > 0$ and $\Delta S > 0$
(d) $\Delta G < 0$

19. In an irreversible process taking place at constant T and P and in which only pressure – volume work is being done, the change in Gibbs energy (dG) and the change in entropy (dS) satisfy the criteria
(a) $(dS)_{W.E} > 0, (dG)_{T.P} < 0$
(b) $(dS)_{W.E} = 0, (dG)_{T.P} = 0$
(c) $(dS)_{W.E} = 0, (dG)_{T.P} > 0$
(d) $(dS)_{W.E} < 0, (dG)_{T.P} < 0$

20. The factor of ΔG is important in metallurgy. The ΔG values for the following reactions at 800°C are given as

$$S_2(g) + 2O_2(g) \rightarrow 2SO_2(g); \quad \Delta G = -544\,KJ$$
$$2Zn(s) + S_2(s) \rightarrow 2ZnS(s); \quad \Delta G = -293\,KJ$$
$$2Zn(s) + O_2(g) \rightarrow 2ZnO(s); \quad \Delta G = -480\,KJ$$

The ΔG for the following reaction will be

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

(a) – 731 KJ (b) – 773 KJ
(c) – 229 KJ (d) – 357 KJ

21. The standard Gibbs energy change ΔG^o is related to equilibrium constant K as
(a) $K = -RT\,\text{In}\,\Delta G^o$ (b) $K = \left(\frac{e^{\Delta G^o}}{RT}\right)$
(c) $K = -\frac{\Delta G^o}{RT}$ (d) $K = e^{-\Delta G^o/RT}$

22. If the standard Gibbs energy change for a reaction is 1.546 KJ mol^{-1} at 500 °C, then the value of standard equilibrium constant for the reaction is
(a) Antilog (0.105) (b) Antilog (– 0.105)
(c) Antilog (0.241) (d) Antilog (– 0.241)

23. The temperature at which the following reaction is at equilibrium is

$Ag_2O(s) \rightarrow 2Ag(s) + \frac{1}{2}O_2(g)$

(Given: ΔH = 35 KJ mol^{-1}; Δ S = 0.066 KJ $K^{-1}mol^{-1}$)
(a) 462.12 K (b) 362.12 K
(c) 262.12 K (d) 562.12 K

24. What is the sign of ΔG for the process of melting of ice at 280 K?
(a) $\Delta G > 0$ (b) $\Delta G = 0$
(c $\Delta G < 0$ (d) None of these

25. Mark the correct statement
(a) For a chemical reaction to be feasible, ΔG should be zero
(b) Entropy is a measure of order in a system
(c) For a chemical reaction to be feasible, ΔG should be positive
(d) The total energy of an isolated system is constant

Answer Key

1. (c)
2. (a)
3. (c)
4. (b)
5. (b)
6. (b)
7. (b)
8. (a)
9. (b)
10. (b)
11. (c)
12. (b)
13. (c)
14. (a)
15. (b)
16. (c)
17. (c)
18. (a)
19. (a)
20. (a)
21. (d)
22. (b)
23. (a)
24. (a)
25. (d)

Examplar Questions

1. Thermodynamics is **not** concerned about______.
(i) energy changes involved in a chemical reaction.
(ii) the extent to which a chemical reaction proceeds.
(iii) the rate at which a reaction proceeds.
(iv) the feasibility of a chemical reaction.

2. Which of the following statements is correct?
(i) The presence of reacting species in a covered beaker is an example of open system.
(ii) There is an exchange of energy as well as matter between the system and the surroundings in a closed system.
(iii) The presence of reactants in a closed vessel made up of copper is an example of a closed system.
(iv) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.

3. The state of a gas can be described by quoting the relationship between___.
(i) pressure, volume, temperature (ii) temperature, amount, pressure
(iii) amount, volume, temperature (iv) pressure, volume, temperature, amount

4. The volume of gas is reduced to half from its original volume. The specific heat will be ______.
(i) reduce to half (ii) be doubled
(iii) remain constant (iv) increase four times

5. During complete combustion of one mole of butane, 2658 kJ of heat is released. The thermochemical reaction for above change is
(i) $2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(l)\ \Delta_cH = -2658.0\,\text{kJ mol}^{-1}$
(ii) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(g)\ \Delta_cH = -1329.0\,\text{kJ mol}^{-1}$
(iii) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)\ \Delta_cH = -2658.0\,\text{kJ mol}^{-1}$
(iv) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)\ \Delta_cH = +2658.0\,\text{kJ mol}^{-1}$

6. $\Delta_fU^\ominus$ of formation of $CH_4(g)$ at certain temperature is -393 kJ mol^{-1}. The value of $\Delta_fU^\ominus$ is
(i) zero (ii) $< \Delta_fU^\ominus$
(iii) $> \Delta_fU^\ominus$ (iv) equal to $\Delta_fU^\ominus$

7. In an adiabatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following.
(i) $q = 0,\ T \neq 0,\ w = 0$ (ii) $q \neq 0,\ T = 0,\ w = 0$
(iii) $q = 0,\ T = 0,\ w = 0$ (iv) $q = 0,\ T < 0,\ w \neq 0$

8. The pressure-volume work for an ideal gas can be calculated by using the expression $w = -\int_{V_i}^{V_f} p_{ex}dV$. The work can also be calculated from the pV– plot by using the area under the curve within the specified limits. When an ideal gas is compressed (a) reversibly or (b) irreversibly from volume V_i to V_f. choose the correct option.
(i) w (reversible) = w (irreversible) (ii) w (reversible) < w (irreversible)
(iii) w (reversible) > w (irreversible) (iv) w (reversible) = w (irreversible) + p_{ex}. V

9. The entropy change can be calculated by using the expression $S = {}_{T}^{rev}$. When water freezes in a glass beaker, choose the correct statement amongst the following :

(i) S (system) decreases but S (surroundings) remains the same.
(ii) S (system) increases but S (surroundings) decreases.
(iii) S (system) decreases but S (surroundings) increases.
(iv) S (system) decreases and S (surroundings) also decreases.

10. On the basis of thermochemical equations (a), (b) and (c), find out which of the algebric relationships given in options (i) to (iv) is correct.

(a) $\text{C(graphite)} + \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)};\ \Delta_r H = x\,\text{kJ mol}^{-1}$

(b) $\text{C(graphite)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)};\ \Delta_r H = y\,\text{kJ mol}^{-1}$

(c) $\text{CO(g)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)};\ \Delta_r H = z\,\text{kJ mol}^{-1}$

(i) $z = x + y$ (ii) $x = y - z$
(iii) $x = y + z$ (iv) $y = 2z - x$

11. Consider the reactions given below. On the basis of these reactions find out which of the algebric relations given in options (i) to (iv) is correct?

(a) $\text{C(g)} + 4\text{H(g)} \longrightarrow \text{CH}_4\text{(g)};\ \Delta_r H = x\,\text{kJ mol}^{-1}$

(b) $\text{C(graphite,s)} + 2\text{H}_2\text{(g)} \longrightarrow \text{CH}_4\text{(g)};\ \Delta_r H = y\,\text{kJ mol}^{-1}$

(i) $x = y$ (ii) $x = 2y$
(iii) $x > y$ (iv) $x < y$

12. The enthalpies of elements in their standard states are taken as zero. The enthalpy of formation of a compound

(i) is always negative (ii) is always positive
(iii) may be positive or negative (iv) is never negative

13. Enthalpy of sublimation of a substance is equal to

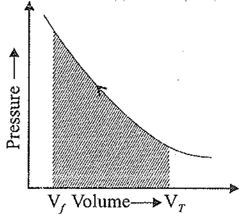
(i) enthalpy of fusion + enthalpy of vapourisation
(ii) enthalpy of fusion
(iii) enthalpy of vapourisation
(iv) twice the enthalpy of vapourisation

14. Which of the following is **not** correct?

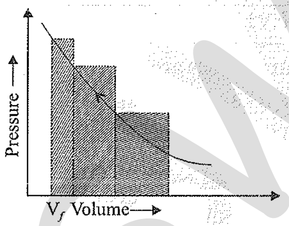
(i) G is zero for a reversible reaction
(ii) G is positive for a spontaneous reaction
(iii) G is negative for a spontaneous reaction
(iv) G is positive for a non-spontaneous reaction

Examplar Solutions

1. (iii) 2. (iii) 3. (iv) 4. (iii) 5. (iii) 6. (ii)
7. (iii)
   Justification : free expansion w = 0
   adiabatic process q = 0
   $\Delta U = q + w = 0$, this means that internal energy remains constant. Therefore, $\Delta T = 0$.
   In ideal gas there is no intermolecular attraction. Hence when such a gas expands under adiabatic conditions into a vaccum no heat is absorbed or evolved since no external work is done to separate the molecules.
8. (ii) w (reversible) < w (irreversible)
   Justification : Area under the curve is always more in irreversible compression as can be seen from (a) and (b).



(a) Reversible compression



(a) Irreversible compression

9. (iii)
   Justification : Freezing is exothermic process. The heat released increases the entropy of surrounding.
10. (iii)
11. (iii)
    Justification : Same bonds are formed in reaction (a) and (b) but bonds between reactant molecules are broken only in reaction (b).
12. (iii) 13. (i) 14. (ii)

JEE and NEET Previous Year

Jee Previous Year

Q.1. 3 gram of acetic acid is mixed in 250 mL of 0.1 M HCl. This mixture is now diluted to 500 mL. 20 mL of this solution is now taken is another container 1/2 mL of 5M NaOH is added to this. Find the pH of this solution. Find the pH of this solution, (log 3 = 0.4771, $pK_a = 4.74$).

[2020 Mains]

Q.2. Calculate $D_f H^\circ$ (In kJ/mol) for $C_2H_6(g)$, if $\Delta_C H^\circ$ $[C_{(graphite)}] = -393.5$ kJ/mol, $\Delta CH^\circ\,[H_2(g)] = -286$ kJ/mol and $\Delta CH^\circ[C_2H_6(g)] = -1560$ kJ/mol.

[2020 Mains]

Q.3. ΔU is equal to **[2017 Mains]**

(a) isochoric work (b) isobaric work

(c) adiabatic work (d) isothermal work

Q.4. The standard state Gibbs free energies of formation of C (graphite) and C(diamond)at T= 298 K are

$\Delta_f G^\circ[C(\text{graphite})] = 0\,\text{kj mol}^{-1}$

$\Delta_f G^\circ[C(\text{diamond})] = 2.9\,\text{kj mol}^{-1}$

The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduced its volume by $2 \times 10^{-6}\ m^3\ mol^{-1}$. If C(graphite)] is covered to C(diamond) isothermally at T= 298 K, the pressure at which C(graphite) is in equilibrium with C(diamond), is

[2017 Jee Adv.]

$[\text{Useful Information}: 1\,j = 1\,kg\,m^2 s^{-2},$

$1\,Pa = 1\,kg\,m^{-1}s^{-2}; 1\,bar = 10^5\,Pa]$

(a) 58001 bar (b) 1450 bar

(c) 14051 bar (d) 29001 bar

Q.5. For a reaction taking place in container in equilibrium with its surrounding, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by

[2017 Jee Adv.]

(a) With increase in temperature the value of K for endothermic reaction increases because unfavorable change in entropy of the surroundings decreases.

(b) With increase in temperature, the value of K for exothermic reaction decreases because favorable change entropy of the surrounding decreases.

(c) With increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative.

(d) With increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system in positive.

Q.6. Given $C_{(graphite)} + O_2\,(g) \rightarrow CO_2\,(g)$,

$\Delta_r H^0 = -\,393.5\ kJmol^{-1}$

$H_2(g) + \frac{1}{2}O_2\,(g) \rightarrow H_2O\,(l);$

$\Delta_r H^0 == 285.8\ kJ\ mol^{-1}$

$CO_2\,(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g);$

$\Delta_r H^0 = +\,890.3\ k\,J\ mol^{-1}$

Based on the above thermochemical equations, the value of $\Delta_r H^0$ at 298 K for the reaction,

$C_{(graphite)} + 2H_2\,(g) \rightarrow CH_4\,(g)$ will be

[2017 Mains]

(a) $+78.8\,kJ\ mol^{-1}$ (b) $+144.0\,kJ\,mol^{-1}$

(c) $-74.8\ kJ\ mol^{-1}$ (d) $-144.0\,kJ\,mol^{-1}$

Q.7. One mole of an ideal gas at 300 K in thermal contact with surrounding expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS) in JK^{-1} is $(1\,L\,atm = 101.3J)$

[2016 Mains]

(a) 5.763 (b) 1.013

(c) −1.013 (d) −5.763

Q.8. The heats of combustion fo carbon and carbon monoxide are −393.5 and − 283.5 kJ , respectively. The heat of formation (in kJ) of carbon monoxide per mole is **[2016 Mains]**

(a) 676.5 (b) −676.5

(c) −110.5 (d) 110.5

Q.9. The following reaction is performed at 298K

$2NO(g) + O_2(g) \rightleftharpoons 2NO(g)$

The standard free energy of formation of NO(g) is 86.6 kj/mol at 298 K. What is the standard free energy of formation $NO_2(g)$ at 298 K? $K_p = 1.6 \times 10^{12}$ **[2015 Mains]**

(a) $R(298)\,\ell n(1.6 \times 10^{12}) - 86600$

(b) $86600 + R(298)\,\ell n(1.6 \times 10^{12})$

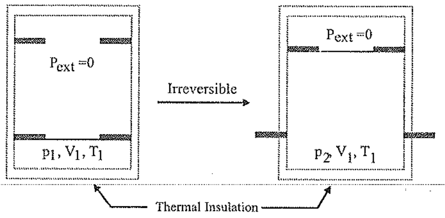
(c) $86600 - \dfrac{\ell n(1.6 \times 10^{12})}{R(298)}$

(d) $0.5[2 \times 86600 - R(298)\ \ell n\,(1.6 \times 10^{12})$

Q.10. For the process, $H_2O(l) \rightarrow H_2O(g)$ at T = 100° C and I atmosphere pressure, the correct choice is **[2014 Jee Adv.]**

(a) $\Delta S_{system} > 0$ and $\Delta S_{surrounding} > 0$
(b) $\Delta S_{system} > 0$ and $\Delta S_{surrounding} < 0$
(c) $\Delta S_{system} < 0$ and $\Delta S_{surrounding} > 0$
(d) $\Delta S_{system} < 0$ and $\Delta S_{surrounding} < 0$

Q.11. A ideal gas in thermally insulated vessel at internal pressure = p_1, volume = V_1 and absolute temperature = T_1 expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are p_2, V_2 and T_2, respectively. For this expansion **[2014 Jee Adv.]**



(a) $q = 0$ (b) $T_2 = T_1$
(c) $p_2V_2 = p_1V_1$ (d) $p_2V_2^y = p_1V_1^y$

Q.12. For the complete combustion of ethanol, $C_2H_5OH(\ell)+3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$, the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol^{-1} at 25^0C. Assuming ideality the enthalpy of combustion $\Delta_C H^0$, for the reaction will be (R=8.314 J $K^{-1}mol^{-1}$ **[2014 Mains]**

(a) –1366.95 kJ mol^{-1}
(b) – 1361,95 kJ mol^{-1}
(c) – 1460.50 kJ mol^{-1}
(d) – 1350.50 kJ mol^{-1}

Q.13. The standard enthalpies of formations and glucose (s) at 25⁰C are – 400 kJ/mol, –300 kJ/mol and – 1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25⁰C is **[2013 Jee Adv.]**

(a) + 2900kJ (b) – 2900 kJ
(c) – 16.11kJ (d) + 16.11kJ

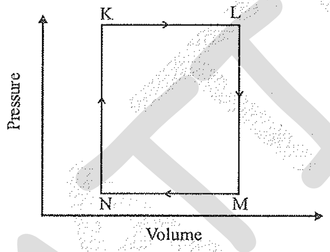
Q.14. Benzene and naphthalene from an ideal solution at room temperature. For this process, the true statement(s) is (are) **[2013 Jee Adv.]**

(a) ΔG is positive (b) ΔS_{system} is positive
(c) $\Delta S_{surroundings} = 0$ (d) $\Delta H = 0$

Q.15. A piston filled with 0.04 mole of an ideal gas expands reversibly form 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and W for the process will be
(R = 8.314 J / mol K. In 7.5 = 2.01)
[2013 Mains]

(a) $q = +208 J, W = -208$
(b) $q = -208 J, W = -208$
(c) $q = -208 J, W = +208$
(d) $q = +208 J, W = +208 J$

A fixed mass m of gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure.



Q.16. The pair of isochoric processes among the transformation of states is **[2013 Adv.]**

(a) K to L and L to M
(b) L to M and N to K
(c) L to M and M to N
(d) M to N and N to K

Q.17. The succeeding operations that enable this transformation of states are **[2013 Adv.]**

(a) heating, cooling, heating, cooling
(b) cooling, heating, cooling, heating
(c) heating, cooling, cooling, heating
(d) cooling, heating, heating, cooling

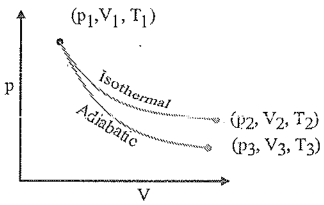
Q.18. Using the data provided, calculated the multiple bond energy (kJ mol^{-1}) of a $C \equiv C$ bond C_2H_2. That energy is (take the bond energy of a C—H bond as 350 kJ mol^{-1})

$2C(s)+H_2(g) \rightarrow C_2H_2(g);\ \Delta H = 225\ kJ\,mol^{-1}$
$2C(s) \rightarrow 2C(g);\ \Delta H = 1410\,kJ\,mol^{-1}$
$H_2(g) \rightarrow 2H(g);\ \Delta H = 330 kJ\,mol^{-1}$

[2012 Mains]

(a) 1165 (b) 837
(c) 865 (d) 815

Q.19. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown is the figure. Which of the following statement(s) is (are) correct? **[2012 Mains]**



(a) $T_1 = T_2$
(b) $T_3 > T_1$
(c) $W_{isothermal} > W_{adiabatic}$

(d) $\Delta U_{isothermal} > \Delta U_{adiabatic}$

Q.20. Match the transformations in Column I with appropriate options in Column II. **[2011 Mains]**

COLUMN I	COLUMN II
A. $CO_2(s) \rightarrow CO_2(g)$	p. phase transition
B. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$	q. Allotropic change
C. $2H \rightarrow H_2(g)$	r. ΔH is positive
D. $P_{(white,solid)} \rightarrow P_{(red,solid)}$	s. ΔS is positive
	t. ΔS is negative

Q.21. Among the following extensive property is (properties are) **[2010 Mains]**

(a) molar conductivity
(b) electromotive force
(c) resistance
(d) heat capacity

Read the following questions and answer as per the direction given below :

(a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I
(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I
(c) Statement I is true; Statement II is false
(d) Statement I is false; Statement III is true

Q.22. Statement I For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.

Statement II At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. **[2008 Mains]**

Q.23. For the process $H_2O(l)(1\,bar, 373K) \rightarrow H_2O(g)$ (1 bar, 373 K), the correct set of thermodynamics parameters is **[2007 Mains]**

(a) $\Delta G = 0, \Delta S = +\,ve$ (b) $\Delta G + 0, \Delta S = -$
(c) $\Delta G = 0, \quad \Delta S = -\,ve$ (d) $\Delta G = -\,ve, \quad \Delta S = 0$

Q.24. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is (Given: $\Delta_r H^\circ = -54.07\,kJ\,mol^{-1}$, $\Delta_r S^\circ(298)$ and $R = 8.314\,JK^{-1}mol^{-1}$; $2.303 \times 8.314 \times 298 = 5705$) **[2007 Mains]**

(a) 5 (b) 10
(c) 95 (d) 100

Q.25. The direct conversion of A to B is difficult, hence it is carried out by the following shown path

$$\begin{tikzcd}
C \arrow[r] & D \arrow[d] \\
A \arrow[u] \arrow[r] & B
\end{tikzcd}$$

Given that $\Delta S_{(A \rightarrow C)} = 50\,eu$
$\Delta S_{(C \rightarrow D)} = 30\,eu$
$\Delta S_{(D \rightarrow B)} = -20\,eu$ where, eu is entropy unit

Then $\Delta S_{(A \rightarrow B)}$ is **[2006 Mains]**

(a) + 100 eu (b) + 60 eu
(c) –100e eu (d) –60 eu

Q.26. One mole of monotomic ideal gas expands adibatically at initial temperature T against a constant external pressure of 1 atm 1L to 2L. Find out the final temperature (R=0.082 L atm $K^{-1}mol^{-1}$) **[2005 Mains]**

(a) T (b) $\dfrac{T}{(2)^{\frac{5}{3}-1}}$
(c) $T - \dfrac{2}{3 \times 0.082}$ (d) $T + \dfrac{2}{3 \times 0.082}$

Q.27. Which of the following reaction defines ΔH_f^0 ? **[2003 Mains]**

(a) $C_{(diamond)} + O_2(g) \rightarrow CO_2(g)$
(b) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \rightarrow HF(g)$
(c) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
(d) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

Q.28. Which of the following statement is false? **[2001]**

(a) Work is a state function
(b) Temperature is a state function
(c) Change in the state is completely defined when the initial and final states are specified
(d) Work appears at the boundary of the system

Q.29. The ΔH_f^0 for $CO_2(g), CO(g)$ and $H_2O(g)$ are $-392.5, -110.5$ and $-241.8\,kJ\,mol^{-1}$ respectively. The standard enthalpy change (in $kJ\,mol^{-1}$) for the reaction $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ is **[2000]**

(a) 524.1 (b) + 41.2
(c) – 262.5 (d) – 41.2

Q.30. Statement I The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.

Statement II The volume occupied by the molecules of an ideal gas is zero. **[2000]**

NEET Previous Year

Q.31. In which case change in entropy is negative? **[2019]**

(a) Sublimation of solid to gas
(b) $2H(g) \rightarrow H_2(g)$
(c) Evaporation of water
(d) Expansion of a gas at constant temperature

Q.32. Under isothermal condition, a gas at 300 K expands from 0.1 L to 0.25 L against a constant external pressure of 2 bar. The work done by the gas is (Given that 1 L bar = 100 J) **[2019]**

(a) 25 J (b) 30 J
(c) –30 J (d) 5 kJ

Q.33. Which of the following is an amphoteric hydroxide? **[2019]**

(a) $Mg(OH)_2$ (b) $Be(OH)_2$
(c) $Sr(OH)_2$ (d) $Ca(OH)_2$

Q.34. A gas at 350 K and 15 bar has molar volume 20 percent smaller than that for an ideal gas under the same conditions. The correct option about the gas and its compressibility factor (Z) is: **[2019]**

(a) $Z < 1$ and attractive forces are dominant
(b) $Z < 1$ and repulsive forces are dominant
(c) $Z > 1$ and attractive forces are dominant
(d) $Z > 1$ and repulsive forces are dominant

Q.35. Conjugate base for Bronsted acids H_2O and HF are: **[2019]**

(a) OH^- and F^-, respectively
(b) H_3O^+ and H_2F^+, respectively
(c) OH^- and H_2F^+, respectively
(d) H_3O^+ and F^-, respectively

Q.36. The bond dissociation energies of X_2, Y_2 and XY are in the ratio of 1: 0.5: 1. ΔH for the formation of XY is -200 kJ mol^{-1}. The bond dissociation energy X_2 will be **[2018]**

(a) 200 kJ mol^{-1} (b) 100 kJ mol^{-1}
(c) 400 kJ mol^{-1} (d) 800 kJ mol^{-1}

Q.37. Which of the following statements is correct for the spontaneous adsorption of a gas?

(a) ΔS is negative and therefore, ΔH should be highly positive.
(b) ΔS is negative and therefore, ΔH should be highly negative.
(c) ΔS positive and therefore, ΔH should be negative.
(d) ΔS is positive and therefore, ΔH should also be highly positive.

Q.38. For the reaction
$X_2O_4(l) \rightarrow 2XO_2(g)$, $\Delta U = 2.1\,kcal$, $\Delta S = 20\,cal\,K$.
Hence ΔG is **[2014]**

(a) 2.7 kcal (b) –2.7 kcal
(c) 9.3 kcal (d) –9.3 kcal

Q.39. The enthalpy of fusion of water is 1.435 kcal/mol. The molar entropy change for the melting of ice at 0^0C is **[2012]**

(a) 10.52 cal/mol K (b) 21.04 cal/mol K
(c) 5.260 cal/mol K (d) 0.526 cak/mol K

Q.40. Enthalpy change for the reaction,
$4H(g) \rightarrow 2H_2(g)$ is $-869.6\,kJ$
The dissociation energy of H-H bond is **[2011]**

(a) –869.6 kJ (b) + 434.8 kJ
(c) +217.4 kJ (d) – 343.8 kJ

Q.41. The values of ΔH and ΔS for the certion, $C_{(graphite)} + CO_2(g) \rightarrow 2H_2(g)$ are 170 kJ and 170 JK^{-1}, respectively. This reaction will be spontaneous at **[2009]**

(a) 710 K (b) 910 K
(c) 1110 K (d) 510 K

Q.42. Form the following bond energies
$H-H$ bond energy: 431.37 kJ mol^{-1}
$C = C$ bond energy: 606.10 kJ mol^{-1}
$C-C$ bond energy: 336.49 kJ mol^{-1}
$C-H$ bond energy: 410.50 kJ mol^{-1}
Enthalpy for the reaction,
$C_2H_4 + H_2 \rightarrow C_2H_6$

(a) 1523.6 kJ mol^{-1} (b) -245 kJ mol^{-1}
(c) -120 kJ mol^{-1} (d) 245 kJ mol^{-1}

Q.43. Consider the following reactions,
(i) $H^+(aq) + OH^-(aq) \rightarrow H_2O(l), -x_1\,kJ\,mol^{-1}$
(ii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l), x_2\,kJ\,mol^{-1}$
(iii) $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(l), -x_3\,kJ\,mol^{-1}$
(iv) $C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l) + x_4\,kJ\,mol^{-1}$
Enthalpy of formation of $H_2O(l)$ is **[2007]**

(a) $-x_2\,kJ\,mol^{-1}$ (b) $+x_3\,kJ\,mol^{-1}$
(c) $-x_4\,kJ\,mol^{-1}$ (d) $+x_1\,kJ\,mol^{-1}$

Q.44. The enthalpy of combustion of H_2 cyclohexene (C_6H_{10}) and cyclohexane ($C_6H'_{12}$) are -241, –3800 and –3920 kJ per mol respectively. Heat of hydrogenation of cyclohexene is **[2006]**

(a) –121 kJ per mol (b) + 121 kJ per mol
(c) + 242 kJ per mol (d) –242 kJ per mol

Q.45. The enthalpy and entropy change for the reaction,
$Br_2(l) + Cl_2(g) \rightarrow BrCl(g)$ are 30 kJ mol^{-1} and 105 JK^{-1} mol^{-1} respectively. The temperature at which the reaction will be in equilibrium is **[2006]**

(a) 285.7 K (b) 273 K
(c) 450 K (d) 300 K

Q.46. Assume each reactions carried out in an open container. For which reaction will $\Delta H = \Delta E$? **[2006]**

(a) $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$
(b) $C(s) + 2H_2O(g) \rightarrow 2H_2(g) + CO_2(g)$
(c) $PCl_5(g) \rightarrow PCl_3(g) + CO_2(g)$
(d) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

Q.47. Identify the correct statement for change of Gibbs free energy for a system (ΔG_{system}) at constant temperature and pressure. **[2006]**

(a) If $\Delta G_{system} > 0$, the process is spontaneous
(b) If $\Delta G_{system} = 0$, the system has attained equilibrium
(c) If $\Delta G_{system} = 0$,the system is still moving in a particular direction
(d) If $\Delta G_{system} = 0$ the process in not spontaneous

Q.48. Standard enthalpy and standard entropy changes for the oxidation of ammonia at 298 K are -382.64 kJ and $-145.6\ JK^{-1}\ mol^{-1}$ respectively, Standard Gibbs energy change for the same reaction at 298 K is **[2004]**

(a) $-221.1\ JK\ mol^{-1}$ (b) $-339\ kJ\ mol^{-1}$
(c) $-439.3\ kJ\ mol^{-1}$ (d) $-523.2\ kJ\ mol^{-1}$

Q.49. For the reaction,
$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ at constant temperature, $\Delta H - \Delta E$ is **[2003]**

(a) $+3RT$ (b) $-RT$
(c) $+RT$ (d) $-3RT$

Q.50. The densities of graphite and diamond at 298 K are 2.25 and 3.31 cm^{-3}, respectively. If the standard free energy difference (ΔG^0) is equal to 1895 J mol^{-1}, the pressure at which graphite will be transformed into diamond at 298 K is **[2003]**

(a) 9.92×10^6 pa (b) 9.92×10^5 pa
(c) 9.92×10^8 pa (d) 9.92×10^7 pa

Q.51. Heat of combustion ΔH^0 for C(s), $H_2(g)$ and $CH_4(g)$ are -94, -68 and -213 kcal/mol. Then, ΔH^0 for C(s) + **[2002]**

(a) -17kcal/mol (b) -111kcal/mol
(c) -170kcal/mol (d) -85kcal/mol

Q.52. 2 moles of an ideal gas at 27^0C temperature is expanded reversibly form 2 L to 20L. Find entropy change (R=2cal/mol K). **[2002]**

(a) 92.1 (b) 0
(c) 4 (d) 9.2

Q.53. Unit of entropy is

(a) $JK^{-1}mol^{-1}$ (b) $J\,mol^{-1}$
(c) $J^{-1}\ K^{-1}\ mol^{-1}$ (d) $JK\ mol^{-1}$

Q.54. $PbO_2 \rightarrow PbO, \Delta G_{298} < 0$
$SnO_2 \rightarrow SnO, \Delta G_{298} > 0$
Most probable oxidation state of Pb and Sn will be **[2001]**

(a) Pb^{4+}, Sn^{4+} (b) Pb^{4+}, Sn^{2+}
(c) Pb^{2+}, Sn^{2+} (d) Pb^{2+}, Sn^{4+}

Q.55. If ΔE is the heat of reaction for
$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
At constant volume, the heat of reaction at constant pressureis , then the correct relation between ΔH and ΔE is **[2000]**

(a) $\Delta H = \Delta E + RT$ (b) $\Delta H = \Delta E - RT$
(c) $\Delta H = \Delta E - 2RT$ (d) $\Delta H = \Delta E + 2RT$

Answer Key

1. (5.22)
2. (–85KJ mol^{-1})
3. (c)
4. (c)
5. (a,b)
6. (c)
7. (c)
8. (c)
9. (d)
10. ()
11. (a,b)
12. (a)
13. (c)
14. (b,c,d)
15. (a)
16. (b)
17. (c)
18. (d)
19. (a,c,d)
20. (a)
21. (c,d)
22. (d)
23. (a)
24. (b)
25. (b)
26. (c)
27. (b)
28. (a)
29. (b)
30. (b)
31. (b)
32. (c)
33. (b)
34. (a)
35. (a)
36. (d)
37. (b)
38. (b)
39. (c)
40. (b)
41. (c)
42. (c)
43. (a)
44. (a)
45. (a)
46. (a)
47. (b)
48. (b)
49. (d)
50. (c)
51. (a)
52. (d)
53. (a)
54. (d)
55. (b)

7

EQUILIBRIUM

EQUILIBRIUM PROCESS AND PHASE EQUILIBRIUM

Reversible Reactions

Reversible reactions are the reactions in which the product can react with one another under suitable conditions to give back the reactants for eg.

$H_2 + I_2 \rightleftharpoons 2HI$

Irreversible Reactions

The chemical reaction in which the products formed do not combine to give back the reactants are known as irreversible reactions for eg. :

$2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$

Active Mass

No. of moles of any substance dissolved in 1 litre of solution is called its active mass or molar concentration

$$[A] = \frac{\text{no. of moles of A}}{\text{Volume (L)}}$$

If $V = 1L$

$\therefore [A] = $ no. of moles of A

Law of mass action (given by Guldberg & Waage) : The rate of chemical reaction is directly proportional to the product of the molar concentration of the reactants at a constant temp. at any given time.

$A + B \qquad C + D$

Rate of change of reaction $\propto [A] \times [B]$

$= k [A] [B]$

k = rate constant or velocity constant.

Rate constant : The rate constant of a reaction at a given temperature may be defined as the rate of the reaction when the concentration of each of the reactant is unity

$[A] = 1$

$[B] = 1$

rate of reaction = k (rate constant)

& $n_1A + n_2B \qquad m_1C + m_2D$

Rate of reaction $\propto [A]^{n_1} [B]^{n_2}$

Acc. to law of mass action, the rate of chemical reaction at any particular temperature is propotional to the product of the molar concentration of reactants with each concentration term raised to the power equal to the no. of molecules of the respective reactants taking part in the reaction.

Chemical Equilibrium

The state in which the measurable properties of the system do not undergo any further noticeable change under given set of conditions is said to be state of equilibrium.

At equilibrium, rate of forward reaction equals rate of backward reaction.

For eg. : $A + B \underset{V_2}{\overset{V_1}{\rightleftharpoons}} C + D$

At chemical equilibrium $V_1 = V_2$

Characteristics of Chemical Equilibrium :

(i) Chemical equilibrium is dynamic in nature.

(ii) The properties of the system become constant at equilibrium and remain unchanged there after.

(iii) The equilibrium can be attained only if the system is closed.

(iv) The equilibrium can be approached from either direction.

Equilibrium constant in terms of law of mass action

$A + B \rightleftharpoons C + D$

Rate of forward reaction $\propto [A] \times [B]$

$= k_1 [A] [B]$

where k_1 is the rate constant of forward reaction

& Rate of backward reaction $\propto [C] \times [D]$

$= k_2 [C] [D]$

where k_2 is the rate constant of backward reaction.

At equilibrium,

Rate of forward reaction = rate of backward reaction

$k_1 [A] [B] = k_2 [C] [D]$

$$\therefore \quad \frac{k_1}{k_2} = \frac{[C][D]}{[A][B]}$$

$$\Rightarrow \quad \frac{K_1}{K_2} = K$$

where K is the equilibrium constant

$$K = \frac{[C][D]}{[A][B]}$$

$\therefore$ We can say that K is the ratio between the product of molar concentration of products to that of product of molar concentration of reactants or, the ratio b/w the rate constant of forward reaction to the rate constant of backward reaction

Also if $n_1A + n_2B \rightarrow m_1C + m_2D$

$$K = \frac{[C]^{m_1}[D]^{m_2}}{[A]^{n_1}[B]^{n_2}}$$

Therefore, we can define **equilibrium constant as the ratio b/w the product of molar concentration of the products to product of the molar concentration of reactants with each concentration term raised to a power equal to the stoichiometric coefficient in the balanced chemical equation at equilibrium at constant temperature is called equilibrium constant.**

Concentration Ratio : (Reaction Quotient) Q

$n_1A + n_2B \rightleftharpoons m_1C + m_2D$

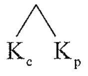
$$Q = \frac{[C]^{m_1}.[D]^{m_2}}{[A]^{n_1}.[B]^{n_2}}$$

If $Q = K$ reaction at equilibrium

$Q < K$ reaction goes in forward direction

$Q > K$ reaction goes in backward direction

*** K is of two types** :



$$\& \; K_c = \frac{[C]^{m_1}[D]^{m_2}}{[A]^{n_1}[B]^{n_2}} \; \& \; K_p = \frac{{p_C}^{m_1}{p_D}^{m_2}}{{p_A}^{n_1}{p_B}^{n_2}}$$

Relationship between K_p and K_c

$n_1A + n_2B \rightleftharpoons m_1C + m_2D$

When $[A]^{n1}$, $[B]^{n2}$, $[C]^{m1}$ $[D]^{m2}$ are the molar concentration of A, B, C & D

$$K_c = \frac{[C]^{m_1}[D]^{m_2}}{[A]^{n_1}[B]^{n_2}} \qquad \text{....(1)}$$

when $p_C^{m_1}$, $p_D^{m_2}$, $p_A^{n_1}$, $p_B^{n_2}$ are the partial pressure of C, D, A, B

$$K_p = \frac{p_C^{m_1} \cdot p_D^{m_2}}{p_A^{n_1} \cdot p_B^{n_2}} \qquad \text{....(2)}$$

Now, PV = nRT [Ideal gas eq^n]

$$\Rightarrow P = \frac{n}{V}RT$$

but $\frac{n}{V} = C$ i.e. molar concentration

$\therefore$ P = CRT

so, $p_A = C_ART$ $\quad p_B = C_BRT$ $\quad p_C = C_CRT$ $\quad p_D = C_DRT$

putting in eq^n (2)

$$K_p = \frac{(C_CRT)^{m_1}.(C_DRT)^{m_2}}{(C_ART)^{n_1}.(C_BRT)^{n_2}}$$

$$K_p = \frac{C_C^{m_1}.C_D^{m_2}}{C_A^{n_1}.C_B^{n_2}} \times [RT]^{(m_1+m_2)-(n_1+n_2)}$$

$$K_p = \frac{[C]^{m_1}[D]^{m_2}}{[A]^{n_1}[B]^{n_2}}.[RT]^{(m_1+m_2)-(n_1+n_2)}$$

But from (1)

$$K_C = \frac{[C]^{m_1}[D]^{m_2}}{[A]^{n_1}[B]^{n_2}}$$

$$\therefore K_P = K_C.[RT]^{(m_1+m_2)-(n_1+n_2)}$$

when $\Delta x = (m_1 + m_2) - (n_1 + n_2)$

= no. of moles of product − no. of moles of reactant

then, $K_P = K_C.[RT]^{\Delta x}$

* Comp. point :

If $\Delta x = (+)$ve $\qquad \Delta x = 0 \quad \Delta x = (-)$ve

$K_p = K(RT)^{\Delta x}$ $\qquad K_p = (RT)^0$

$K_p > K_c$ $\quad K_p = K_c$ $\quad K_p < K_c$

For Δx solids molecule are not counted.

Units of Kc and Kp :

Unit of $K_c = (mol/L)^{\Delta x}$

Unit of $K_p = (atm)^{\Delta x}$

Note : If no. of moles of products is equal to the no. of moles of reactants i.e. $\Delta x = 0$, then equilibrium constant has no units.

Note : Units of Equilibrium Constant

The value of equilibrium constant *K*c can be calculated by substituting the concentration terms in mol/L and for *Kp* partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same.

For the reactions,
$H_2(g) + I_2(g) \rightleftharpoons 2HI$, *Kc* and *Kp* have no unit.

$N_2O_4(g) \rightleftharpoons 2NO_2\ (g)$, *Kc* has unit mol/L and *Kp* has unit bar

Equilibrium constants can also be expressed as dimensionless quantities if the standard state of reactants and products are specified.

For a pure gas, the standard state is 1bar. Therefore a pressure of 4 bar in standard state can be expressed as 4 bar/1 bar = 4, which is a dimensionless number. Standard state (c_0)
for a solute is 1 molar solution and all concentrations can be measured with respect to it. The numerical value of equilibrium constant depends on the standard state chosen. Thus, in this system both *Kp* and *Kc* are dimensionless quantities but have different numerical values due to different standard states.

Types of chemical equilibrium : Chemical equilibrium are of following types :

(i) **Homogenous equilibrium :** The equilibrium reaction in which all the reactant and the product are in the same phase are called homogeneous equilibrium reaction for eg.
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(ii) **Heterogeneous equilibrium :** The equilibrium reaction in which the reactants and products are present in different phase are called heterogeneous equilibrium reactions. For eg.
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
* For pure liquids and solids, concentration is always one. i.e.
[Solid] = 1, [liquid] = 1
For eg. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$\therefore\ K = \frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]}$$

But $[CaO(s)] = 1$ & $[CaCO_3(s)] = 1$
$\Rightarrow \qquad K = [CO_2(g)]$
or $\qquad K = p_{CO2}$

Calculate K (equilibrium constant) for :

(i) $N_2O(g) + O_2(g) \rightleftharpoons 2NO(g)$

$$K = \frac{[NO(g)]^2}{[N_2O(g)][O_2(g)]}$$

$$= \frac{(P_{NO})^2}{P_{N_2O} \cdot P_{O_2}}(\text{atm})^0 = \frac{(P_{NO})^2}{P_{N_2O} \cdot P_{O_2}}$$

(ii) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$K_c = \frac{[PCl_3(g)][Cl_2(g)]}{[PCl_5(g)]}[\text{mol/lit}]$$

(iii) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

$$K = \frac{[Fe_3O_4][H_2]^4}{[Fe]^3[H_2O]^4}[\text{mol / lit}]^0 = \frac{[H_2]^4}{[H_2O]^4}[\text{mol / lit}]^0$$

Characteristics of Equilibrium Constant :

(i) The value of equilibrium constant is independent of the original concentration of the reactant.

(ii) The equilibrium constant has a definite value for every reaction at particular temperature.

(iii) For a reversible reaction, the equilibrium constant for the forward reaction is inverse of the equilibrium constant for the backward reaction
For eg. $\quad H_2 + I_2 \rightleftharpoons 2HI \qquad K = 48$
$2HI \rightleftharpoons H_2 + I_2 \quad K' = 1/48$

(iv) The value of an equilibrium constant tells the extent to which a reaction proceeds in the forward or reverse reaction. If the value of K is large, the reaction proceeds to a greater extent in the forward direction and if it is small, the reverse reaction proceeds to a large extent and the progress in the forward direction is small.

(v) The equilibrium constant is independent of the presence of catalyst.

SPECIAL NOTE:

$$H_2 + I_2 \rightleftharpoons 2HI \qquad K$$

(i) For reverse reaction,

$$\text{New } K = \frac{1}{old\ K}$$

(ii) If equation is divided by 2

New K = (old K)$^{1/2}$

$\frac{1}{2} H_2 + \frac{1}{2} I_2 \rightleftharpoons HI$

(iii) If equation is multiply by 2

New K = (old K)^2

Eg. $2NO_2 + O_2 \rightleftharpoons 2NO_2$ $\qquad K = K_1$

$\therefore$ For, $4NO_2 \rightleftharpoons 4NO_2 + 2O_2$

$$K_2 = \frac{1}{K_1^2}$$

Predicting the Extent of a Reaction

The numerical value of the equilibrium constant for a reaction indicates the extent of the reaction. But it is important to note that an equilibrium constant does not give any information about the rate at which the equilibrium is reached. The magnitude of Kc or Kp is directly proportional to the concentrations of products (as these appear in the numerator of equilibrium constant expression) and inversely proportional to the concentrations of the reactants (these appear in the denominator).

This implies that a high value of K is suggestive of a high concentration of products and vice-versa.

We can make the following generalizations concerning the composition of equilibrium mixtures:

- If **Kc > 10^3**, products predominate over reactants, i.e., if Kc is very large, the reaction proceeds nearly to completion.

Consider the following examples:

(a) The reaction of H_2 with O_2 at 500 K has a very large equilibrium constant, Kc = 2.4×10^{47}.

(b) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ at 300K has Kc = 4.0×10^{31}.

(c) $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ at 300 K, Kc = 5.4×10^{18}

- If **Kc < 10^{-3}**, reactants predominate over products, i.e., if Kc is very small, the reaction proceeds rarely.

Consider the following examples:

(a) The decomposition of H_2O into H_2 and O_2 at 500 K has a very small equilibrium constant, Kc = 4.1×10^{-48}

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, at 298 K has Kc = 4.8×10^{-31}.

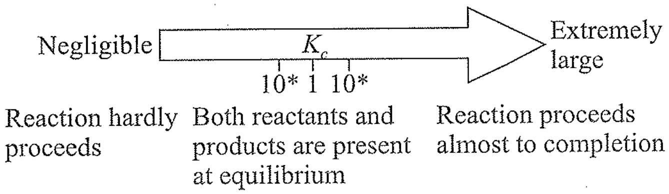
- If **Kc is in the range of 10^{-3} to 10^3**, appreciable concentrations of both reactants and products are present.

Consider the following examples:

(a) For reaction of H_2 with I_2 to give HI, Kc = 57.0 at 700K.

(b) Also, gas phase decomposition of N_2O_4 to NO_2 is another reaction with a value of Kc = 4.64×10^{-3} at 25°C which is neither too small nor too large. Hence, equilibrium mixtures contain appreciable concentrations of both N_2O_4 and NO_2.

These generarlisations are illustrated in



Dependence of extent of reaction on K_c

RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANT (K), REACTION QUOTIENT (Q) AND GIBBS ENERGY (G)

The value of Kc for a reaction does not depend on the rate of the reaction. it is directly related to the thermodynamics of the reaction and in particular, to the change in Gibbs energy, ΔG. If,

- ΔG is negative, then the reaction is spontaneous and proceeds in the forward direction.
- ΔG is positive, then reaction is considered non-spontaneous. Instead, as reverse reaction would have a negative ΔG, the products of the forward reaction shall be converted to the reactants.
- ΔG is 0, reaction has achieved equilibrium; at this point, there is no longer any free energy left to drive the reaction.

A mathematical expression of this thermodynamic view of equilibrium can be described by the following equation :

$$\Delta G = \Delta G^0 + RT \ln Q \qquad ....(1)$$

where, G^0 is standard Gibbs energy.
At equilibrium, when $\Delta G = 0$ and Q = Kc,
the equation (1) becomes,

$$\Delta G = \Delta G^0 + RT \ln K = 0$$

$$\Delta G^0 = -RT \ln K \qquad ....(2)$$

$$\ln K = -\Delta G^0 / RT$$

Taking antilog of both sides, we get,

$$K = e^{-\Delta G^0/RT} \qquad ....(3)$$

Hence, using the equation (3), the reaction spontaneity can be interpreted in terms of the value of ΔG^0.

• If $\Delta G^0 < 0$, then $-\Delta G^0 / RT$ is positive, and $e^{-\Delta G^0/RT} > 1$, making K >1, which implies a spontaneous reaction or the reaction which proceeds in the forward direction to such an extent that the products are present predominantly.

• If $\Delta G^0 > 0$, then $-\Delta G^0 / RT$ is negative, and $e^{-\Delta G^0/RT} < 1$, that is , K < 1, which implies a non-spontaneous reaction or a reaction which proceeds in the forward direction to such a small degree that only a very minute quantity of product is formed.

Le-Chaterlier Principle

If an equilibrium is subjected to any kind of stress, (change in concentration, pressure, and temp. etc.) equilibrium shifts in such a way so as to cancel (undo) the effect of stress imposed.

Favourable conditions for some forward reactions (temp. & pressure).

(1) $N_2 + 3H_2 \rightleftharpoons 2NH_3 + 22400$ cal.
low temp & High pressure

(2) $2SO_2 + O_2 \rightleftharpoons 2SO_3 + 47$ Cal
low temp & high pressure

(3) Ice $\rightleftharpoons$ Water – x Cal
High temp. High pressure

* If temp. is (+ve) eg : +47 cal, then low temp. & vice versa. If volume is decreasing, then high pressure and vice versa.

Effect of change in concentration : If concentration of one or all the reactants species is increased, the equilibrium shifts in forward direction and more of the products are formed.

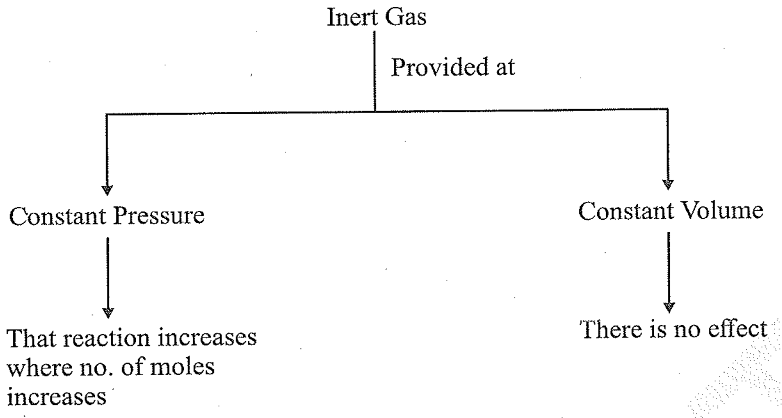
If concentration of one or all the product species is increased, the equilibrium shift in the backward direction forming more reactants.

Effect of change of temperature : The equilibrium will shift in the direction of endothermic reaction with increase in temp. The decrease in temp. will shift the equilibrium towards the direction in which heat is produced, therefore will favour endothermic reaction.

Effect of change of pressure : Increase in pressure will shift the direction of lesser number of gaseous moles formed. Decrease in pressure shifts the equilibrium in the direction of large number of gaseous moles formed.

Effect of catalyst : Catalyst does not shift the equilibrium in any direction.

Effect of adding an inert gas



Henry Law : The mass of a gas dissolved in a given mass of a solvent at a particular temperature is proportional to the pressure of the gas above the solvent.

$$m \propto p$$
$$m = Kp$$

IONIC EQUILIBRIUM

Electrolyte

The substance which conduct electricity in their molten state or in the form of their aqueous solution are called electrolytes for eg. : Acids, Base and Salts are electrolytes.

➡ NON ELECTROLYTE

The substance which do not conduct electricity in their molten state or in the form of their aqueous solutions are called non-electrolytes for eg. Sugar, Urea, Glycerine.

Electrolytes are divided into two classes :

1. **STRONG ELECTROLYTES :** The substance which ionised almost completely into ions in aqueous solutions are called strong electrolyte. For eg. : HCl, HNO_3, H_2SO_4, NaOH, KOH, NaCl, KCl, Na_2CO_3, CH_3COONa, NH_4Cl.
   ($X^-_{(Halides)}$, SO_4^{--}, NO_3^-, K, Na)
2. **WEAK ELECTROLYTES :** The substance which ionise to a small extent in aqueous solution are called weak electrolytes. For eg. H_2S, CH_3COOH, H_3PO_4, NH_4OH, $Fe(OH)_3$, $Cu(OH)_2$.
   IONIC EQUILIBRIUM : Equilibrium which is establish b/w the unionised molecule and the ions in solution of weak electrolyte.
   $AB \rightleftharpoons A^+ + B^-$

Acid Base Concepts

I. **ARRHENIUS CONCEPT OF BASE AND ACID (1887) :** Acc. to Arrhenius concept, an acid is a substance which dissociate in aqeous solution to give hydrogen ions & Base is a substance which dissociate in aqueous solutions to give Hydroxyl ion (OH^-).

Eg. For acid, $HCl \longrightarrow H^+ + Cl^-$

For base, $NaOH \longrightarrow Na^+ + OH^-$

The strength of an acid or base depends upon its capacity of ionisation to H^+ or OH^- respectively.

II. **BRONSTED-LOWRY CONCEPT (1923) :** Acc. to Bronsted-lowry concept, an acid is a substance which can donate proton while a base is a substance which can accept a proton. In other words, acid is a proton donor & base is a proton acceptor.

The base formed from an acid is reffered to as the conjugate base of the acid. Similarly, the acid formed from a base is reffered to as the conjugate acid of the base. For eg. : Cl^- is the conjugate base of HCl acid and NH_4^+ is the conjugate acid of NH_3 base.

The pairs of acid and base which are formed from each other by the gain or loss of a proton are called conjugate acid-base pair.

III. LEWIS CONCEPT OF ACID AND BASE : Acc. to this concept, an acid is a substance (molecule or ion or atom) which can accepts electron pair while a base is a substance which can donates an electron pair.

LEWIS BASE : Acc. to lewis concept, the following species can act as lewis base□

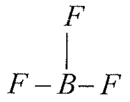
(i) Neutral species having at least one lone pair of electron for eg.

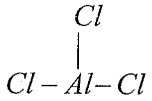
Ammonia : $(\ddot{N}H_3)$, Alcohol : $(R-\underset{\cdot\cdot}{\ddot{O}}-H)$, Amines : $(R-\ddot{N}H_2)$, H_2O : $(H-\underset{\cdot\cdot}{\ddot{O}}-H)$

(ii) Negatively charged ions.

For eg. Cl^-, CN^-, OH^- etc.

LEWIS ACID : (i) Molecules in which the central atom has incomplete octate :

Eg. **(1)** BF_3 :

$F-\overset{\overset{F}{|}}{B}-F$

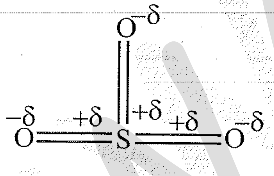
(2) $AlCl_3$:

$Cl-\overset{\overset{Cl}{|}}{Al}-Cl$

(ii) Simple cation can act as Lewis acid for eg. : Ag^+, H^+ etc.

(iii) Molecules in which the central atom has empty *d*-orbitals. eg. SiF_4, $SnCl_4$ etc.

(iv) molecules in which atoms of dissimilar electronegativities are joined by multiple bonds.

For eg. CO_2, SO_2, SO_3 etc.



Dissociation constant or Ionisation constant of acids in H_2O

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

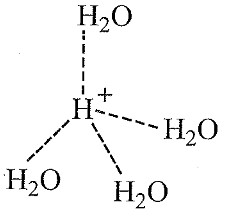
Since water is present in a large quantity, its concentration remains practically constant. The concentration of H_2O may be combined with K & gives another constant K_a.

$$K[H_2O] = \frac{[H_3O^+][A^-]}{[HA]} \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

K_a is called dissociation or ionisation constant of an acid.

Note : The larger the value of K_a, higher is the concentration of Hydronium ion & therefore stronger is the acid.

Note : H^+ exists in H_2O in the form of Hydronium ion (H_3O^+) or $H_9O_4^+$.



Comp. Point. * Lesser will be the value of pK_a, stronger will be the acid.

Comp. Point. $pK_a = -\log K_a$

General $[pK_x = -\log K_x]$

$pK_w = -\log K_w$

$pH = -\log [H^+]$

$pOH = -\log [OH^-]$

DEGREE OF DISSOCIATION OR IONISATION : The fraction of the total no. of molecules of an electrolyte (acid or base) which ionise into ions is called degree of dissociation.

Degree of dissociation (α) = $\dfrac{\text{no. of molecules of the electrolyte which ionise}}{\text{total no. of molecule of the electrolyte}}$

CONCENTRATION OF H^+ OR HYDRONIUM ION FOR WEAK ACIDS

$$\begin{array}{lcccc} HA & + & H_2O \rightleftharpoons & H_3O^+ & + \quad A^- \\ 1 & & & 0 & 0 \\ 1-\alpha & & & \alpha & \alpha \\ c(1-\alpha) & & & c\alpha & c\alpha \end{array}$$

$$\boxed{H_3O^+ = c.\alpha}$$

Now, $K_a = \dfrac{[H_3O^+][A^-]}{[HA]} = \dfrac{c\alpha.c\alpha}{c(1-\alpha)} = \dfrac{\alpha^2 c}{(1-\alpha)}$

$$\boxed{K_a = \frac{\alpha^2 c}{(1-\alpha)}}$$

for weak acid α is very small so that $1 - \alpha \cong 1$

$K_a = \alpha^2 c$

$\Rightarrow \quad \boxed{\alpha = \sqrt{\dfrac{K_a}{c}}}$

Now, $[H_3O^+] = c.\alpha = c\sqrt{\dfrac{K_a}{c}}$

$\Rightarrow \quad \boxed{[H_3O^+] = \sqrt{K_\alpha.c}}$

Dissociation or Ionisation constants of bases in water (H_2O)

$$BOH \rightleftharpoons B^+ + OH^-$$

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

$$K_b = \boxed{\frac{\alpha^2 c}{(1-\alpha)}}$$

$$\boxed{[OH^-] = \sqrt{K_b.c}}$$

Special Note : Relative strength of Acid & Base.

For acid, $\dfrac{S_1}{S_2} = \sqrt{\dfrac{K_{a_1}}{K_{a_2}}}$ & for base, $\dfrac{S_1}{S_2} = \sqrt{\dfrac{K_{b_1}}{K_{b_2}}}$

Ionisation of water Or Ionic product of water

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Since the degree of ionisation of H_2O is very small, the concentration of unionized water may be practically taken as constant

$K[H_2O]^2 = [H_3O^+][OH^-]$

$$\boxed{K_w = [H_3O][OH^-]}$$

K_w is known as ionic product of water at 298 K.

$$K_w = 1.008 \times 10^{-14}$$

$$\Rightarrow \quad K_w \cup 1.0 \times 10^{-14}$$

Note : The value of K_w increases with increase in temperature.

$ln K = \log_e K$,

$\log K = \log_{10} K$

$\log_e K = 2.303 \times \log_{10} K$

The pH Scale

Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the pH scale.

The pH of a solution is defined as the negative logarithm to base 10 of the activity (a_{H^+}) of hydrogen ion.

In dilute solutions (< 0.01 M), activity of hydrogen ion (H+) is equal in magnitude to molarity represented by [H+]. It should be noted that activity has no units and is defined as:

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

From the definition of pH, the following can be written,

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

Thus, an acidic solution of HCl (10^{-2}M) will have a pH = 2. Similarly, a basic solution of NaOH having $[OH-] = 10^{-4}$ M and $[H_3O+] = 10^{-10}$ M will have a pH = 10.

At 25 °C, pure water has a concentration of hydrogen ions,

[H+] = 10–7 M. Hence, the pH of pure water is given as:

$$pH = -\log(10^{-7}) = 7$$

Acidic solutions possess a concentration of hydrogen ions, $[H+] > 10^{-7}$M,

while basic solutions possess a concentration of hydrogen ions, $[H+] < 10^{-7}$ M.

thus, we can summarise that

Acidic solution has pH < 7

Basic solution has pH > 7

Neutral solution has pH = 7

Now again, consider the equation (7.28) at 298 K

$K_w = [H_3O+] [OH^-] = 10^{-14}$

Taking negative logarithm on both sides of equation, we obtain

$-\log K_w = -\log \{[H_3O+] [OH^-]\}$

$= -\log [H_3O+] - \log [OH^-]$

$= -\log 10^{-14}$

$$pK_w = pH + pOH = 14$$

Note that although K_w may change with temperature the variations in pH with temperature are so small that we often ignore it.

pK_w is a very important quantity for aqueous solutions and controls the relative concentrations of hydrogen and hydroxyl ions as their product is a constant.

It should be noted that as the pH scale is logarithmic, a change in pH by just one unit also means change in [H+] by a factor of 10. Similarly, when the hydrogen ion concentration, [H+] changes by a factor of 100, the value of pH changes by 2 units. Now you can realise why the change in pH with temperature is often ignored.

The pH of a solution can be found roughly with the help of pH paper that has different colour in solutions of different pH.

For greater accuracy pH meters are used.

pH meters of the size of a writing pen are now available in the market

$$[H^+] = 10^{-pH}$$

$$[H_3O^+] = 10^{-pH}$$

$\log_{10} [H_3O^+] = \log_{10} 10^{-pH}$

$\log_{10} [H_3O^+] = -pH \log_{10} 10$

$\text{pH} = -\log_{10}[H_3O^+]$

$\text{pH} = \log_{10}\dfrac{1}{[H_3O^+]}$

Acid	Neutral	Base
$[H_3O^+] > 10^{-7}$	$[H_3O^+] = 10^{-7}$	$[H_3O^+] < 10^{-7}$
$pH < 7$	$pH = 7$	$pH > 7$

$0 \xleftarrow[\text{Strong acid}]{} 7 \xrightarrow[\text{Strong base}]{} 14$

$*pH = -\log[H_3O^+]$ $\quad pOH = -\log[OH^-]$

at 25°C $\boxed{\text{pH} + \text{pOH} = 14}$

pH of Some Common Substances

Name of the Fluid	pH	Name of the Fluid	pH
Saturated solution of $NaOH$	~ 15	Black Coffee	5.0
$0.1M$ $NaOH$ solution	13	Tomato Juice	~ 4.2
Lime water	10.5	Soft drinks and vinegar	~ 3.0
Milk of magnesia	10	Lemon juice	~ 2.2
Egg white, sea water	7.8	Gastric juice	~ 1.2
Human blood	7.4	$1M$ HCl solution	~ 0
Milk	6.8	Concentrated HCl	~ 1.0
Human Saliva	6.4		

Relation between K_a and K_b

(i) $K_a \times K_b = K_w$

(ii) **pKa + pKb = pKw = 14 (at 298K)**

The ionization Constant of Some Common Polyprotic Acids (298 K)

Acid	K_{a_1}	K_{a_2}	K_{a_3}
Oxalic Acid	5.9×10^{-2}	6.4×10^{-4}	
Ascorbic Acid	7.4×10^{-4}	1.6×10^{-12}	
Sulphurous Acid	1.7×10^{-2}	6.4×10^{-3}	
Sulphuric Acid	Very large	1.2×10^{-2}	
Carbonic Acid	4.3×10^{-7}	5.6×10^{-21}	
Citric Acid	7.4×10^{-4}	1.7×10^{-6}	4.0×10^{-2}
Phosphoric Acid	7.5×10^{-3}	6.2×10^{-3}	4.0×10^{-23}

It can be seen that higher order ionization constants (Ka_2, Ka_3) are smaller than the lower order ionization constant (Ka_1) of a polyprotic acid.

The reason for this is that it is more difficult to remove a positively charged proton from a negative

ion due to electrostatic forces.

This can be seen in the case of removing a proton from the uncharged H_2CO_3 as compared from a negatively charged HCO_3^-.

Similarly, it is more difficult to remove a proton from a doubly charged HPO_4^{2-}anion as compared to $H_2PO_4^-$.

Polyprotic acid solutions contain a mixture of acids like H_2A, HA^- and A^{2-} in case of a diprotic acid. H_2A being a strong acid, the primary reaction involves the dissociation of H_2A, and H_3O+ in the solution comes mainly from the first dissociation step.

Factors Affecting Acid Strength

Why should some acids be stronger than others?

What factors are responsible for making them stronger?

The answer lies in its being a complex phenomenon. But, broadly speaking we can say **that the extent of dissociation of an acid depends on the strength and polarity of the H-A bond.**

In general, **when strength of H-A bond decreases, that is, the energy required to break the bond decreases, HA becomes a stronger acid.**

Also, **when the H-A bond becomes more polar i.e., the electronegativity difference between the atoms H and A increases and there is marked charge separation, cleavage of the bond becomes easier thereby increasing the acidity.**

But it should be noted that while **comparing elements in the same group of the periodic table, H-A bond strength is a more important factor** in determining acidity than its polar nature. As the size of A increases down the group,

H-A bond strength decreases and so the acid strength increases. For example,

Size increases

HF << HCl << HBr << HI

Acid strength increases Similarly, H_2S is stronger acid than H_2O.

But, when we discuss **elements in the same row of the periodic table, H-A bond polarity becomes the deciding factor for determining the acid strength.**

As the electronegativity of A increases, the strength of the acid also increases. For example, Electronegativity of A increases

$CH_4 < NH_3 < H_2O < HF$

Acid strength increases

SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

As a general rule , for a salt to be able to dissolve in a particular solvent its **solvation enthalpy must be greater than its lattice enthalpy** so that the latter may be overcome by former.

Category I	Soluble	Solubility $> 0.1M$
Category II	Slightly soluble	$0.1M <$ Solubility $< 0.1M$
Category III	Sparingly soluble	Solubility $< 0.01M$

SOLUBILITY PRODUCT CONSTANT

$$AB(s) \rightleftharpoons A^+(aq) + B^-(aq)$$

$$K = \frac{[A^+][B^-]}{[AB]}$$

$$K[AB] = [A^+][B^-]$$

$$K_{sp} = [A^+][B^-]$$

Eg. $A_2B_3 \rightleftharpoons 2A^{+++} + 3B^{--}$

$$K = \frac{[A^{+++}]^2[B^{--}]^3}{[A_2B_3]}$$

$$K[A_2B_3] = [A^{+++}]^2[B^{--}]^3$$

$$\boxed{K_{ab} = [A^{+++}]^2[B^{--}]^3}$$

The solubility product of a salt at a given temperature is equal to the product of the concentration of its ions in the saturated solution with each concentration term raised to the power equal to the no. of ions produced on dissociation of one mole of the substance.

RELATION BETWEEN SOLUBILITY AND SOLUBILITY PRODUCT

For a Binary solution

$$\begin{array}{llll} AB(s) & \rightleftharpoons A^+ (aq) & + & B^- (aq) \\ S & \quad 0 & & \quad 0 \\ & \quad S & & \quad S \end{array}$$

$K_{sp} = [A^+]\,[B^-]$

$K_{sp} = S.\,S$

$K_{sp} = S^2$

$S = \sqrt{K_{sp}}$

For a ternary solution

$$\begin{array}{llll} CaF_2 & \rightleftharpoons Ca^{++} & + & 2F^- \\ S & \quad 0 & & \quad 0 \\ & \quad S & & \quad 2S \end{array}$$

$$\boxed{K_{sp} = 4S^3}$$

* Unit of solubility = mol/L

If given in gm/L, convert in mol/L

$$\text{mole} = \frac{wt.in\,gm}{mol.wt.}$$

Predicting the precipitation in reaction

$AB \rightleftharpoons A^+ + B^-$

Ionic product $[A^+]\,[B^-] = K_{sp}$ (Saturated solution)

$[A^+]\,[B^-] > K_{sp}$ (ppt.)

$[A^+]\,[B^-] < K_{sp}$ (solution)

COMMON ION EFFECT

The suppression of the degree of dissociation of a weak acid or a weak base by the addition of strong electrolyte containing a common ion is called common ion effect.

$$\begin{array}{llccc} \text{* (Strong)} & AB \rightleftharpoons & A^+ & + & B^- \\ \text{(Weak)} & AC \rightleftharpoons & A^+ & + & C^- \\ & & \text{Common and excess} & & \text{Less} \end{array}$$

⇒ HYDROLYSIS OF SALTS

The reaction of anion or cation of the salt with water to produce an acidic or basic solution.

Hydrolysis is the reverse of neutralization.

The equilibrium constant of such a reaction is called hydrolysis constant. The fraction of the total salt that gets hydrolyzed at equilibrium is called degree of hydrolysis.

Note : Strong acid + Strong base = neutral

weak + strong = Sol^n acc. to strong

RELATION OF HYDROLYSIS CONSTANT AND K_a AND K_b

HYDROLYSIS OF SALTS OF WEAK ACID AND STRONG BASE : The examples of these types of salts are sodium acetate, sodium carbonate & sodium phosphate etc. The resulting solution will be basic in character and having pH > 7.

Eq. $CH_3COONa + H_2O \rightleftharpoons \underset{\text{(Weak acid)}}{CH_3COOH} + \underset{\text{(Strong base)}}{NaOH}$

$CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$ $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

Since water is reacting with anion, the hydrolysis will be **anionic hydrolysis.**

$$K = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-][H_2O]}$$

$$K[H_2O] = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$K_H = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \qquad ...(1)$$

where, K_H is the hydrolysis constant for weak acid CH_3COOH

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

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \qquad ...(2)$$

Multiply (1) × (2)

$$K_H.K_a = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \times \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \qquad K_H.K_a = [OH^-][H^+] = K_w$$

But $\quad [OH^-][H^+] = K_w$

$\therefore$

$$K_H.K_a = K_w$$

$$K_H = \frac{K_w}{K_a}$$

Hydrolysis constant of the salt is inversely proportional to the dissociation constant of weak acid, therefore **weaker is the acid, Greater is the hydrolysis constant of the salt.**

DEGREE OF HYDROLYSIS : Let the original concentration of the salt in the solution be 'C' mole L^{-1} and 'h' is the degree of Hydrolysis at that concentration.

Eg. $CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$

$$\begin{array}{lccc} CH_3COO^- + H_2O & \rightleftharpoons & CH_3COOH + & OH^- \\ 1 & & 0 & 0 \\ 1-h & & h & h \\ c(1-h) & & ch & ch \end{array}$$

$$K_H = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{ch.ch}{c(1-h)}$$

$$K_H = \frac{ch^2}{1-h}$$

If h is very small as compared to 1 we can assume,

$1 - h \cup 1$

$\therefore$ $K_H = ch^2$

$$h^2 = \frac{K_h}{c} \qquad h = \sqrt{\frac{K_H}{c}}$$

But, $K_H = \dfrac{K_w}{K_a}$

$$\therefore \quad h = \sqrt{\frac{K_w}{K_a.c}}$$

pH of the hydrolysed salt solution

$$[OH^-] = ch$$

$$[H_3O^+]\,[OH^-] = K_w.$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{K_w}{ch}$$

$$= \frac{K_w}{c}\sqrt{\frac{K_a.c}{K_w}}$$

$$[H_3O^+] = \sqrt{\frac{K_w.K_a}{c}}$$

Now, $\quad pH = -\log\,[H_3O^+]$

$$= -\log\left(\frac{K_w.K_a}{c}\right)^{1/2} \qquad = -\frac{1}{2}\log\left(\frac{K_w.K_a}{c}\right)$$

$$= -\frac{1}{2}[\log K_w + \log K_a - \log c] \qquad = \frac{1}{2}[-\log K_w - \log K_a + \log c]$$

$$\boxed{pH = \frac{1}{2}[pK_w + pK_a + \log c]}$$

Salt of	Example	Hydrolys is constant	Degree of Hydrolysis	pH =
Strong base + Weak acid	CH_3COONa	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_w}{K_a.C}}$	$\frac{1}{2}[pK_w + pK_a + \log c]$
Strong acid + Weak base	NH_4Cl	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_w}{K_b.c}}$	$\frac{1}{2}[pK_w - pK_a - \log c]$
Weak acid + Weak base	CH_3COONH_4	$K_h = \frac{K_w}{K_a.K_b}$ D	$h = \sqrt{\frac{K_w}{K_b.K_a}}$	$\frac{1}{2}[pK_w + pK_a + pK_b]$
Strong acid + Strong base	$NaCl$	does not hydrolysed		

BUFFER SOLUTIONS

Many body fluids e.g., blood or urine have definite pH and any deviation in their pH indicates malfunctioning of the body. The control of pH is also very important in many chemical and biochemical processes.

The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.

Human blood is an excellent example of natural buffer solution. Blood maintains its pH value about 7.35.

Buffer solution are of two types :

(i) **Acidic buffer solution :** It contains equimolar quantities of a weak acid and its salt with strong base. For eg. Acetic acid and Sodium acetate i.e.

$CH_3COOH \quad + \quad CH_3COONa$

(Weak acid + Salt of its acid with strong base)

(ii) **Basic buffer solution :** It contains equimolar quantities of a weak base and its salt with a strong acid. For eg. Ammonium Hydroxide and Ammonium chloride. i.e.

NH_4OH + NH_4Cl

(Weak base + Salt of its base with strong acid)

Buffer solution of known pH can be prepared from the knowledge of pK_a of the acid or pK_b of base and by controlling the ratio of the salt and acid or salt and base.

A mixture of acetic acid and sodium acetate acts as buffer solution around pH 4.75 and a mixture of ammonium chloride and ammonium hydroxide acts as a buffer around pH 9.25.

⇒ Buffer Action

The ability of the buffer solution to resist the changes in pH value on the addition of small amount of an acid or a base is called buffer action. For eg.

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

$$Acid \longrightarrow H^+$$

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

(Undissociated molecule)

Handerson's Equation :

For acidic buffer

$$\boxed{pH = pK_a + \log\frac{[salt]}{[acid]}}$$

For basic buffer

$$\boxed{pOH = pK_b + \log\frac{[salt]}{[base]}}$$

Common Ion Effect on Solubility of Ionic Salts :

It is expected from Le Chatelier's principle that if we increase the concentration of any one of the ions, it should combine with the ion of its opposite charge and some of the salt will be precipitated till once again $K_{sp} = Q_{sp}$.

Similarly, if the concentration of one of the ions is decreased, more salt will dissolve to increase the concentration of both the ions till once again $K_{sp} = Q_{sp}$.

This is applicable even to soluble salts like sodium chloride except that due to higher concentrations of the ions, we use their activities instead of their molarities in the expression for Q_{sp}.

Thus if we take a saturated solution of sodium chloride and pass HCl gas through it, then sodium chloride is precipitated due to increased concentration (activity) of chloride ion available from the dissociation of HCl. Sodium chloride thus obtained is of very high purity and we can get rid of impurities like sodium and magnesium sulphates. The common ion effect is also used for almost complete precipitation of a particular ion as its sparingly soluble salt, with very low value of solubility product for gravimetric estimation. Thus we can precipitate silver ion as silver chloride, ferric ion as its hydroxide (or hydrated ferric oxide) and barium ion as its sulphate for quantitative estimations. The solubility of salts of weak acids like phosphates increases at lower pH. This is because at lower pH the concentration of the anion decreases due to its protonation. This in turn increase the solubility of the salt so that $K_{sp} = Q_{sp}$. We have to satisfy two equilibria simultaneously.

⇒ Indicators

Indicators are the substances which indicate end point of a chemical reaction by change in colour. For eg. In volumetric analysis, during the titration of sodium hydroxide and HCl, Phenolphthalein turns pink to colourless when total sodium hydroxide has been neutralized by HCl.

⇒ Acid-Base Indicators

The object of an acid-base titration is to determine the amount of acid which is exactly equivalent chemically to the amount of some standard base, the point at which equivalence is raised is called endpoint.

⇒ Acid-Base Indicators Behaviour

The first successful theory was developed by Ostwald which offered a simple explanation for the colour change with change in pH.

Acc. to Ostwald, all acid-base indicator are weak organic acid or base which possesses different colours in unionized and ionised states. Eg.

For acidic indicators

$$\underset{\text{(Phenolphthalin)}}{HPh} \rightleftharpoons H^+ + \underset{\text{(Pink) coloured ion}}{Ph^-}$$

HPh can be written as HIn.

For basic indicators.

$$\underset{\text{Methylorange}}{MeOH} \rightleftharpoons \underset{\substack{\text{(Red)}\\ \text{coloured ion}}}{Me^+} + OH^-$$

MeOH can also be written as InOH (In-Indicators)

QUESTIONS

NCERT EXERCISE & EXAMPLES

Based on K_p and K_c

1. What is K_c for the following equilibrium when the equilibrium concentration of each substance is :
$[SO_2] = 0.60$ M, $[O_2] = 0.82$ M and $[SO_3] = 1.90$ M

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

2. At a certain temperature and total pressure of 10^5Pa, iodine vapour contains 40% by volume of I atoms $[I_2(g) \rightleftharpoons 2I(g)]$.
Calculate K_p for the equilibrium.

3. Write the expression for the equilibrium constant, K_c for each of the following reactions :

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

(ii) $2Cu(NO_3)_2(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$

(iii) $CH_3COOC_2H_5(aq) + H_2O(\ell) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$

(iv) $Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$

(v) $I_2(s) + 5F_2 \rightleftharpoons 2IF_5$

4. Find out the value of K_c for each of the following equilibria from the value of K_p :

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$; $K_p = 1.8 \times 10^{-2}$ at 500 K

(ii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; $K_p = 167$ at 1073 K.

5. For the following equilibrium $K_c = 6.3 \times 10^{14}$ at 1000 K for the following equilibrium.

$$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$$

Both the forward and reverse reaction in the equilibrium are elementary bimolecular reactions. What is K_c, for the reverse reaction ?

6. Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression ?

7. Reaction between N_2 and O_2 takes place as following:

$$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$$

If a mixture of 0.482 mol N_2 and 0.933 mol of O_2 is placed in a reaction vessel of volume 10L and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$. Determine the composition of equilibrium mixture.

Based on Applications of Law of Equilibrium

8. Nitric oxide reacts with Br_2 and give nitrosyl bromide as per reaction given below :

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$$

When 0.087 mol of NO and 0.0437 mol of Br_2 are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of NO and Br_2.

9. At 450K, $K_p = 2.0 \times 10^{10}$/bar for the given reaction at equilibrium.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

What is K_c at this temperature ?

10. A sample of HI(g) is placed in a flask at a pressure of 0.2 atm. At equilibrium the partial pressure of III (g) is 0.04 atm. What is K_p for the given equilibrium ?

11. A mixture of 1.57 mol of N_2, 1.92 mol of H_2 and 8.13 mol of NH_3 is introduced into a 20 litre reaction vessel at 500K. At this temperature, the equilibrium constant K_c for the reaction; $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 1.7×10^2. Is the reaction mixture at equilibrium ? If not, what is the direction of the net reaction ?

12. The equilibrium constant expression for a gas reaction is $K_c = \dfrac{[NH_3]^4[O_2]^5}{[NO]^4[H_2O]^6}$

Write the balanced chemical equation corresponding to this expression.

13. One mol of H_2O and one mol of CO are taken in 10 L vessel and heated to 725 K. At equilibrium 40% of water (by mass) reacts with CO according to the equation,

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Calculate the equilibrium constant for the reaction ?

14. At 700 K equilibrium constant for the reaction :

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

is 54.8. If 0.5 mol L^{-1} of HI(g) is present at equilibrium at 700 K, what are the concentration of $H_2(g)$ and $I_2(g)$ assuming that we initially started with HI(g) and allowed it to reach equilibrium at 700 K ?

15. What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M ?

$2ICl(g) \rightleftharpoons I_2(g) + Cl_2(g);\ K_c = 0.14$

16. $K_p = 0.04$ atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of C_2H_6 when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium ?

$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$

17. Ethyl acetate is formed by the reaction between ethanol and acetic acid and equilibrium is represented as:

$CH_3COOH(\ell) + C_2H_5OH(\ell) \rightleftharpoons$
$CH_3COOC_2H_5(\ell) + H_2O(\ell)$

(i) Write the concentration ratio (reaction quotient), Qc, for this reaction (note : water is not in excess and is not a solvent in this reaction)

(ii) At 293K, if one starts with 1.00 mol of acetic acid and 9.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293K, 0.214 mol of ethyl acetate is found after sometime. Has equilibrium been reached ?

18. A sample of pure PCl_5 was introduced into and evacuated vessel at 473K. After equilibrium was attained concentration of PCl_5 was found to be 0.5×10^{-1} mol L^{-1}. If value of K_c is 8.3×10^{-3}, what are the concentration of PCl and Cl_2 at equilibrium ?

19. One of the reaction that takes place in producing steel from iron ore is the reduction of iron (II) oxide by carbon monoxide to give iron metal and CO_2.

$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g);$
$K_p = 0.265$ at 1050K

What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are $p_{CO} = 1.4$ atm and $p_{CO_2} = 0.80$ atm ?

20. Equilibrium constant K_c for the reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500K is 0.061.

At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L^{-1} N_2, 2.0 mol L^{-1} H_2 and 0.5 mol L^{-1} NH_3. Is the reaction at equilibrium ? If not in which direction does the reaction tend to proceed to each equilibrium ?

21. Bromine monochloride, BrCl, decomposes into bromine and chlorine and reaches the equilibrium :

$2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$ for which K_c = 32 at 500 K, if initially pure BrCl is present at a concentration of 3.3×10^{-3} mol L^{-1}, what is its molar concentration in the mixture at equilibrium?

22. At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90.55% CO by mass in the reaction,

$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$.

Calculate K_c for this reaction at the above temperature?

23. Calculate (a) ΔG^o and (b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298 K.

$$NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$$

Where

$\Delta_f G^o(NO_2) = 52.0\,kJ/mol;$
$\Delta_f G^o(NO) = 87.0\,kJ/mol;$
$\Delta_f G^o(O_2) = 0\,kJ/mol$

24. The equilibrium constant for the following reaction is 1.6×10^5 at 1024 K.

$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$

Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K ?

25. Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction :

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

(a) Write as expression for K_p for the above reaction.

(b) How will the values of K_p and composition of equilibrium mixture be affected by
  (i) increasing the pressure
  (ii) increasing the temperature
  (iii) using a catalyst.

26. Describe the effect of : (a) addition of H_2 (b) addition of CH_3OH (c) removal of CO (d) removal of CH_3OH, on the equilibrium of the reaction :

$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$

27. At 473 K, equilibrium constant K_c for decomposition of phosphorus pentachloride PCl_5 is 8.3×10^{-3}. If decomposition is depicted as,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g);$$

$$\Delta_r H^\circ = 124.0\,kJ\,mol^{-1}$$

(a) write an expression for K_c for the reaction

(b) what is the value of K_c for the reverse reaction at the same temperature ?

(c) what would be the effect on K_c if (i) more PCl_5 is added (ii) pressure is increased (iii) the temperature is increased ?

28. Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The 1st stage of two stage reaction involves the formation of CO and H_2. In 2nd stage, CO formed in 1st stage is reacted with more steam in water gas shift reaction,

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g).$$

If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that $P_{CO} = P_{H_2O} = 4.0$ bar, what will be the partial pressure of H_2 at equilibrium ? $K_p = 10.1$ at 400°C.

29. The value of K_c of the reaction;

$3O_2(g) \rightleftharpoons 2O_3(g)$, **is** 2.0×10^{-50} **at 25°C.**

If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2}, what is the concentration of O_3 ?

30. The reaction,

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g),$$

is at equilibrium at 1300 K in a 1L flask. It also contain 0.30 mol of CO, 0.10 mol of H_2 and 0.02 mol of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration of CH_4 in the mixture. The equilibrium constant, K_c for the reaction at the given temperature is 3.90.

Based on Le Chatelier's Principle

31. A liquid in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.

(a) What is the initial affect of the change on vapour pressure ?

(b) How do rates of evaporation and condensation change initially ?

(c) What happens when equilibrium is restored finally and what will be the final vapour pressure ?

32. Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume ?

(a) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(b) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

(c) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

33. Which of the following reactions will get affected by increasing of pressure ? Also mention whether change will cause the reaction to go into forward or backward direction ?

(i) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

(ii) $CH_4(s) + 2S_2(g) \rightleftharpoons CS_2(g) + 2H_2S(g)$

(iii) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

(iv) $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$

(v) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(vi) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

34. Predict which of the following reaction will have appreciable concentration of reactants and products :

(a) $Cl_2(g) \rightleftharpoons 2Cl(g);\ K_c = 5 \times 10^{-39}$

(b) $Cl_2(g) + 2NO(g) \rightleftharpoons 3NO_2Cl(g);$ $K_c = 3.7 \times 10^8$

(c) $Cl_2(g) + 2NO_2(g) \rightleftharpoons 2NO_2Cl(g);$ $K_c = 1.8$

Based on Bronsted Lowry Acids and Bases

35. What is meant by the conjugate acid base pair ? Find the conjugate acid/base for the following species :

HNO_2, CN^-, $HClO_4$, F^-, OH^-, CO_3^{2-} and S^{2-}.

36. Which of the following are lewis acids ?

H_2O, BF_3, H^+, NH_4^+.

37. What will be the conjugate bases for the following Bronsted acids : HF, H_2SO_4 and HCO_3^- ?

38. Write the conjugate acids for the following Bronsted bases : NH_2^-, NH_3 acid $HCOO^-$.

39. The species : H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and base.

Based on Lewis Acids and Bases

40. Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base :

(a) OH^- (b) F^-

(c) H^+ (d) BCl_3 ?

41. Predict if the solution of the following salts are neutral, acidic or basic :

NaCl, KBr, NaCN, NH_4NO_3, $NaNO_2$ and KF.

Based on pH Scale

42. The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3} M. What is its pH ?

43. The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

44. The ionization constant of HF, HCOOH and HCN at 298 K are 6.8×10^{-4}, 1.8×10^{-4} and 4.8×10^{-9} respectively. Calculate the ionization constants of the corresponding conjugate base.

45. The ionization constant of acetic acid is 1.74×10^{-5}. Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.

46. It has been found that the pH of a 0.01 M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its pKa.

47. Assuming complete dissociation calculate the pH of the following solutions :

(a) 0.003 M HCl (b) 0.005 M NaOH

(c) 0.002 M HBr (d) 0.002 M KOH

48. Calculate the pH of the following solutions :

(a) 2g of TlOH dissolved in water to give 2 litre of solution.

(b) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution.

(c) 0.3 g of NaOH dissolved in water to give 200 mL of solution.

(d) 1 mL of 13.6 M HCl is diluted with water to give 1 litre of solution.

49. The degree of ionization of a 0.1 M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pKa of bromoacetic acid.

50. The pH of 0.005 M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate its ionization constant and pKb.

51. What is the pH of 0.001 M aniline solution. The ionization constant of aniline can be taken from Table 7.7. Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline ? (given $K_b = 4.27 \times 10^{-10}$)

52. Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below :

(a) Human muscle – fluid = 6.83

(b) Human stomach fluid = 1.2

(c) Human blood = 7.38

(d) Human saliva = 6.4.

53. The pH of milk, black coffee, tomato juice, lemon juice, and egg white are 6.8, 5.0, 4.2, 2.2 and 7.8 respectively. Calculate corresponding hydrogen ion concentration in each.

54. If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH ?

55. The solubility of $Sr(OH)_2$ at 298K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

56. The ionization constant of propanoic acid is 1.32×10^{-5}. Calculate the degree of ionization of the acid in its 0.05 M solution and also its pH. What will be its degree of ionization if the solution is 0.01 M in HCl also ?

57. The pH of 0.1 M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

58. The ionization constant of nitrous acid is 4.5×10^{-4}. Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.

59. A 0.02 M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine.

60. The ionization constant of chloroacetic acid is 1.35×10^{-3}. What will be the pH of 0.1 M acid and its 0.1 M sodium salt solution ?

61. Ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature ?

62. Calculate the pH of the resultant mixtures :
- (a) 10 mL of 0.2 M $Ca(OH)_2$ + 25 mL of 0.1 M HCl
- (b) 10 mL of 0.01 M H_2SO_4+10 mL of 0.01M $Ca(OH)_2$
- (c) 10 mL of 0.1 M H_2SO_4 + 10 mL of 0.1 M KOH.

Based on Ostwald Dilution Law

63. The ionization constant of phenol is 1.0×10^{-10}. What is the concentration of phenolate ion in 0.05 M solution of phenol ? What will be its degree of ionization if the solution is also 0.01 M in sodium phenolate ?

64. The first ionization constant of H_2S is 9.1×10^{-8}. Calculate the concentration of HS^- ion in its 0.1 M solution and how will this concentration be effected if the solution is 0.1 M in HCl also. If the second dissociation constant of H_2S is 1.2×10^{-13}, calculate the concentration of S^{2-} under both conditions.

65. Calculate the degree of ionization of 0.05 M acetic acid if its pKa value is 4.74. How is the degree of dissociation affected when its solution is also
(a) 0.01 M HCl (b) 0.1 M in HCl ?

66. The ionization constant of dimethylamine is 5.4×10^{-4}. Calculate its degree of ionization in its 0.02 M solution. What percentage of dimethylamine is ionized if the solution is also 0.1 M in NaOH ?

Based on Solubility Product

67. Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298 K from their solubility product constants given in table 7.9. Determine also the molarities of individual ions.

68. The solubility product constant of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.

69. Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate ? (For cupric iodate $K_{sp} = 7.4 \times 10^{-8}$).

70. The ionization constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water ?

71. What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide ? (For iron sulphide $K_{sp} = 6.3 \times 10^{-18}$).

72. What is the minimum volume of water required to dissolve 1g of calcium sulphate at 298 K ? (For calcium sulphate, K_{sp} is 9.1×10^{-6}).

73. The concentration of sulphide ion in 0.1 M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19} M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following : $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$, in which solutions precipitation will take place?
Given K_{sp} for FeS = 6.3×10^{-18}; MnS = 2.5×10^{-13}
ZnS = 1.6×10^{-24}; and CdS = 8.0×10^{-27}

SOLUTIONS

NCERT EXERCISE & EXAMPLES

Sol.1 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K_C = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

$$= \frac{(1.9)^2}{(0.6)^2\,(0.82)} = 12.229\,\text{L mol}^{-1}$$

Sol.2 $I_2(g) \rightleftharpoons 2I(g)$

total pressure = 10^5 Pa

Since out of total volume, 40% by volume are I atoms

$\therefore$ 60% are I_2 molecules (gaseous)

$$\therefore \text{ Partial pressure of I(g) } = \frac{40}{100} \times 10^5\,\text{Pa}$$

$$\text{Partial pressure of } I_2(g) = \frac{60}{100} \times 10^5\,\text{Pa}$$

$$\therefore\ K_P = \frac{p_I^2}{p_{I_2}} = \frac{(0.4 \times 10^5)^2}{0.60 \times 10^5} = 2.67 \times 10^4\,\text{Pa}$$

Sol.3 (i) $K_c = \dfrac{[NO(g)]^2\ Cl_2(g)]}{[NOCl(g)]^2}$

(ii) $K_c = \dfrac{[CuO(s)]^2\,[NO_2(g)]^4\,[O_2(g)]}{[Cu(NO_3)_2(s)]^2}$

$= [NO_2(g)]^2\,[O_2(g)]$

(iii) $K_c = \dfrac{[CH_3COOH(aq)]\,[C_2H_5OH(aq)]}{[CH_3COOC_2H_5(aq)]\,[H_2O(\ell)]}$

(iv) $K_c = \dfrac{[Fe(OH)_3(s)]}{[Fe^{3+}(aq)]\,[OH^-(aq)]^3}$

$= \dfrac{1}{[Fe^{3+}(aq)][OH^-(aq)]^3}$

(v) $K_c = \dfrac{[IF_5]^2}{[I_2(s)][F_2]^5} = \dfrac{[IF_5]^2}{[F_2]^5}$

Sol.4 (i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

$K_p = 1.8 \times 10^{-2}$ at 500 K

Δn = change in the no. of amoles (gaseous)

= [2 + 1] – 2 = 1

$\therefore\ K_P = K_C \times (RT)^{\Delta n}$ [R = 0.08211 atm/K/Mol]

or $1.8 \times 10^{-2} = K_C \times (RT)^1$

or $K_C = \dfrac{1.8 \times 10^{-2}}{RT} = \dfrac{1.8 \times 10^{-2}}{0.0821 \times 500} = 4.4 \times 10^{-4}$

(ii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$;

$K_p = 167$ at 1073 K ; Here $\Delta n = 1$

$$\therefore\ K_C = \frac{K_P}{RT} = \frac{167}{0.0821 \times 1073} = 1.90$$

Sol.5 $K_c = 6.3 \times 10^{14}$ at 1000 K for the equilibrium.

$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$

i.e., $K_C = \dfrac{[NO_2][O_2]}{[NO][O_3]} = 6.3 \times 10^{14}$ (given)

The reverse reaction will be

$NO_2(g) + O_2(g) \rightleftharpoons NO(g) + O_3(g)$

$$K_C = \frac{[NO][O_3]}{[NO_2][O_2]} = \frac{1}{K_C}$$

$$= \frac{1}{6.3 \times 10^{14}} = 1.59 \times 10^{-15}$$

Sol.6 $[\text{Pure liquid}] \text{ or } [\text{Pure solid}] = \dfrac{\text{No.of moles}}{\text{Volume in L}}$

$$= \frac{\text{Mass / mol.mass}}{\text{Volume}} = \frac{\text{Mass}}{\text{Volume}} \times \frac{1}{\text{Mol.mass}} = \frac{\text{Density}}{\text{Mol.mass}}$$

As density of a pure liquid or pure solid is a constant at constant temperature and molecular mass is also constant, therefore, their molar concentrations are constant and included into the equilibrium constant.

Sol.7 Given reaction is

	$2N_2(g)$	+ $O_2(g)$	$\rightleftharpoons 2N_2O(g)$
Inital	0.482 mol	0.933 mol	
At eqm.	0.482 – x	0.933 – x / 2	x
Molar conc.	$\dfrac{0.482 - x}{10}$	$\dfrac{0.933 - x/2}{10}$	$\dfrac{x}{10}$

Where x is the no. of moles reacting of N_2 with $\dfrac{x}{2}$ of O_2 to form x moles of N_2O.

As $K_c = 2.0 \times 10^{-37}$ is very small, this means that the amount of N_2 and O_2 reacted (x) is very small.

Hence at equilibrium, we have

$[N_2] = 0.0484$ mol L^{-1}

$[O_2] = 0.0933$ mol L^{-1}

and $[N_2O] = 0.1$ x

$$\therefore\ K_c = \frac{(0.1x)^2}{(0.0482)^2\,(0.0933)} = 2.0 \times 10^{-37} \text{ (Given)}$$

On solving $x = 6.6 \times 10^{-20}$

Hence $[N_2O] = 0.1x = 6.6 \times 10^{-21}$ mol L^{-1}

Sol.8 0.0518 mol of NOBr is formed from

$0.0518\,\text{mol}$ of NO and $0.0518/2 = 0.0259\,\text{mol}$ of Br_2.

$\therefore$ At equilibrium,

Amount of $NO = 0.087 - 0.0518 = 0.0352\,\text{mol}$

Amount of $Br_2 = 0.0437 - 0.0259 = 0.0178\,\text{mol}$

Sol.9 This given equation is

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$\Lambda n = 2 - [2 + 1] = -1$

$\therefore\ K_P = K_C \times (RT)^{-1}$

$\therefore\ K_C = K_P \times (RT)^1 = = 2.0 \times 10^{10} \times 0.0831 \times 450.$

$= 7.47 \times 10^{11}\ \text{Mol L}^{-1}$

$\therefore K_C$ for the reaction at $450\,K = 7.47 \times 10^{11}\ \text{L Mol}^{-1}$

Sol.10

	$2HI(g) \rightleftharpoons$	$H_2(g)$	$+\ I_2(g)$
Initial pressure	0.2 atm	0	0
At eqm.	0.04 atm	$\frac{0.16}{2}$ atm $= 0.08$ atm	$\frac{0.16}{2}$ atm $= 0.08$ atm

(Decrease in the pressure of $HI = 0.2 - 0.04 = 0.16\,\text{atm}$.)

$$\therefore\ K_p \frac{p_{H_2} \times p_{I_2}}{p^2_{HI}} = \frac{0.08\,\text{atm} \times 0.08\,\text{atm}}{(0.04\,\text{atm})^2} = 4.0.$$

Sol.11 The reaction is

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$Q_c = \frac{[NH_3]}{[N_2][H_2]^3} = \frac{\left(\frac{8.13}{20}\,\text{mol L}^{-1}\right)^2}{\left(\frac{1.57}{20}\,\text{mol L}^{-1}\right)\left(\frac{1.92}{20}\,\text{mol L}^{-1}\right)^3}$$

$= 2.38 \times 10^3$

As $Q_c \neq K_c$, the reaction mixture is **not in equilibrium.**

As $Q_c > K_c$, the net reaction will be in the **backward direction.**

Sol.12 $4NO(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 5O_2(g)$.

Sol.13 At equilibrium, $[H_2O] = \frac{1 - 0.40}{10}\,\text{mol L}^{-1}$

$= 0.06\,\text{mol L}^{-1}$, $[CO] = 0.06\,\text{mol L}^{-1}$,

$[H_2] = \frac{0.4}{10}\,\text{mol L}^{-1} = 0.04\,\text{mol L}^{-1}$,

$[CO_2] = 0.04\,\text{mol L}^{-1}$

$$K = \frac{[H_2][CO_2]}{[H_2O][CO]} = \frac{0.04 \times 0.04}{0.06 \times 0.06} = 0.444.$$

Sol.14 The equilibrium constant (K_C) for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is given as 54.8

$\therefore$ For the reaction; $2HI(g) \rightleftharpoons H_2 + I_2(g)$ the equilibrium constant (K'_C) will be $= \frac{1}{K_C} = \frac{1}{54.8}$

at eqbm. $[HI] = 0.5\ \text{mol L}^{-1}$

Let $[H_2] = [I_2] = x\ \text{Mol L}^{-1}$

$$K'_C = \frac{1}{54.8} = \frac{x \times x}{(0.5)^2}$$

This gives the value of $x = 0.068$

$[H_2] = [I_2] =$ **0.068 Mol L^{-1}.**

Sol.15 Suppose at equilibrium, $[I_2] = [Cl_2] = x\,\text{mol L}^{-1}$. Then

	$2ICl \rightleftharpoons$	$I_2(g)$	$+\ Cl_2(g)$
Initial	0.78 M	0	0
At eqm.	$0.78 - 2x$	x	x

$$K_c = \frac{[I_2][Cl_2]}{[ICl]^2}\ \therefore\ 0.14 = \frac{x \times x}{(0.78 - 2x)^2}$$

or $x^2 = 0.14(0.78 - 2x)^2$

or $0.14 \frac{x \times x}{(0.78 - 2x)^2}$

or $x^2 = 0.14(0.78 - 2x)^2$

or $\frac{x}{0.78 - 2x} \sqrt{0.14} = 0.374$

or $x = 0.292 - 0.748\,x$

or $1.748x = 0.292$ or $x = 0.167$

Hence, equilibrium, $[I_2] = [Cl_2] = 0.167\,M$, $[ICl] = 0.78 - 2 \times 0.167\,M = 0.446\,M$

Sol.16

	$C_2H_6(g) \rightleftharpoons$	$C_2H_4(g)$	$+\ H_2(g)$
Initial pressure	4.0 atm	0	0
At eqm.	$4 - p$	p	p

$$K_p = \frac{p_{C_2H_4} \times p_{H_2}}{p_{C_2H_6}}\ \therefore\ 0.04 = \frac{p^2}{4 - p}$$

or $p^2 = 0.16 - 0.04p$

or $p^2 + 0.04 - 0.16 = 0$

$$\therefore\ p = \frac{-0.04 \pm \sqrt{0.016 - 4(-0.16)}}{2} = \frac{-0.04 \pm 0.89}{2}$$

Taking positive value, $p = \frac{0.80}{2} = 0.40$

$\therefore\ [C_2H_6]_{eq} = 4 - 0.40\,\text{atm} = 3.60\,\text{atm}.$

Sol.17 (i) $Q_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$

(ii)

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Initial $1.00\,\text{mol}$ $0.180\,\text{mol}$

At eqm. $1-0.171$ $0.180-0.171$ $0.171\,\text{mol}$ $0.171\,\text{mol}$

Molar conc. $\frac{0.829}{V}$ $\frac{0.009}{V}$ $\frac{0.171}{V}$ $\frac{0.171}{V}$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$= \frac{(0.171/V)(0.171/V)}{(0.829/V)(0.009/V)} = 3.92$$

(iii)

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Initial $1.000\,\text{mol}$ $0.500\,\text{mol}$

At eqm. $1-0.214$ $0.500-0.214$ $0.214\,\text{mol}$ $0.214\,\text{mol}$

$=0.786\,\text{mol}$ $=0.286\,\text{mol}$

Reaction quotient

$$(Q_c) = \frac{(0.214/V)(0.214/V)}{(0.786/V)(0.286/V)} = 0.204$$

As $Q_c \neq K_c$, equilibrium has not been attained.

Sol.18

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

At eqm. $0.5\times10^{-1}\,\text{mol}\,L^{-1}$ $x\,\text{mol}\,L^{-1}$ $x\,\text{mol}\,L^{-1}$ (suppose)

$\therefore K_c = \frac{x^2}{0.5\times10^{-1}} = 8.3\times10^{-3}$ (Given)

or $x^2 = (8.3\times10^{-3})(0.5\times10^{-1}) = 4.15\times10^{-4}$

or $x = \sqrt{4.15\times10^{-4}} = 2.04\times10^{-2}\,M = 0.02\,M$

Hence, $[PCl_3]_{eq} = 0.02\,M$.

Sol.19

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$$

Initial pressures $1.4\,\text{atm}$ $0.80\,\text{atm}$

$$Q_p = \frac{p_{CO_2}}{p_{CO}} = \frac{0.80}{1.4} = 0.571$$

As $Q_p > K_p$, reaction will move in the backward direction, i.e., pressure of CO_2 will decrease and that of CO will increase to attain equilibrium. Hence, if p is the decrease in pressure of CO_2, increase in pressure of $CO = p$.

$\therefore$ At equilibrium, $p_{CO_2} = (0.80 - p)\,\text{atm}$,

$p_{CO} = (1.4 + p)\,\text{atm}$

$K_p = \frac{p_{CO_2}}{p_{CO}}$ $\therefore 0.265 = \frac{0.80 - p}{1.4 + p}$

or $0.265(1.4 + p) = 0.80 - p$

or $0.371 + 0.265p = 0.80 - p$

or $1.265p = 0.429$ or $0.339\,\text{atm}$

$\therefore (p_{CO})_{eq} = 1.4 + 0.339\,\text{atm} = 1.739\,\text{atm}$,

$(p_{CO_2})_{eq} = 0.80 - 0.339\,\text{atm} = 0.461\,\text{atm}$.

Sol.20 $Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.5)^2}{(3.0)(2.0)^3} = 0.0104$

As $Q_c \neq K_c$, reaction is **not in equilibrium.**

As $Q_c < K$ reaction will proceed in the **forward direction.**

Sol.21

$$2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$$

Initial $3.30\times10^{-3}\,\text{mol}\,L^{-1}$

At eqm. $(3.30\times10^{-3} - x)$ $x/2$ $x/2$

$K_c = \frac{(x/2)(x/2)}{(3.30\times10^{-3} - x)^2} = 32$ (Given)

$\therefore \frac{x^2}{4(3.30\times10^{-3} - x)} = 32$

or $\frac{x}{2(3.30\times10^{-3}) - x} = \sqrt{32} = 5.60$

$x = 11.32(3.30\times10^{-3} - x)$

or $12.32x = 11.32\times3.30\times10^{-3}$

or $x = 3.0\times10^{-3}$

$\therefore$ At eqm. $[BrCl] = (3.30\times10^{-3} - 3.0\times10^{-3})$

$= 0.30\times10^{-3} = 3.0\times10^{-4}\,\text{mol}\,L^{-1}$

Sol.22 If total mass of the mixture of CO and CO_2 is 100g, then

$CO = 90.55\,g$ and $CO_2 = 100 - 90.55 = 9.45\,g$

$\therefore$ Number of moles of $CO_2 = 90.55/3.234$

(molecular mass of $CO = 28$)

Number of moles of $CO_2 = 9.45/44 = 0.215$

(molecular mass of $CO_2 = 44$)

$\therefore p_{CO} = \frac{3.234}{3.234 + 0.215} \times 1\,\text{atm} = 0.938\,\text{atm}$,

$p_{CO_2} = \frac{0.215}{3.234 + 0.215} \times 1\,\text{atm} = 0.062\,\text{atm}$

$K_p = \frac{p^2_{CO}}{p_{CO_2}} = \frac{(0.938)^2}{0.062} = 14.19$.

$\Delta n_g = 2 - 1 = 1$ $\therefore K_p = K_c(RT)$

or $K_c = \frac{K_p}{RT} = \frac{14.19}{0.0821\times1127} = 0.153$.

Sol.23 (a)

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{Products}) - \sum \Delta_f G^\circ(\text{Reactants})$$

$$= \Delta_f G^\circ(NO_2) - \left[\Delta_f G^\circ(NO + \frac{1}{2}\Delta_f G^\circ(O_2)\right]$$

$$= 52.0 - \left(87.0 + \frac{1}{2}\times 0\right) = -35.0\,\text{kJ}\,\text{mol}^{-1}$$

(b) $-\Delta_f G^\circ = 2.303RT\log K$. Hence,

$$-(-35000) = 2.303\times8.314\times298\times\log K$$
$$\text{or } \log K = 6.1341 \text{ or } K = 1.361\times10^6$$

Sol.24

$$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g), K = \frac{1}{(1.6\times10^5)}$$

Initial $10\,\text{bar}$

At eqm. $10-p \qquad p/2 \qquad p/2$

$$K_p = \frac{(p/2)(p/2)}{(10-p)^2} = \frac{1}{1.6\times10^5}\frac{p^2}{4(10-p)^2} = \frac{1}{1.6\times10^5}$$

Taking square root of both sides, we get

$$\frac{p}{2(10-p)} = \frac{1}{4\times10^2} \text{ or } 4\times10^2 p = 2(10-p)$$

$$\text{or } 402p = 20 \text{ or } p = \frac{20}{402} = 4.98\times10^{-2}\,\text{bar}$$

Hence, at equilibrium $p_{H_2} = p_{Br_2} = p/2$ $= 2.5\times10^{-2}\,\text{bar}, p_{HBr} = 10 - p \cong 10\,\text{bar}$

Sol.25 (a) $K_p = \dfrac{p_{CO}\times p_{H_2}^3}{p_{CH_4}\times p_{H_2O}}$

(b)

(i) By Le Chatelier's principle, equilibrium will shift in the backward direction (as $n_r < n_p$)

(ii) As the given reaction is endothermic, by Le Chatlier's principle, equilibrium will shift in the forward direction.

(iii) Equilibrium composition will not be disturbed but equilibrium will be attained quickly.

Sol.26 (a) Equilibrium will shift in the forward direction

(b) Equilibrium will shift in the backward direction

(c) Equilibrium will shift in the backward direction

(d) Equilibrium will shift in the forward direction

Explain on the basis of Le Chatelier's principle in each case.

Sol.27 (a) $K_c = \dfrac{[PCl_3(g)][Cl_2(g)]}{[PCl_5(g)]}$

(b) $K' = \dfrac{1}{8.3\times10^{-3}} = 120.48$

(c)

(i) No effect as K_c is constant at temperature.

(ii) No effect

(iii) As given reaction is endothermic, on increasing the temperature, k_f will increase. As $K_c = \dfrac{k_f}{k_b}$, K_c will increase with increase of temperature.

Sol.28 Suppose the partial pressure of H_2 at equilibrium $= p\,\text{bar}$

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Initial pressure $4.0\,\text{bar} \qquad 4.0\,\text{bar}$

At eqm. $(4-p) \qquad (4-p) \qquad p \qquad p$

$$K_p = \frac{p^2}{(4-p)^2} = 0.1 \text{ (Given) } \therefore \frac{p}{4-p} = \sqrt{0.1} = 0.316$$

$p = 1.264 - 0.316p$ or $1.316p = 1.264$ or $p = 0.96\,\text{bar}$. Hence, $(p_{H_2})_{eq} = 0.96\,\text{bar}$

Sol.29 $K_c = \dfrac{[O_3]^2}{[O_2]^3}$

$$\therefore 2.0\times10^{-50} = \frac{[O_3]^2}{(1.6\times10^{-2})^3}$$

or $[O_3]^2 = (2.0\times10^{-50})(1.6\times10^{-2})^3 = 8.192\times10^{-56}$

or $[O_3] = 2.86\times10^{-28}\,M$

Sol.30 $K_c = \dfrac{[CH_4][H_2O]}{[CO][H_2]^3}$

$$\therefore 3.90 = \frac{[CH_4](0.02)}{(0.03)(0.10)^3}$$

(Molar conc = No. of moles because volume of flask =1L)

or $[CH_4] = 0.0585M = 5.85\times10^{-2}\,M$

Sol.31 (a) The vapour pressure on the surface of the liquid initially decreases by the sudden increase in the volume of the container. V.P. will decrease.

(b) On increasing the volume of the container suddenly, initially the rate of evaporation remains constant. However, due to increase in the volume of the vapour, the rate of condensation decreases.

(c) When equilibrium is restored finally, the rate of evaporation will again be equal to the rate of condensation. The final vapour pressure will be the same as it was before the sudden increase in the volume of the container.

Sol.32 Applying Le Chatelier's principle, on decreasing the pressure, equilibrium shifts to the direction in which pressures increases, i.e., number of moles of gaseous substances is more. Thus, moles of reaction products will (a) increase (b) decrease (c) remain same ($\because$ $n_p = n_r$ gaseous)

Sol.33 Reactions affected will be those in which $(n_p \neq n_r)_{gaseous}$. Hence, reactions (i), (iii), (iv), (v) and (vi) will be affected. By applying Le Chatelier's principle, we can predict the direction. Increase of pressure will shift the equilibrium to the side in which the number of moles is less.

(i) $n_p = 2, n_r = 1$, i.e., $n_p = n_r$, reaction will go in the backward direction

(ii) $n_p = 3, n_r = 3$, i.e., $n_p > n_r$, reaction will not be affected by pressure.

(iii) $n_p = 2, n_r = 1$, i.e., $n_p > n_r$, reaction will go in the backward direction.

(iv) $n_p = 1, n_r = 3$, i.e., $n_p < n_r$, reaction will go in the forward direction.

(v) $n_p = 1, n_r = 0$, i.e., $n_p > n_r$, reaction will go in the backward direction.

(vi) $n_p = 10, n_r = 9$, i.e., $n_p > n_r$, reaction will go in the backward direction.

Sol.34 For reaction (c), as K_c is neither high nor very low, reactants and products will be present in comparable amounts.

Sol.35 An acid-base pair which differ by a proton is called conjugate acid base pair.

Sol.36 BF_3, H^+ (Remember that all cations are Lewis acids).

Sol.37 Conjugate acid $\rightleftharpoons$ Conjugate base $+H^+$ or

Conjugate base = Conjugate acid $-H^+$

$\therefore$ Conjugate bases of the given acids will be F^-, HSO_4^-, CO_3^{2-}.

Sol.38 $NH_3, NH_4^+, HCOOH$

Sol.39 Conjugate acids : $H_3O^+, H_2CO_3, H_2SO_4, NH_4^+$

Conjugate bases : $OH^-, CO_3^{2-}, SO_4^{2-}, NH_2^-$.

Sol.40 (a) OH^- can donate electron pair. Hence, it is a Lewis base

(b) F^- can also donate electron pair. Hence, it is a Lewis base

(c) H^+ can accept electron pair. Hence, it is a Lewis base

(d) BCl_3 is deficient in electrons. Hence, it can accept electron pair and is, therefore, a Lewis acid.

Sol.41 $NaCN, NaNO_2, KF$ solutions are basic, as they are salts of strong base, weak acid.

$NaCl, KBr$ solutions are neutral, as they are salts of strong acid, strong base.

NH_4NO_3 solution is acidic, as it is a salt of strong acid, weak base.

Sol.42 $pH = -\log [H_3O^+]$

$= -\log (3.8 \times 10^{-3})$

$= -\log 3.8 + 3 = 3 - 0.5798$

$= 2.4202 = 2.42$

Sol.43 $pH = -\log [H^+]$

$3.76 = -\log [H^+]$

or $\log [H^+] = -3.76 = \bar{4}.24$

$\therefore$ $[H^+] = \text{antilog } = \bar{4}.24 = 1.74 \times 10^{-4}$ M

Thus hydrogen ion concentration $[H^+]$ = 1 .74×10^{-4} M.

Sol.44 $K_a \times K_b = K_w$

where

K_a = dissociation ionization constant of a weak acid

K_b = Ionisation constant of its conjugate base

K_w = Ionic product of water = 1.0×10^{-14} at 298 K

HF/F^- $K_{HF} \times K_F = 1.0 \times 10^{-14}$

$6.8 \times 10^{-4} \times K_F = 1.0 \times 10^{-14}$

$$\therefore K_F = \frac{1.0\times10^{-14}}{6.8\times10^{-4}} = 1.5 \times 10^{-11}$$

$HCOOH/HCOO^-$

$$\therefore K_{HCOO^-} = \frac{1.0\times10^{-14}}{1.8\times10^{-4}} = 5.6\times10^{-11}$$

HCN/CN^-

$$\therefore K_{CN^-} = \frac{1.0\times10^{-14}}{4.8\times10^{-9}} = 2.08 \times 10^{-6}.$$

Sol.45 $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{[H^+]^2}{[CH_3COOH]}$$

or $[H^+] = \sqrt{K_a(CH_3COOH)}$

$= \sqrt{(1.74\times10^{-5})(5\times10^{-2}} = 9.33\times10^{-4}$M

$[CH_3COO^-] = [H^+] = 9.33\times10^{-4}$M

$pH = -\log(9.33\times10^{-4}) = 4 - 0.9699$

$= 4 - 0.97 = 3.03$

Sol.46 Organic acid $HA \rightleftharpoons H^+ + A^-$

pH = 4.15 (given); c = [HA] = 0.01 M.

$\therefore$ $[H^+] = +10^{-pH}$ or $-\log [H^+] = 4.15$

$\log [H^+] = -4.15 = \bar{5}.85$

$\therefore$ $[H^+] = \text{antilog } \bar{5}.85 = 7.079 \times 10^{-5}$

$\therefore$ Conc. of anion $[A^-] = [H^+] = 7.08 \times 10^{-5}$ M.

$\therefore$ $K_a = (7.08 \times 10^{-5})^2 / 0.01 = 5.08 \times 10^{-7}$

$pKa = -\log K_a = -\log 5.08 \times 10^{-7} = 6.29.$

Sol.47 (a) $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

$[HCl] = 0.003$ M

As HCl is completely dissociated into H^+ ions

$\therefore$ $[H^+] = [HCl] = 0.003$ M

$pH = -\log [H^+] = -\log 3 \times 10^{-3}$

$= -(-3) \log 3 = 3 - \log 3$

$= 3 - 0.477 = 2.523.$

(b) $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

$[NaOH] = 0.005 = 5 \times 10^{-3}$ M

$[OH^-] = [NaOH] = 5 \times 10^{-3}$ M

$$\therefore [H^+] = \frac{K_W}{[O\bar{H}]} = \frac{1.0 \times 10^{-14}}{0.002}$$

$[H^+] = 2.0 \times 10^{-12}$

$\therefore$ $pH = -\log 2 \times 10^{-12} = -(-12) - \log 2$

$= 12 - 0.30 = 11.70$ $[\log 2 = 0.30]$

(c) $HBr \rightarrow H^+ + Br^-$ completely dissociated

0.002 M

$[HBr] = 0.002$ M

$[H^+] = [HBr] = 0.002 \text{ M} = 2.0 \times 10^{-3}$ M

$pH = -\log [H^+] = -\log 2 \times 10^{-3}$

$= -(-3) \log 2 = 3 - \log 2$

$= 3 - 0.3 = 2.70.$

(d) $KOH \rightarrow K^+ + OH^-$ completely dissociated

.002 M .002 M

$[OH^-] = 0.002$ M

$$[H^+] = \frac{K_W}{[O\bar{H}]} = \frac{1.0 \times 10^{-14}}{0.002} = 5 \times 10^{-12} \text{ M}$$

$pH = -\log [H^+] = -(-12) - \log 5$

$= 12 - 0.70 = 11.30$

Sol.48 (a) $TlOH \rightleftharpoons Tl^+ + OH^-$

$$[TlOH] = \frac{2}{221 \times 2} = \frac{1}{221} \text{ mol L}^{-1}$$

$[TlOH = 204 + 16 + 1 = 221]$

$$\therefore [O\bar{H}] = \frac{1}{221} \text{M}$$ assuming complete dissociation

$$\therefore \quad [H^+] = \frac{K_W}{[O\bar{H}]} = \frac{1.0 \times 10^{-14}}{1/221}$$

$= 221 \times 10^{-14}$ M

$\therefore$ $pH = -\log [H^+] = -\log 221 \times 10^{-14}$

$= -(-14) \log 221 = 14 - 2.3 = 11.70$

(b) $Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2\,OH^-$

assuming complete dissociation

1 Mol 2 Mol

= 74 gm.

$$[Ca(OH)_2] = \frac{0.3 \times 2}{74} = \frac{0.6}{74} = 8.0 \times 10^{-3}$$

$[O\bar{H}] = 2 \times 8.0 \times 10^{-3} = 16.0 \times 10^{-3}$

$= 1.60 \times 10^{-2}$ M.

$$\therefore [H^+] = \frac{K_W}{[O\bar{H}]} = \frac{1.0 \times 10^{-14}}{1.6/10^{-2}} = 6.25 \times 10^{-13}$$

$pH = -\log 6.25 \times 10^{-13} = -(-13) - \log 6.25$

$= 13 - 0.796$

$pH = 12.204.$

(c) $NaOH(aq) \rightarrow Na^+(aq) + OH(aq)^-$

1 Mol 1 Mol

= 40.0 gm

$[NaOH] = [OH]^-$ assuming complete dissociation.

$$[O\bar{H}] = \frac{0.3 \times 5}{40} = \frac{1.5}{40} = 0.0375$$

$$\therefore \quad [H^+] = \frac{1.0 \times 10^{-14}}{.0375} = 26.67 \times 10^{-14}$$

$pH = -(-14) - \log 26.67 = 14 - 1.43$

$= 12.57.$

(d) 1 ml of 13.6 M HCl is diluted to give 1 litre of solution HCl is completely dissociated to give H^+ ions

$[HCl] = ?$

$M_1V_1 = M_2V_2$

1 ml of 13.6 M HCl = 100 ml of M_2 molarity

$$\therefore \quad M_2 = \frac{1 \times 13.6}{1000} = 0.0136 \text{ M}$$

$\therefore$ $[HCl] = [H^+] = 0.0136$ M

$\therefore$ $pH = -\log [H^+] = -\log 1.36 \times 10^{-2}$

$= -(-2) \log 1.36 = 2 - 0.13 = 1.87$

Sol.49 α (Degree of ionization) = 0.132

C (Molar conc.) = 0.1 M

$BrCH_2COOH$	$\rightleftharpoons$	$BrCH_2COO^-$	$+ H^+$
Initial conc.	1	0	0
	$(1-\alpha)$	α	α
	$c(1-\alpha)$	$c\alpha$	$c\alpha$

$[H^+] = c \times \alpha = 0.1 \times 0.132$

$= 0.0132.$

$pH = -\log [H^+] = -\log 1.32 \times 10^{-2}$

$= -(-2) - \log 1.32 = 2 - 0.12 = 1.88$

$pKa = -\log K_a$

Now $K_a = c\alpha^2$

$K_a = 0.1 \times (.132)^2 = 1.74 \times 10^{-3}$

$pKa = -\log 1.74 \times 10^{-3}$

$= -(-3) - \log 1.74 = 3 - 0.30 = 2.70.$

Sol.50 Molar conc. of codeine = 0.005 M

pH = 9.95

$\therefore$ $\log[H^+] = -9.95 = \overline{10}.05$

$\therefore$ $[H^+] = 1.12 \times 10^{-10}$;

$$[O\overline{H}] = \frac{K_w}{[H^+]} = \frac{1.0\times10^{-14}}{1.12\times10^{-10}} = 8.92 \times 10^{-5}$$

$$[OH^-] = \sqrt{K_b C}$$

$$\therefore \quad K_b = \left(\frac{8.92\times10^{-5}}{0.005}\right)^2 = 1.59\times10^{-6}$$

$pKb = -\log K_b$

$= -\log 1.59 \times 10^{-6}$

$= -(-6) - \log 1.59$

$\therefore$ $pKb = 5.8$.

Sol.51 (i) $C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$

$$K_b = \frac{[C_6H_5NH_3^+]\cdot}{[C_6H_5NH_2]} = \frac{[OH^-]^2}{[C_6H_5NH_2]}$$

$$[OH^-] = \sqrt{K_b[C_6H_5NH_2]}$$

$$= \sqrt{(4.27\times10^{-10})(10^{-3})}$$

$$= 6.534\times10^{-7}\,M$$

$$pOH = -\log(6.534\times10^{-7})$$

$$= 7 - 0.8152 = 6.18$$

$$\therefore \; pH = 14 - 6.18 = 7.82$$

(ii) Conc. (c) of aniline solution = 0.001 M

K_b (aniline) = 4.2×10^{-10}

$$\alpha = \sqrt{\frac{K_b}{c}} = \sqrt{\frac{4.2\times10^{-10}}{0.001}}$$

$$= \sqrt{42\times10^{-8}}$$

$\therefore$ Degree of Ionisation = 6.53×10^{-4} = (α)

(iii) If K_a = Ionisation constant of the conjugate acid of aniline then

$K_a \times K_b = K_w$

$$\therefore \; K_a = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{4.2\times10^{-10}} = 2.34 \times 10^{-5}.$$

Sol.52 (a) pH of **human muscle** – fluid = 6.83

$pH = -\log[H^+]$

$6.83 = -\log[H^+]$

$\log[H^+] = -6.83$

$\therefore$ $[H^+] = \text{antilog } \overline{7}.17 = 1.48 \times 10^{-7}$ M

(b) **Stomach fluid**

$-\log[H^+] = 1.2$

$\therefore$ $[H^+] = \text{antilog } \overline{2}.8 = 6.3 \times 10^{-2} = 0.063$ M.

(c) **Human blood**

$pH = 7.38$

$-\log[H^+] = 7.38$

or $\log[H^+] = -7.38 = \overline{8}.62$

$\therefore$ $[H^+] = \text{antilog } \overline{8}.62 = 4.17 \times 10^{-8}$ M

(d) **Human saliva**

$pH = 6.4$

$-\log[H^+] = 6.4$

$\therefore$ $[H^+] = \text{antilog } \overline{7}.6 = 3.98 \times 10^{-7}$ M

Sol.53 (a) **Milk** pH = 6.8

$-\log[H^+] = 6.8$ or $\log[H^+] = -6.8 = \overline{7}.2$

$\therefore$ $[H^+] = \text{antilog } \overline{7}.2 = 1.5 \times 10^{-7}$ M

(b) **Black coffee** pH = 5.0

$-\log[H^+] = 5.0$ or $\log[H^+] = -5 = \overline{5}.0000$

$\therefore$ $[H^+] = 10^{-5}$ M.

(c) **Tomato juice** pH = 4.2

$-\log[H^+] = 4.2$

or $\log[H^+] = -4.2 = \overline{5}.8$

$\therefore$ $[H^+] = \text{antilog } \overline{5}.8 = 6.31 \times 10^{-5}$ M.

(d) **Lemon juice** pH = 2.2

$-\log[H^+] = 2.2$

$\therefore$ $\log[H^+] = -2.2 = \overline{3}.8$

$\therefore$ $[H^+] = \text{antilog } \overline{3}.8 = 6.31 \times 10^{-3}$ M.

(e) **Egg white** pH = 7.8

$-\log[H^+] = 7.8$

$\therefore$ $\log[H^+] = -7.8 = \overline{8}.2$

$= 1.5 \times 10^{-8}$ M.

Sol.54 Molar conc. of KOH $= \dfrac{0.561\times1000}{56.1\times200}$

$= 0.05$ mol L^{-1}

KOH, being a strong electrolyte, is completely ionized in aqueous solution.

$\therefore$ $KOH(aq) \rightarrow K^+(aq) + OH^-(aq)$

$[KOH] = [K^+] = [OH^-] = 0.05$ mol L^{-1}

$$\text{Now, } [H^+] = \frac{K_w}{[O\overline{H}]} = \frac{1.0\times10^{-14}}{0.05} = 2.0 \times 10^{-13}\,M$$

$\therefore$ $pH = -\log[H^+] = -\log 2.0 \times 10^{-13}$

$= -(-13) - \log 2 = 13 - 0.30$

$pH = 12.70$.

Sol.55 The solubility of $Sr(OH)_2$ at 298K = 19.23 gL^{-1}

Molar concentrations of dissolved

$$Sr(OH)_2 = \frac{19.23}{121.6} = 0.1581 \text{ mol } L^{-1}$$

$\therefore$ $Sr(OH)_2 \rightleftharpoons Sr^{2+} + 2OH^-$

$\therefore$ $[Sr^{2+}] = [Sr(OH)_2]_{dist.} = 0.1581$ mol L^{-1}

$[OH^-] = 2 \times 0.1581 = 0.3162$ mol L^{-1}

$$\therefore \; [H^+] = \frac{K_w}{[O\overline{H}]} = \frac{1.0\times10^{-14}}{0.3162} = 3.1625\times10^{-14}\,M$$

$\therefore$ $pH = -\log[H^+] = -\log 3.1625 \times 10^{-14}$

$= -(-14) - \log 3.1625$

$= 14 - \log 3.1625 = 13.50$

Sol.56 $CH_3CH_2COOH \rightleftharpoons CH_3CH_2COO^- + H^+$

If α = degree of ionization of propanoic acid

$\alpha = \sqrt{\frac{K_a}{c}}$ where K_a = Ionization constant and c = Molar conc.

$\alpha = 1.62 \times 10^{-2}$

$\therefore$ Degree of ionization $= 1.62 \times 10^{-2}$

$[H^+] = c\alpha = 0.05 \times 1.62 \times 10^{-2}$

$= 8.1 \times 10^{-4}$

$pH = -\log [H^+] = -\log 8.1 \times 10^{-4} = -(-4) - \log 8.1$

$= 4 - \log 8.1$

$pH = 3.09.$

Degree of ionization if the solution is 0.01 M in HCl also.

In presence of HCl, eqbm. will shift in backward direction i.e. concentration of CH_3CH_2COOH will decrease.

If c is the initial concentration and x is the amount of CH_3CH_2COOH now dissociated, then at eqbm.

$[CH_3CH_2COOH] = c - x$

$[CH_3CH_2COO^-] = x; [H^+] = 0.01 + x$

$\therefore\ K_a = \frac{x(0.01+x)}{c-x}$

$= \frac{x(0.01)}{c-x}$

or $\frac{x}{c} = \frac{K_a}{0.01} = \frac{1.32\times10^{-5}}{0.01} = 1.32 \times 10^{-3}$

$\alpha = \frac{x}{c} = 1.32 \times 10^{-3}$

Sol.57 $pH = 2.34$

Molar conc. (c) = 0.1 M

$HCNO \rightleftharpoons H^+ + CNO^-$

$-\log [H^+] = 2.34$

$\therefore\ \log [H^+] = -2.34 = \bar{3}.66$

$\therefore\ [H^+] = \text{antilog } \bar{3}.66 = 4.57 \times 10^{-3}$ M.

$[H^+] = \sqrt{K_aC}$

$\therefore\ 4.57 \times 10^{-3} = \sqrt{K_aC}$

$\therefore\ K_aC = 2.088 \times 10^{-5}$

$\therefore\ K_a = \frac{2.088\times10^{-5}}{0.1} = 2.088 \times 10^{-4}$

$\therefore$ Degree of ionization $\alpha = \frac{\sqrt{K_a}}{c}$

$= \sqrt{\frac{2.088\times10^{-4}}{0.1}}$

$= 0.0457$

Sol.58 Hydrolysis constant $K_h = \frac{K_W}{K_a}$

Where K_w = Ionic product of water

K_a = ionization constant of the acid

$K_h = \frac{1.0\times10^{-14}}{4.5\times10^{-4}} = 2.22 \times 10^{-11}$

$\therefore$ Degree of ionization $= h = \sqrt{\frac{K_h}{c}}$

$= \sqrt{\frac{2.22\times10^{-11}}{0.04}} = \sqrt{55\times10^{-10}}$

$= 2.36 \times 10^{-5}$

now $[OH^-] = \sqrt{K_bc} = \sqrt{2.22\times10^{-11}\times0.04}$

$= 9.42 \times 10^{-7}$.

$pOH = -\log 9.42 \times 10^{-7} = 7 - 0.97 = 6.03$

$\therefore\ pH = 14 - pOH = 14 - 6.03 = 7.97.$

Or, $pH = \frac{1}{2}\left[pk_w + pk_a + \log C\right]$

Sol.59 Pyridinium hydrochloride is the salt of a weak base pyridine and a strong acid HCl. Hence

$pH = \frac{1}{2}[pK_w - pK_b - \log c]$

$3.44 = \frac{1}{2}[14 - pK_b - \log 2\times10^{-2}]$

$6.88 = [14 - pK_b - \log 2 - \log 10^{-2}]$

$6.88 = [14 - pK_b - 0.3010 + 2]$

$pK_b = 14 + 1.6990 - 6.88 = 8.819$

$-\log K_b = 8.819$

$\log K_b = -8.819 = \bar{9}.181$

$K_b = \text{Antilog}(\bar{9}.181) = 1.5\times10^{-9}$

Sol.60 The given reaction is

$CH_2ClCOOH \rightleftharpoons CH_2ClCOO^- + H^+$

$[\overset{+}{H}] = \sqrt{K_aC} = \sqrt{1.35\times10^{-3}\times0.1}$

$= 1.16 \times 10^{-2}$

$\therefore\ pH = -\log [\overset{+}{H}] = -\log 1.16 \times 10^{-2}$

$= 2 - 0.06 = 1.94.$

Sodium salt chloroacetic acid is a salt of strong base NaOH and a weak acid chloroacetic acid ($ClCH_2COOH$)

$pH = \frac{1}{2}[pK_w + pK_b + \log c]$

$pK_b = -\log K_b = -\log 1.35\times10^{-3}$

$= -\log 1.36 \log 10^{-3}$

$= -0.130 + 3 = 2.87$

$pH = \frac{1}{2}[14 + 2.87 + \log 10^{-1}]$

$= \frac{1}{2}[14 + 2.87 - 1] = 7.935$

Hence pH = 7.94.

Sol.61 At 310 K; Ionic product of water

$K_w = 2.7 \times 10^{-14}$

$\therefore\ [H^+] \times [OH^-] = 2.7 \times 10^{-14}$

But in neutral water $[H^+] = [OH^-]$

$\therefore\ [H^+]^2 = 2.7 \times 10^{-14}$

or $[H^+] = \sqrt{2.7 \times 10^{-14}}$

$= 1.64 \times 10^{-7}$ M

$pH = -\log [H^+] = -\log 1.64 \times 10^{-7}$

$= -(-7) - \log 1.64$

$= 7 - 0.215 = 6.785.$

Sol.62 (a) 10 mL of 0.2 M $Ca(OH)_2$

$= 10 \times 0.2$ millimoles = 2 millimoles of $Ca(OH)_2$

25 mL of 0.1 M HCl = 25 × 0.1 millimoles

= 2.5 millimoles of HCl

$Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O$

1 millimoles of $Ca(OH)_2$ reacts with 2 millimoles of HCl

∴ 2.5 millimoles of HCl will react with 1.25 millimoles of $Ca(OH)_2$

∴ $Ca(OH)_2$ left $= 2 - 1.25 = 0.75$ millimoles

(HCl is the limiting reactant)

Total volume of the solution $= 10 + 25\,mL = 35\,mL$

∴ Molarity of $Ca(OH)_2$ in the mixture solution

$= \frac{0.75}{35} M = 0.0214M$

$\therefore\ [OH^-] = 2 \times 0.0214\,M$

$= 0.0428M = 4.28 \times 10^{-2}$

$pOH = -\log(4.28 \times 10^{-2})$

$= 2 - 0.6314 = 1.3686 = 1.37$

$\therefore\ pH = 14 - 1.37 = 12.63$

(b) 10 mL of 0.01 M $H_2SO_4 = 10 \times 0.01$ millimole

= 0.1 millimole

10 mL of 0.01 M $Ca(OH)_2 = 10 \times 0.01$ millimole

= 0.1 millimole

$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$

1 mole of $Ca(OH)_2$ reacts with 1 mole of H_2SO_4

∴ 0.1 millimole of $Ca(OH)_2$ will react completely with 0.1 millimole of H_2SO_4. Hence, solution will be neutral with pH = 7.0

(c) 10 mL of 0.1 M H_2SO_4 = 1 millimole

10 mL of 0.1 M KOH = 1 millimole

$2KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O$

1 millimole of KOH will react with 0.5 millimole of H_2SO_4

∴ H_2SO_4 left $= 1 - 0.5 = 0.5$ millimole

Volume of reaction mixture $= 10 + 10 = 20\,mL$

∴ Molarity H_2SO_4 in the mixture solution

$= \frac{0.5}{20}$

$= 2.5 \times 10^{-12}$ M

$[H^+] = 2 \times (2.5 \times 10^{-2}) = 5 \times 10^{-2}$

$pH = -\log(5 \times 10^{-2}) = 2 - 0.699 = 1.3$

Sol.63

	$C_6H_5OH \rightleftharpoons$	$C_6H_5O^- +$	H^+
Initial	0.05 M		
After disso.	0.05 − x	x	x

$\therefore K_a = \frac{x \times x}{0.05 - x} = 1.0 \times 10^{-10}$ (Given) or

$\frac{x^2}{0.05} = 1.0 \times 10^{-10}$

or $x^2 = 5 \times 10^{-12}$ or $x = 2.2 \times 10^{-6}$ M

In presence of 0.01 C_6H_5ONa, suppose y is the amount of phenol dissociated, then at equilibrium

$[C_6H_5OH] = 0.05 - y \simeq 0.05$,

$[C_6H_5O^-] = 0.01 + y \simeq 0.01M$, $[H^+] = y\,M$

$\therefore\ K_a = \frac{(0.01)(y)}{0.05} = 1.0 \times 10^{-10}$ (Given) or $= 5 \times 10^{-10}$

$\therefore\ \alpha = \frac{y}{c} = \frac{5 \times 10^{-10}}{5 \times 10^{-2}} = 10^{-8}.$

Sol.64 **To calculate** $[HS^-]$

	$H_2S \rightleftharpoons$	$H^+ +$	HS^-
Initial conc.	0.1 M	0	0
After disso.	$0.1 - x \simeq 0.1$	x	x

$K_a = \frac{x \times x}{0.1} = 9.1 \times 10^{-8}$ or $x^2 = 9.1 \times 10^{-9}$ or

$x = 9.54 \times 10^{-5}$.

In presence of 0.1 M HCl, suppose H_2S dissociated is y. Then at equilibrium,

$[H_2S] = 0.1 - y \simeq 0.1$, $[H^+] = 0.1 + y \simeq 0.1$,

$[HS^-] = y\,M$

$K_a = \frac{0.1 \times y}{0.1} = 9.1 \times 10^{-8}$ (Given) or $y = 9.1 \times 10^{-8}$ M

To calculate $[S^{2-}]$

$H_2S \xrightleftharpoons{K_{a1}} H^+ + HS^-$; $HS^- \xrightleftharpoons{K_{a2}} H^+ + S^{2-}$

For the overall reaction, $H_2S \rightleftharpoons 2H^+ + S^{2-}$

$K_a = K_{a_1} \times K_{a_2} = (9.1\times10^{-8})\times(1.2\times10^{-13})$
$= 1.092\times10^{-20}$

But $K_a = \dfrac{[H^+][S^{2-}]}{[H_2S]}$

In the absence of $0.1\,M\,HCl, [H^+] = 2[S^{2-}]$

Hence, if $[S^{2-}] = x$, $[H^+] = 2x$

$\therefore \dfrac{(2x)^2(x)}{0.1} = 1.092\times10^{-20}$

or $4x^3 = 1.092\times10^{-21}$ or
$x^3 = 273\times10^{-24}$
$3\log x = \log 273 - 24 = 2.362 - 24$
$\log x = 0.8127 - 8 = \bar{8}.8127$ or
$x = \text{Antilog}\,\bar{8}.8127$
$= 6.497\times10^{-8} = 6.5\times10^{-8}\,M.$

In presence of $0.1\,M\,HCl$, suppose $[S^{2-}] = y$, then
$[H_2S] = 0.1 - y \simeq 0.1\,M\,[H^+] = 0.1 + y \simeq 0.1\,M$

$K_a = \dfrac{(0.1)^2\times y}{0.1} = 1.09\times10^{-20}$

or $y = 1.09\times10^{-19}\,M.$

Sol.65 $pK_a = 4.74$, i.e., $-\log K_a = 4.74$ or
$\log K_a = -4.74 = \bar{5}.26 \;\therefore\; K_a = 1.82\times10^{-5}$
$\alpha = \sqrt{K_a / C} = \sqrt{(1.82\times10^{-5})/(5\times10^{-2})}$
$= 1.908\times10^{-2}$

In presence of HCl, due to high concentration of H^+ ion, dissociation equilibrium will shift backward, i.e., dissociation of acetic acid will decrease.

(a) In presence of $0.01\,M\,HCl$, if x is the amount dissociated, then

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

	CH_3COOH	CH_3COO^-	H^+
Initial conc.	0.05M		
After disso.	$0.05 - x$ $\simeq 0.05$	x	$0.01 + x$ $= 0.01M$

($0.01\,M\,H^+$ ions are obtained from $0.01\,M\,HCl$)

$\therefore K_a = \dfrac{x(0.01)}{0.05}$ or $\dfrac{x}{0.05} = \dfrac{K_a}{0.01} = \dfrac{K_a}{0.01} = \dfrac{1.82\times10^{-5}}{10^{-2}}$

$= 1.82\times10^{-3}$. But $\dfrac{x}{0.05} = \alpha$

Hence, $\alpha = 1.82\times10^{-3}$ $\left(\because \alpha = \dfrac{\text{Amount dissociated}}{\text{Amount taken}}\right)$

(b) In the presence of $0.1\,M\,HCl$, if y is the amount of acetic acid dissociated, then at equilibrium,

$[CH_3COOH] = 0.05 - y \simeq 0.05\,M$
$[CH_3COO^-] = y$, $[H^+] = 0.1\,M + y \simeq 0.1\,M$

$K_a = \dfrac{y(0.1)}{0.05}$ or $\dfrac{y}{0.05} = \dfrac{K_a}{0.1} = \dfrac{1.82\times10^{-5}}{10^{-1}}$
$= 1.82\times10^{-4}$,
i.e., $\alpha = 1.82\times10^{-4}$

Sol.66 K_b for dimethylamine = 5.4×10^{-4}
Molar conc. (c) = 0.02 M
Degree of ionization = α

$= \sqrt{\dfrac{K_b}{c}} = \sqrt{\dfrac{5.4\times10^{-4}}{0.02}} = 0.164$

In the presence of 0.01 NaOH, if x is the amount of dimethylamine dissociated,
$[MOH] = 0.02 - x = 0.02\,M$
$[OH^-] = 0.1 + x = 0.1$
$[M^+] = x\,M$

$\therefore K_b = \dfrac{[M^+]\times[OH^-]}{[MOH]} = \dfrac{x\times0.1}{0.02}$

Now,
$K_b = 5.4\times10^{-4}$

$\therefore \dfrac{x\times0.1}{0.02} = 5.4\times10^{-4}$

$x = 1.08\times10^{-4}\,M$

$\therefore \alpha = \dfrac{x}{c} = \dfrac{1.08\times10^{-4}}{0.02} = 0.0054.$

Sol.67 $Ag_2CrO_4 = 2Ag^+ + CrO_4^{2-}$
$\quad s \qquad\quad 2s \qquad s$
$K_{sp}(Ag_2CrO_4) = 1.1\times10^{-12}$ (given)
Let the solubility of Ag_2CrO_4 = s mols L^{-1}
$\therefore K_{sp} = [Ag^+]^2\,[CrO_4^{2-}]$
$= (2s)^2\,(s) = 4s^3$

$\therefore s = \sqrt[3]{\dfrac{K_{sp}}{4}} = \left[\dfrac{1.1\times10^{-12}}{4}\right]^{1/3}$

$= [0.275\times10^{-12}]^{1/3}$
$\therefore s = 0.65\times10^{-4}\,M$

Molarity of $Ag^+ = 2s = 1.30\times10^{-4}$ M and $CrO_4^{2-} = 0.65\times10^{-4}$.

Barium Chromate

$BaCrO_4 \rightleftharpoons Ba^{2+} + CrO_4^{2-}$
$\quad s \qquad\quad s \qquad s$
$K_{sp} = 1.2\times10^{-10}$ (given)
$K_{sp} = [Ba^{2+}]\,[CrO_4^{2-}] = s\times s = s^2$
$\therefore s = \sqrt{K_{sp}} = \sqrt{1.2\times10^{-10}} = 1.1\times10^{-5}\,M$

Molarity of both Ba^{2+} and $CrO_4^{2-} = s = 1.1\times10^{-5}$ M

Ferric hydroxide

$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$

$K_{sp} = 1.0 \times 10^{-38}$

$s \quad s \quad 3s$

$K_{sp} = s \times (3s)^3 = 27\,s^4$

$27\,s^4 = K_{sp} = 1.0 \times 10^{-38}$

$\therefore \; s = \sqrt[4]{\frac{1.0\times10^{-38}}{27}}$

$= \sqrt[4]{3.70\times10^{-40}} = 1.39 \times 10^{-10}$ M.

Molarity of $Fe^{3+} = s = 1.39 \times 10^{-10}$ M;

$[OH^-] = 3s = 4.17 \times 10^{-10}$ M.

Lead Chloride $PbCl_2$

$PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-$

$s \quad s \quad 2s$

$K_{sp}\,(PbCl_2) = 1.6 \times 10^{-5}$ (given)

$K_{sp} = [Pb^{2+}]\,[Cl^-]^2$

$= s \times (2s)^2 = 4s^3$

$\therefore \; s = \sqrt[3]{K_{sp}/4}$

$= \sqrt[3]{\frac{1.6\times10^{-5}}{4}}$

$s = 1.59 \times 10^{-2}$ M.

Molarities of $Pb^{2+} = s = 1.59 \times 10^{-2}$ M

Molarities of $Cl^- = 2s = 3.18 \times 10^{-2}$ M

Mercurous Iodine

$Hg_2I_2 \rightleftharpoons Hg_2^{2+} + 2I^-$

$s \quad s \quad 2s$

$K_{sp} = 4.5 \times 10^{-29}$ (given)

$K_{sp} = s \times (2s)^2 = 4s^3$

$\therefore \; s = \sqrt[3]{K_{sp}/4}$

$= \sqrt[3]{\frac{4.5\times10^{-29}}{4}}$

$= 2.24 \times 10^{-10}$ M

Molarities of $Hg_2^{2+} = 2.24 \times 10^{-10}$ M

Molarities of $I^- = 2s = 4.48 \times 10^{-10}$ M.

Sol.68 Suppose the solubility of AgBr is 5M

K_{sp} of AgBr $= 5.0 \times 10^{-13}$ (given)

$AgBr \rightleftharpoons Ag^+ + Br^-$

$S \quad S \quad S$

$K_{sp} = [Ag^+]\,[Br^-] = S \times S$

Or $S^2 = K_{sp}$

or $\quad S = \sqrt{K_{sp}}$

Or $S = \sqrt{5.0\times10^{-13}} = 0.71 \times 10^{-6}$ M

Solubility of AgBr $= 0.71 \times 10^{-6}$ M

$Ag_2CrO_4 = 2Ag^+ + CrO_4^{2-}$

$S \quad 2S \quad S$

$K_{sp} = [Ag^+]^2\,[CrO_4^{2-}]; \quad K_{sp} = 1.1 \times 10^{-12}$ (given)

$= (2s)^2 \times s = 4s^3$

$\therefore \; S = \sqrt[3]{K_{sp}/4} = \sqrt{\frac{1.1\times10^{-12}}{4}} = 6.5 \times 10^{-5}$ M

$\therefore$ Solubility of $Ag_2CrO_4 = 6.5 \times 10^{-5}$ M

It is clear from above that solubility of Ag_2CrO_4 is more than that of AgBr

The ratio of their molarities in their saturated solutions is 91.9 in favour of Ag_2CrO_4.

$= 6.5\times10^{-5} / 7.07\times10^{-7} = 91.9$

Sol.69 $2NaIO_3 + Cu(ClO_3)_2 \rightarrow Cu(IO_3)_2 + 2NaClO_3$

Molar conc. of both solutions before mixing = 0.002

Molar conc. of both solutions after mixing

$[IO_3^-] = [Cu^{2+}] = \frac{0.002}{2} = 0.001$ M.

(as they have equal volumes)

$2[IO_3^-] + Cu^{2+} \rightarrow Cu(IO_3)_2$

K_{sp} for $(CuIO_3)_2 = 7.4 \times 10^{-8}$

$[Cu^{2+}] = 0.001$ M

$[IO_3^-] = 0.001$ M

IONIC PRODUCT $= [Cu^{2+}]\,[IO_3^-]^2$

$= 10^{-3} \times (1 \times 10^{-3})^2 = 1.0 \times 10^{-9}$

Since the Ionic product is less than the solubility product.

$\therefore$ no. precipitation will occur.

Sol.70 $C_6H_5COOAg \rightleftharpoons C_6H_5COO^- + Ag^+$

Solubility in water

Suppose solubility of silver benzoate in water $= x$ mol L^{-1}

Then $[C_6H_5CO\bar{O}] = [Ag^+] = x$ mol L^{-1}

$\therefore K_{sp} = [Ag^+]\,[C_6H_5CO\bar{O}]$

$= x \times x$

or $\; x^2 = K_{sp} = 2.5 \times 10^{-13}$ (given)

or $\quad x = \sqrt{K_{sp}}$

$= \sqrt{25\times10^{-13}}$

$= 5.0 \times 10^{-7}$ mol L^{-1}

Solubility in buffer of pH = 3.19

$3.19 = -\log\,[H^+]$

$\therefore \; \log\,[H^+] = -3.19 = \bar{4}.81$

$\therefore \; [H^+] = \text{antilog } \bar{4}.81 = 6.457 \times 10^{-4}$

$C_6H_5CO\bar{O}$ ions now combine with H^+ ions to form benzoic acid but $[H^+]$ remains almost constant because we have buffer solution.

Now $C_6H_5COOH \rightleftharpoons C_6H_5CO\bar{O} + H^+$

$$K_a = \frac{[C_6H_5CO\bar{O}]\times[H^+]}{[C_6H_5COOH]}$$

or $\frac{[C_6H_5COOH]}{[C_6H_5CO\bar{O}]} = \frac{[H^+]}{K_a}$

$\frac{6.457\times10^{-4}}{6.46\times10^{-5}} = 10$ ...(i)

Suppose solubility in the buffer solution is y mol L^{-1}. Then as most of the benzoate ions are converted to benzoate acid molecules which remain almost ionised], we have

$Y = [Ag^+] = [C_6H_5CO\bar{O}] + [C_6H_5COOH]$

$= [C_6H_5CO\bar{O}] + 10\,[C_6H_5CO\bar{O}]$,

using equation (i) above

$\therefore [C_6H_5CO\bar{O}] = \frac{Y}{11}$

$\therefore K_{sp} = [C_6H_5CO\bar{O}][Ag^+]$

i.e. $2.5 \times 10^{-3} = \frac{Y}{11} \times y$ or $y^2\ 2.5 \times 10^{-12}$

or $y = 1.66 \times 10^{-6}$

$\therefore \frac{Y}{x} = \frac{1.66\times10^{-6}}{5\times10^{-7}} = 3.32$

Thus silver benzoate is 3.32 times more soluble at lower pH.

Sol.71 Suppose the concentration of each of $FeSO_4$ and Na_2S is x mol L^{-1}. Then after mixing equal volumes,

$[FeSO_4] = [Na_2S] = \frac{x}{2}M$

i.e. $[Fe^{++}] = [s^{--}] = \frac{x}{2}M$

K_{sp} for $FeS = 6.3 \times 10^{-18}$

$\therefore K_{sp} = [Fe^{++}]\,[S^{2-}] = \frac{x}{2}\times\frac{x}{2}$

or $6.3 \times 10^{-18} = \frac{x^2}{2}$

or $x^2 = 25.2 \times 10^{-18}$

or $x = 5.02 \times 10^{-9}$ M

Sol.72 $CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$

If s is the solubility of $CaSO_4$ in mol L^{-1}, then

$K_{sp} = [Ca^{2+}]\,[SO_4^{2-}]$

$= s \times s = s^2$,

K_{sp} for $CaSO_4 = 9.1 \times 10^{-6}$

$\therefore\ s^2 = 9.1 \times 10^{-6}$

or $= 3.02 \times 10^{-3}$ mol L^{-1}

Now molecular mass of $CaSO_4$ = 40+32+4×16

= 136 g

$\therefore\ s = 3.02 \times 10^{-3} \times 136$ g L^{-1}

= 0.411 g L^{-1}

Thus for dissolving 0.411 g, water required = 1 L

$\therefore$ For dissolving 1 gm, water required $= \frac{1}{0.411}$ L

= 2.43 L.

Sol.73 Precipitation will take place in the solution for which ionic product is greater than the solubility product. As 10 mL of solution containing S^{2-} ion is mixed with 5 mL of metal salt solution, after mixing.

$[S^{2-}] = 1.0 \times 10^{-19} \times \frac{10}{15} = 6.67 \times 10^{-20}$

$[Fe^{2+}] = [Mn^{2+}] = [Zn^{2+}] = [Cd^{2+}]$

$= \frac{5}{15}\times 0.04 = 1.33 \times 10^{-2}$ M.

Ionic product for each of these will be = $[M^{2+}] = [S^{2-}]$

$= (1.33 \times 10^{-2}) \times (6.67 \times 10^{-20}) = 8.87 \times 10^{-22}$

Thus Ionic product for each of these species = 8.87×10^{-22}

This value of Ionic product is greater than the solubility products (K_{sp}) of ZnS (1.6×10^{-24}) and CdS [8.0×10^{-27}] and less than the values of FeS [6.3×10^{-18}] and that of MnS [2.5×10^{-13}]. Therefore out of the 4 species, only $ZnCl_2$ and $CdCl_2$ solutions will be precipitated.

QUESTION ALIKE

Calculation of solubility of sparingly Soluble Salts

1. The solubility product for silver chloride is $\mathbf{1.2\times10^{-10}}$ at 298 K. Calculate the solubility of silver chloride at 298 K.

2. Calculate the solubility of silver chloride in water at room temperature if the solubility product of $AgCl$ is 1.6×10^{-10}

3. If solubility product for CaF_2 is 1.7×10^{-10} at 298 K, calculate the solubility in mol L^{-1}.

4. How many moles of $AgBr$ ($K_{sp}=5\times10^{-13}$ $mol^2\,L^{-2}$) will dissolve in 0.01 M $NaBr$ solution ?

Predicting Ionic or Percipitation Reaction

5. If 20 ml of 2×10^{-5} $BaCl_2$ solution is mixed with 20 ml of 1×10^{-5} M Na_2SO_4 solution, will a ppt. form ? (K_{sp} for $BaSO_4$ is 1.0×10^{-10})

6. 003 mole of Ca^{2+} ions is added to a litre of 0.01 M SO_4^{2-} solution. Will it cause precipitation of $CaSO_4$? K_{sp} for $CaSO_4=2.4\times10^{-5}$.

7. $PbCl_2$ has a solubility product of 11.7×10^{-8}. Will a precipitate of $PbCl_2$ form, when 0.010 mole of lead nitrate and 0.010 mole of potassium chloride are mixed and water added upto to 1 litre ?

Calculation of pH of Completely Ionized Acids

8. Calculate the pH value of

(i) 10^{-2} molar HNO_3 solution 0.03 N HCl solution

(ii) 0.001 N H_2SO_4 solution.

9. The concentration of hydronium ions in a cup of black coffee is $\mathbf{1.3\times10^{-5}M}$. Find the pH of the coffee. Is this coffee acidic or alkaline ?

10. A solution is found to contain 0.63 g of nitric acid per 100 ml of the solution. What is the pH of the solution. If the acid is completely dissociated ?

11. Calculate the pH value of 0.001 N HNO_3 solution

12. Calculate the pH value of 10^{-3} M HCl solution

pH of very Dilute Acid or Alkali Solutions

13. What will the pH of the resulting solution if to a 100 ml of HCl solution of pH = 1.0, 900 ml of distilled water is added ?

14. The pH of a solution is 5. Its hydrogen ion concentration is increased 100 times. What is the pH of the resulting solution ?

15. Calculate the pH of a solution obtained by diluting 25 ml of N/100 HCl to 500 ml.

16. 1 ml of 13.6 HCl is diluted with water to give 1 litre of the solution. Calculate pH of the resulting solution.

Calculation of pH of Acids and Bases not completely Ionized

17. Calculate the pH of a 0.01 N solution of acetic acid. K_a for CH_3COOH is 1.8×10^{-5} at 25°C.

18. A 0.05 N solution of acetic acid is found to be 1.9% ionized at 25°C. Calculate (i) K_a for acetic acid and (ii) the pH of the solution.

19. Calculate the pH value of a solution of 0.1 M NH_3 ($K_b=1.8\times10^{-5}$)

20. A sample of sour milk was found to be 0.1 M solution of lactic acid $CH_3CH(OH)COOH$. What is the pH of the sample milk ? K_a for latic acid at 25°C is 1.37×10^{-4}.

Calculation of pH of completely Ionized Alkalies

21. Calculate the pH value of (a) 0.001 M $NaOH$ (b) 0.01 M $NaOH$ and (c) 0.04 M $NaOH$ solution at 25°C.

22. Calculate the pH of a solution containing 2 g caustic soda/litre of water.

23. How many grams of sodium hydroxide must be dissolved in one litre of water to prepare its N/10 solution ? What will be its pH value ?

Calculation of pH of Mixtures of Acids and Bases

24. Calculate the pH of the solution obtained by mixing 100 cm^3 of solution with pH = 3 with 400 cm^3 of solution with pH = 4.

25. Calculate the pH of a solution obtained by mixing 50 ml of 0.2 M HCl with 49.9 ml of 0.2

M $NaOH$ solution

26. Calculate the pH of a solution obtained by mixing equal volumes of N/10 $NaOH$ and N/20 HCl.

27. Calculate the pH value of a mixture containing 50 ml of 1 N HCl and 30 ml of 1 N $NaOH$ solution, assuming both to be completely dissociated.

28. A 50 ml solution of pH = 1 is mixed with 50 ml solution of pH = 2. What will be the pH of the mixture ?

Calculation of pH of Water from its Ionic Product

29. The value of K_W is $\mathbf{9.55\times10^{-14}}$ at a certain temperature. Calculate the pH of water at this temperature.

Calculation of H^+ ion conc. or OH^- ion conc. or Ionization Constant (K_a or K_b) from given Value of PH

30. A sample of fresh apple juice has a pH of 3.76. Calculate $[H^+]$.

31. Lemon juice has pH = 2.1. If all the acid in lemon is citric acid $\left(H\,Cit. \rightleftharpoons H^+ + Cit^{-1}\right)$ and K_a for citric acid is 8.4×10^{-4} moles/litre, what is the concentration of citric acid in lemon juice ?

32. Calculate the dissociation constant of an acid, 1 M solution of which has a pH value of 4.

33. The pH of 0.1 M solution of an organic acid is 3.0. Calculate the dissociation constant of the acid.

34. 0.01 M solution of an organic acid is found to have a pH of 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its pK_a.

35. The pH of 0.005 M codeine $\left(C_{18}H_{21}NO_3\right)$ solution is 9.95. Calculate its ionization constant and pK_b.

Buffer Solutins

36. How much volume of 0.1 M H Ac should be added to 50 mL of 0.2 M NaC solution if we want to prepare a buffer solution of pH 4.91. Given pK_a for acetic acid is 4.76.

37. How much of 0.3 M ammonium hydroxide should be mixed with 30 mL of 0.2 M solution of ammonium chloride to give a buffer solution of pH 10. Give pK_a for NH_4OH is 4.75.

38. The ionization constant of formic acid is 1.8×10^{-4}. Calculate the ratio of sodium formate and acid sodium formic acid in a buffer of pH 4.25.

Calculation Degree of Ionisation, pH of Weak Acid/Base and Equilibrium Concentrations of all Species

39. The ionization constant of HF is $\mathbf{3.2\times10^{-4}}$. Calculate the degree of dissociation of HF in its 0.02 M solution. Calculate the concentration of all the species present (H_3O^+, F^-, HF) in the solution and its pH

40. Calculate the pH of 0.08 M solution of hypohclorous acid, $HOCl$. The ionization constant of the acid is 2.5×10^{-5}. Determine the percent dissociation of $HOCl$.

41. The pH of 0.04 M hydrazine solution is 9.7. Calculate its ionization constant K_b and pK_b.

Calculation of Degree of Dissociation

42. Calculate the degree of dissociation and concentration of H_3O^+ ions in 0.01 M solution of formic acid. $K_a = 2\times10^{10-4}$ at 298 K.

43. Calculate the degree of ionization and $[H_3O^+]$ of 0.01 M CH_3COOH solution. The equilibrium constant of acetic acid is 1.8×10^{-5}

44. A 0.01 M solution of acetic acid is 1.34% ionized (degree of dissociation = 0.0134) at 298 K. What is the ionization constant of acetic acid ?

45. What will be percentage of dissociation in 1.0 M CH_3COOH at equilibrium having dissociation constant 1.8×10^{-5} ?

On the Calculation and $[H_3O^+]$ and $[OH^-]$

46. Calculation and $[H_3O^+]$ and $[OH^-]$ ion concentrations at 25°C in
(i) 0.02 n HCl solution
(ii) 0.005 N NaOH solution

47. Calculate the concentration of H_3O^+ ions in a mixture of 0.02 M acetic acid and 0.2 M sodium acetate. Given that the ionization constant (K_a) for acetic acid is 1.8×10^{-5}.

Involving Common Ion Effect

48. Calculate the pH of a 0.10 M ammonia solution. Calculate the pH after 50.0 mL this solution treated with 25.0 mL of 0.10 HCl. The dissociation constant of ammonia, $K_b = 1.77 \times 10^{-5}$

Calculation of pH of Salts Solutions

49. The dissociation of aniline $(C_6H_5NH_2)$ as a base is 5.93×10^{-10}. The ionic product of water at 25°C is 1.02×10^{-14}. Calculate the percentage hydrolysis of aniline hydrochloride in 1.0 N solution at 25°C. Also calculate the pH of the solution.

50. At 25°C, the ionization constant of anilinium hydroxide is 4.6×10^{-10}. Taking ionic product of water as 1×10^{-14}, calculate (a) hydrolysis constant of anilinium chloride (b) the degree of hydrolysis and (c) pH value of 0.2 molar solution of the salt.

51. calculate the pH of 0.05 M solution acetate solution if the pK_a of acetic acid is 4.74.

52. The pK_a of acetic acid and pK_b of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the hydrolysis constant of ammonium acetate at 298 K and also the degree of hydrolysis and pH of (a) 0.01 M and (b) 0.04 M solutions.

QUESTION ALIKE SOLUTIONS

Sol.1 Silver chloride dissociates according to the equation

$$AgCl(s) \rightleftharpoons AgCl(aq) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

Let s be the solubility of $AgCl$ in moles per litre.

Consequently, the molar concentration of Ag^+ and Cl^- will also be x each. Substituting in the expression for solubility product of $AgCl$

$K_{sp} = [Ag^+][Cl^-]$

$= s \times s = s^2$

But $K_{sp} = 1.2\times10^{-10}$ (Given)

$\therefore\ x^2 = 1.2\times10^{-10}$

or $s = \sqrt{1.2\times10^{-19}}$

$\mathbf{= 1.1\times10^{-5}\ mol\ L^{-1}}$

Sol.2 $1.26\times10^{-5}\ mol\ L^{-1}$

Sol.3 3.5×10^{-4}

Sol.4 Suppose solubility of $AgBr$ in 0.01 M $NaBr$ $= s$ mol L^{-1}. Then as

$AgBr \longrightarrow Ag^+ + Br^-$

$[Ag^+] = s\ mol\ L^{-1}$ and

Total $[Br^-] = 0.01 + s = 0.01\text{M}$

$K_{sp} = [Ag^+][Br^-]$

i.e., $5\times10^{-13} = s\times0.01$

or $s = 5\times10^{-11}\ mol\ L^{-1}$

Sol.5 No

Sol.6 In the final solution, $[Ca^{2+}]$ = 0.03 M and $[SO_4^{2-}]$ = 0.01 M. Hence, ionic product of $CaSO_4 = 0.03(0.01) = 3\times10^{-4}$ which is greater than K_{sp}. Hence, precipitation will occur.

Sol.7 As final volume of the solution = 1 L, therefore

$[Pb^{2+}] = 0.01M = 10^{-2}M$

$[Cl^-] = 0.01M = 10^{-2}M.$

Ionic product of $PbCl_2 = [Pb^{2+}][Cl^-]^2$

$= (10^{-2})(10^{-2}) = 10^{-6}$

which is greater than K_{sp}. Hence, ppt. of $PbCl_2$ will be formed.

Sol.8 (i) HNO_3 completely ionizes as

$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$

$\therefore [H_3O^+] = [HNO_3] = 10^{-2}M$ (Given)

$pH = -\log[H_3O^+] = -\log(10^{-2})$

$= -(-2\log10) = 2$

(ii) HCl completely ionizes as

$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

$\therefore [H_3O^+] = [HCl] = 0.03N$ (Given)

$= 3\times10^{-2}N = 3\times10^{-2}M$ (HCl is monobasic)

$\therefore\ pH = -\log[H_3O^+]$ (Eq. mass = Mol. Mass)

$= -[\log 3\times10^{-2}]$

$= -(\log3 + \log10^{-2})$

$= -(0.4.771 - 2) = \mathbf{1.5229}$

(iii) H_2SO_4 completely ionizes as

$H_2SO_4 + 2H_2O \longrightarrow 2H_3O^+ + SO_4^{2-}$

$[H_3O^+] = 2\times[H_2SO_4]$

[1 molecule of H_2SO_4 gives $2H_3O^+$ ions]

But H_2SO_4 = 0.001 N = 0.001×49 g/litre (Eq. mass of H_2SO_4 = 49)

$= \frac{0.001\times49}{98}$ moles/litre

($\because$ Mol. Mass of $H_2SO_4 = 98$)

$= 0.0005\,M$

$\therefore [H_3O^+] = 2\times[H_2SO_4]$

$= 2\times0.005M$

$= 0.001M = 10^{-3}M$

$\therefore\ pH = -\log[H_3O^+]$

$= -\log(10^{-3}) = \mathbf{3}$

Sol.9 Here, we are given that

$[H_3O^+] = 1.3\times10^{-5}$

$pH = -\log[H_3O^+] = -\log(1.3\times10^{-5})$

$= -(\log1.3 + \log10^{-5})$

$= -0.1139 + 5 = 4.8861$

= 4.89

As pH is less than 7, the black coffee is acidic.

Sol.10 Concentration of HNO_3 solution

= 0.63 g per 100 ml (Given)

$= 6.3\,g\ per\ litre = \frac{6.3}{3}\,moles\,/\,litre = 10^{-1}M$

($\because$ Mol. Mass of $HNO_3 = 63$)

Now, HNO_3 completely ionizes as

$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$

$\therefore\ \left[H_3O^+\right]=\left[HNO_3\right]$

$=10^{-1}M$

$\therefore\ pH=-\log\left[H_3O^+\right]$

$=-\log 10^{-1}=\mathbf{1}$

Sol.11 3

Sol.12 3

Sol.13 100 ml has been diluted to 1000 ml. Hence, dilution, = 10 times.

Now, $\left[H^+\right]=10^{-1}/10=10^{-2}$ M

$\therefore$ pH = 2

Sol.14 pH = 5 means $\left[H^+\right]=10^{-5}$ M. On increasing 100 times, new $\left[H^+\right]=10^{-3}$ M. So pH = 3.

Sol.15 $N_1V_1=N_2V_2, 25\times 1/100=N_2\times 500$

or $N_2=5\times 10^{-4}$ N

$\left[H^+\right]=\left[HCl\right]=5\times 10^{-4}$ M

$pH=-\log\left(5\times 10^{-4}\right)$

$=4-\log 5=4-0=3.301.$

Sol.16 1.67

Sol.17 CH_3COOH ionizes as

$CH_3COOH+H_2O \rightleftharpoons CH_3COO^-+H_3O^+$

Applying the law of chemical equilibrium, we get

$$K_a=\frac{\left[CH_3COO^-\right]\left[H_3O^+\right]}{\left[CH_3COOH\right]}$$

But $\left[CH_3COO^-\right]=\left[H_3O^+\right]$

$$\therefore\ K_a=\frac{\left[H_3O^+\right]^2}{\left[CH_3COOH\right]}$$

[$\because$ one molecules of CH_3COOH gives one CH_3COO^- ion and one H^+ ion or H_3O^+ ion]

or $\left[H_3O^+\right]=\sqrt{K_a\left(CH_3COOH\right)}$

But $K_a=1.8\times 10^{-5}$

and $\left[CH_3COOH\right]=0.01M=10^{-2}M$

$\therefore\ \left[H_3O^+\right]=\sqrt{\left(1.8\times 10^{-5}\right)\times\left(10^{-2}\right)}$

$=\sqrt{1.8\times 10^{-7}}=\sqrt{18\times 18^{-8}}$

$=\sqrt{18}\times 10^{-4}$ g ions/litre

$=4.242\times 10^{-4}$ g ions/litre

$\therefore\ pH=-\log\left[H_3O^+\right]$

$=-\log\left(4.242\times 10^{-4}\right)$

$=-\left(0.6376-4\right)=3.3727=\mathbf{3.37}.$

Sol.18 (i) 1.8×10^{-5}

(ii) 3.0223

Sol.19 11.12

$NH_3+H_2O \rightleftharpoons NH_4^++OH^-$

$$K_b=\frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]}=\frac{\left[OH^-\right]^2}{\left[NH_3\right]}$$

$\therefore\ \left[OH^-\right]=\sqrt{K_b\times\left[NH_3\right]}$

$\left[H^+\right]=\dfrac{K_b}{\left[OH^-\right]},\ pH=-\log\left[H^+\right]$

Sol.20 3.42

Sol.21 (a) 10 (b) 12

(c) 12.60

Sol.22 12.699

$\left[NaOH\right]=\dfrac{2}{40}mol\,L^{-1}=5\times 10^{-2}M$

ie., $\left[OH^-\right]=5\times 10^{-2}M$

$\therefore\ \left[H_3O^+\right]=\dfrac{10^{-14}}{5\times 10^{-2}}=2\times 10^{-13}.$

$pH=-\log\left(2\times 10^{-13}\right)$

Sol.23 4g, 13

For 1 L of 1 N $NaOH$ solution, $NaOH$ dissolved = 1 g eg. = 40 g

$\therefore$ For 1 L of N/10 $NaOH$ solution., $NaOH$ dissolved

$=40\times\dfrac{1}{10}=4g$

$\left[OH^-\right]=10^{-1}M$

$\therefore\ \left[H_3O^+\right]=10^{-13}M.$

$pH=-\log 10^{-13}=\mathbf{13}.$

Sol.24 100 cm^3 of solution with pH = 3 contains H^+

$=\dfrac{10^{-3}}{1000}\times 100=10^{-4}$ mole

400 cm^3 of solution with pH = 4 contains H^+

$=\dfrac{10^{-4}}{1000}\times 400=4\times 10^{-5}$ mole

Total $H^+=10^{-4}+4\times 10^{-5}$

$=10^{-4}\left(1+0.4\right)$

$=1.4\times 10^{4}$

Total volume $= 500\,cm^3$

$\therefore \left[H^+\right] = \dfrac{1.4\times10^{-4}}{500}\times1000M$

$= 2.8\times10^{-4}$ M

$pH = -\log\left(2.8\times10^{-4}\right)$

$= 4 - 0.4472 = \mathbf{3.55}$

Sol.25 3.699

Sol.26 12.398

Suppose 1 L of N/10 $NaOH$ is mixed with 1 L of N/20 HCl.

1 L of N/10 $NaOH$ contains $NaOH$

$= \dfrac{1}{10}$ g eq. = 0.1 g eq.

1 L of N/20 HCl contains HCl

$= \dfrac{1}{20}$ g eq. = 0.05 g eq.

0.05 g. eq. of HCl will neutralize 0.05 g eq. of $NaOH$

$\therefore$ $NaOH$ left unneutralised = 0.05 g eq.

Volume of solution = 2 L

$\therefore$ Concentration of $NaOH$ in the final solution

$= \dfrac{0.05}{2}$ g eq L^{-1} = 0.025 N

$\left[NaOH\right] = \left[OH^-\right] = 0.025$ M $= 2.5\times10^{-2}$

$\therefore \left[H_3O^+\right] = 10^{-14}/\left(2.5\times10^{-2}\right)$

$= 4\times10^{-13}$ M

Sol.27 0.6021

Sol.28 In the mixture, $\left[H^+\right] = \left(10^{-1}+10^{-2}\right)/2$

$= \dfrac{0.11}{2} = 0.55 = 5.5\times10^{-2}$

pH $= -\log\left(5.5\times10^{-2}\right) = 2 - 0.74 = 1.26$

Sol.29 Here, we are given

$K_w = 9.55\times10^{-14}$

Now, as for water $\left[H_3O^+\right] = \left[OH^-\right]$

$\therefore K_w = \left[H_3O^+\right]\left[OH^-\right]$

$= \left[H_3O^+\right]\left[H_3O^+\right] = \left[H_3O^+\right]^2$

i.e. $\left[H_3O^+\right]^2 = 9.55\times10^{-14}$

or $\left[H_3O^+\right] = \sqrt{9.55\times10^{-14}}$

$= \left[H_3O^+\right]\left[OH^-\right]$

$= \left[H_3O^+\right]\left[H_3O^+\right] = \left[H_3O^+\right]^2$

$= 3.09\times10^{-7}$ M

$\therefore\ pH = -\log\left[H_3O^+\right]$

$= -\log\left(3.09\times10^{-7}\right)$

$= -\left[\log 3.09 + \log 10^{-7}\right]$

$= -\left[0.49 - 7\right] = \mathbf{6.51}.$

Sol.30 1.74×10^{-4}

Sol.31 pH = 2.1 i.e., $-\log\left[H^+\right] = 2.1$

or $\log\left[H^+\right] = -2.1 = \bar{3}.9$

or $\left[H^+\right] = 7.943\times10^{-3}$

$HCit \rightleftharpoons H^+ + Cit^{-1}$

$K_a = \dfrac{\left[H^+\right]\left[Cit^{-1}\right]}{\left[HCit\right]}$

$8.4\times10^{-4} = \dfrac{\left(7.943\times10^{-3}\right)\left(7.943\times10^{-3}\right)}{\left[H\,Cit\right]}$

or $\left[H\,Cit\right] = 7.5\times10^{-2}$ M

Sol.32 pH = 4 means $\left[H^+\right] = 10^{-4}$ M

$$\begin{array}{lccccc} & HA & \rightleftharpoons & H^+ & + & A^- \\ At\,eqm & 1-10^{-4}\approx 1M & & 10^{-4}M & & 10^{-4}M \end{array}$$

$K_a = \dfrac{10^{-4}\times10^{-4}}{1} = 10^{-8}$

Sol.33 $RCOOH \rightleftharpoons RCOO^- + H^+$

$\left[H^+\right] = \left[RCOO^-\right] = 10^{-3}$ M $\quad (\because$ pH = 3)

$\left[RCOOH\right] = 0.1 - 10^{-3} \approx 0.1M$

$K_a = \dfrac{\left[RCOO^-\right]\left[H^+\right]}{\left[RCOOH\right]} = \dfrac{10^{-3}\times10^{-3}}{0.1} = 10^{-5}$

Sol.34 pH = 4.15 means $-\log\left[H^+\right] = 4.15$

or $\log\left[H^+\right] = -4.15 = \bar{5}.85$

or $\left[H^+\right] = 7.08\times10^{-5}$ M

$HA \rightleftharpoons H^+ + A^-$

Hence, at equilibrium

$\left[H^+\right] = \left[A^{-1}\right] = 7.08\times10^{-5}$ M

$\simeq 7.1\times10^{-5}$ M

$\left[HA\right] = \left(0.01 - 7.1\times10^{-5}\right)$

= (0.01 – 0.000071) M = 0.009929 M

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$= \frac{(7.1\times10^{-5})^2}{9.929\times10^{-3}} = 5.08\times10^{-7}$$

$$pK_a = -\log K_a = -\log(5.08\times10^{-7}) = 6.29.$$

Sol.35 $K_b = 1.6\times10^{-6}, pK_b = 5.8$

Codeine + water $\rightleftharpoons$ codenium ion + OH^-

From given $pH, [H^+] = 1.12\times10^{-10}$ M

$\therefore [OH^-] = K_w/[H^+] = 8.93\times10^{-10}$ M

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

$$= \frac{(8.93\times10^{-5})^2}{0.05} = 1.6\times10^{-6}.$$

Sol.36 $pH = pK_a + \log\frac{[Salt]}{[Acid]}$

i.e., $4.91 = 4.76 + \log\frac{[Salt]}{[Acid]}$

or $\log\frac{[Salt]}{[Acid]} = 0.15$

or $\frac{[Salt]}{[Acid]} = Anti\log 0.15 = 1.41$

$$\frac{Moles\ of\ Salt}{Moles\ of\ Acid} = 1.41$$

i.e. $\dfrac{\frac{0.2}{1000}\times50}{\frac{0.1}{1000}\times V} = 1.41$ or $\dfrac{0.01}{0.001V} = 1.41$

or $V = 100/1.41$
$= 70.92$ mL

Sol.37 $pOH = 14 - pH = 14 - 10 = 4$

$$pOH = pK_b + \log\frac{[Salt]}{[Base]}$$

$$4 = 4.75 + \log\frac{[Salt]}{[Base]}$$

or $\log\frac{[Salt]}{[Base]} = 0.75 = \bar{1}.25$

or $\frac{[Salt]}{[Base]} = 0.1778$

i.e., $\frac{Moles\ of\ salt}{Moles\ of\ base} = 0.1778$

or $\dfrac{\frac{0.2}{1000}\times30}{\frac{0.3}{1000}\times V} = 0.1778$ **or** $V = 112.5$ **ml**

Sol.38 $pK_a = -\log(1.8\times10^{-4}) = 3.74$

$$\log\frac{[Salt]}{[Acid]} = pH - pK_a = 4.25 - 3.74 = 0.51$$

or $[Salt]/[Acid] = Anti\log 0.51 = 3.24.$

Sol.39 (i)

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$

Initial conc. $0.02M$

Eqm.conc. $0.002 - 0.02\alpha$ $\quad 0.021\alpha \quad 0.02\alpha$

$= 0.02(1-\alpha)$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

$$\therefore 3.2\times10^{-4} = \frac{(0.02\alpha)^2}{0.02(1-\alpha)} = \frac{0.02\alpha^2}{1-\alpha} \simeq 0.02\alpha^2$$

(Neglecting α in comparison to 1)

$$\therefore \alpha^2 = \frac{3.2\times10^{-4}}{0.02} = 1.6\times10^{-2}$$

or $\alpha =$ **0.12**

Note. If α is not neglected in comparison to 1, solve as follows (solution of quadratic equation.)

or $0.02\alpha^2 = 3.2\times10^{-4} - 3.2\times10^{-4}\alpha$

or $2\times10^{-2}\alpha^2 + 3.2\times10^{-4}\alpha - 3.2\times10^{-4} = 0$

or $\alpha^2 + 1.6\times10^{-2}\alpha - 1.6\times10^{-2} = 0$

$$\alpha = \frac{-b\pm\sqrt{b^2-4ac}}{2}.$$

Neglecting – ve value.

(ii) Equilibrium concentrations

$[HF] = 0.02(1-0.12) = \mathbf{1.76\times10^{-3}M}$

$[H_3O^+] = [F^-] = 0.02\times0.12 = \mathbf{2.4\times10^{-3}}$ **M**

(iii) $pH = -\log[H_3O^+] = -\log(2.4\times10^{-3}) = 2.62$

Sol.40

$$HOCl + H_2O \rightleftharpoons H_3O^+ + ClO^-$$

Initial conc. 0.08

Eqm.conc. $0.08 - x$ $\quad x \quad x$

$\simeq 0.08$ (x = Amount of $HOCl$ dissociated)

$$K_a = \frac{x^2}{0.08}$$

or $x = \sqrt{\left(2.5\times10^{-5}\right)(0.08)} = 1.41\times10^{-3}$

$pH = -\log\left[H_3O^+\right] = -\log\left(1.41\times10^{-3}\right)$

$\mathbf{= 2.85}$

$$\%\ \text{dissociation} = \frac{\textit{Amount dissociated}}{\textit{Amount taken}}\times100$$

$$= \frac{1.41\times10^{-3}}{0.08}\times100 = 1.76\%$$

Thus, $K_a = \dfrac{0.01\alpha\times0.01\alpha}{0.01}$

$= 0.01\alpha^2$

$\therefore\ 0.01\alpha^2 = 2.1\times10^{-4}$

$[K_a = 2.1\times10^{-4}$, given$]$

or $\alpha^2 = \dfrac{2.1\times10^{-4}}{0.01}$

$= 2.1\times10^{-2}$

$\therefore$ Degree of ionization, α

$= \dfrac{2.1\times10^{-2}}{0.15}$

$\mathbf{= 0.14}$

Concentration of H_3O^+ ions

$C_\alpha = 0.14\times0.01$

$\mathbf{= 1.4\times10^{-3}\ mol\ L^{-1}}$

Sol.41 $8.96\times10^{-7}, 6.04$

$NH_2NH_2 + H_2O \rightleftharpoons NH_2NH_3^+ + OH^-$

pH = 9.7

$\therefore\ \log\left[H^+\right] = -9.7 = \overline{10}.3$

or $\left[H^+\right] = 1.67\times10^{-10}$

$\therefore\ \left[OH^-\right] = K_w / \left[H^+\right]$

$= 10^{-14}/\left(1.67\times10^{-10}\right)$

$= 5.98\times10^{-5}$

$K_b = \left[NH_2NH_3^+\right]\left[OH^-\right]/\left[NH_2NH_2\right]$

$= \left(5.98\times10^{-5}\right)^2/(0.004)$

$= 8.96\times10^{-7}$

$pK_a = -\log K_b = \log\left(8.96\times10^{-7}\right)$

$= 6.04$

Sol.42 Formic acid is weak electrolyte and ionizes in water to give H_3O^+ ions according to the equation

$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$

Let α be the degree of ionization. Then the concentration of the various species present at equilibrium would be as under:

$$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$$

Initial conc.	0.01	0	0
*Conc.*0.01	$(1-\alpha)$	0.01α	0.01α
at eqm.	$\simeq 0.01$		

[$\because\ \alpha$ is very small and can be neglected in comparison to 1]

Sol.43 4.24×10^{-2}, $4.24\times10^{-4}\ mol\ L^{-1}$

Sol.44

$$CH_3COOH \rightleftharpoons CHCOO^- + H^+$$

Initial conc.	$C\ mol\ L^{-1}$	0	0
At eqm.	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$K_c = \frac{C\alpha.C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

$$= \frac{0.01\times(0.0134)^2}{1-0.01} = 1.8\times10^{-6}$$

Sol.45 $K_c = \dfrac{C\alpha^2}{C(1-\alpha)}$ i.e, $1.8\times10^{1-5} = \dfrac{1\times\alpha^2}{1-\alpha} = \alpha^2$

or $\alpha = \sqrt{1.8\times10^{-5}} = 4.24\times10^{-3}$

% dissociation $= \left(4.24\times10^{-3}\right)\times100 = 0.424$

Sol.46 (i) HCl completely ionizes as

$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

$\therefore \left[H_3O^+\right] = [HCl]$

$= 0.02N$ (Given)

$= 0.02M$

($\because$ HCl is monobasic)

$= 2\times10^{-2}M$

Now, as $\left[H_3O^+\right]\left[OH^-\right] = K_w = 10^{-14}$

$\mathbf{= 5\times10^{-13}\ M}$

(ii) $NaOH$ completely ionizes as

$NaOH \longrightarrow N^+ + OH^-$

$\therefore \left[OH^-\right] = [NaOH]$

$= 0.005$ N (Given)

($\because$ $NaOH$ is monoacidic)

$= 5\times10^{-3} M$

Now as, $\left[H_3O^+\right]\left[OH^-\right] = K_w = 10^{-14}$

$$\therefore \left[H_3O^+\right] = \frac{K_w}{\left[OH^-\right]} = \frac{10^{-14}}{5\times10^{-3}}$$

$$= \mathbf{2\times10^{-12} M}$$

Sol.47 Acetic acid ionizes to a small extent whereas sodium acetate (being a salt) ionizes completely. Suppose acetic ionized at equilibrium $= x$ moles. Then

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Initial moles	0.02	0	0
Moles at eqm.	$0.02 - x$	x	x

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Initial moles	0.02	0	0
Moles at eqm.	0	0.2	0.2

Thus, in the mixture solution,

$\left[CH_3COO^-\right] = 0.2\times x \simeq 0.2 M$

(CH_3COO^- are obtained mainly from CH_3COONa, therefore $x << 0.2$)

$\left[CH_3COOH\right] = 0.02 - x \simeq 0.02M$

$$K_a = \frac{\left[CH_3COO^-\right]\left[H_3O^+\right]}{\left[CH_3COOH\right]}$$

$$1.8\times10^{-5} = \frac{0.2\times\left[H_3O^+\right]}{0.02}$$

$$\text{or } \left[H_3O^+\right] = \frac{1.8\times10^{-5}\times0.02}{0.2}$$

$$= \mathbf{1.8\times10^{-6} M}$$

Sol.48 (i) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]} = \frac{\left[OH^-\right]^2}{\left[NH_3\right]}$$

$\left(\because \left[NH_4^+\right] = \left[OH^-\right]\right)$

$$\therefore \left[OH^-\right] = \sqrt{K_b\left[NH_3\right]}$$

$$= \sqrt{\left(1.77\times10^{-5}\right)\left(0.10\right)}$$

$$= 1.33\times10^{-3} M$$

$$pOH = -\log\left(1.35\times10^{-3}\right) = 3 - 0.12 = 2.88$$

$$\therefore pH = 14 - pOH = 14 - 2.88 = \mathbf{11.12}$$

(ii) 50.0 mL of 0.10 M NH_3 = 5.0 mmol of NH_3

25.0 mL of 0.10 HCl = 2.5 mmol of HCl

2.5 mmol of HCl will neutralize 2.5 mmol of NH_3 forming 2.5 of NH_4Cl and 2.5 mmol of NH_3 will be left un-neutralized. Thus, now the solution contains 2.5 mmol of NH_3 and 2.5 mmol of NH_4Cl

Total volume of the solution = 50 + 25 = 75 mL.

$\therefore$ In the final solution, we have

$$\left[NH_3\right] = \frac{2.5}{75} M = 0.033 M$$

$$\left[NH_4Cl\right] = \frac{2.5}{75} M = 0.033 M$$

The dissociation of NH_3 now will be less due to common ion effect. If x is the amount of NH_3 now dissociated, then

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

$$0.033 M$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Initial conc.	$0.033 M$		
In presence of NH_4Cl	$0.33 - x$ $\simeq 0.033$	$0.033 + x$ $\simeq 0.033$	x

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_2\right]}$$

$$1.77\times10^{-5} = \frac{0.033(x)}{0.033}$$

$$\therefore x = 1.77\times10^{-5} M$$

$$\therefore \left[OH^-\right] = 1.77\times10^{-5}$$

$$pOH = -\log\left(1.77\times10^{-5}\right)$$

$$= 5 - 0.2480 = 4.75$$

$$\therefore pH = 14 - 4.75 = \mathbf{9.25}$$

Sol.49 Aniline hydrochloride $\left(C_6H_5\overset{+}{N}H_3Cl^-\right)$ is a salt of weak base $\left(C_6H_5NH_2\right)$ and strong acid (HCl).

$$K_h = \frac{K_w}{K_b} = \frac{1.02\times10^{-14}}{5.93\times10^{-10}} = 1.72\times10^{-5}$$

$$C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + H_3O^+$$

$$\text{or } C_6H_5NH_3^+ \rightleftharpoons CH_5NH_2 + H^+$$

$$h=\sqrt{\frac{K_h}{c}}=\sqrt{\frac{1.72\times10^{-5}}{1.0}}=4.15\times10^{-3}$$

or, $4.15\times10^{-3}\times100\%=0.415\%$

$$\left[H^+\right]=\sqrt{K_h\times c}\sqrt{1.72\times10^{-5}\times1.0}$$

$$=4.15\times10^{-3}M$$

$$pH=-\log\left(4.15\times10^{-3}\right)=3-0.618$$

$$=2.382=2.38$$

Sol.50 (a) 2.17×10^{-5}
(b) 3.9×10^{-2}
(c) 3.18

Sol.51 8.72

Sol.52 $K_a=3.25\times10^{-5}, h=5.7\times10^{-3}$ and pH = 7.005
(same in both cases)

Objective Questions

1. In any chemical reaction, equilibrium is supposed to be established when
(a) mutual opposite reactants undergo.
(b) velocity of mutual reactions become equal.
(c) concentration of reactants and resulting products are equal.
(d) the temperature of mutual opposite reactions become equal.

2. In any chemical reaction, at which factor equilibrium constant depends
(a) Concentration of the reactant
(b) Pressure
(c) Temperature
(d) Volume

3. Theory of active mass indicates that the rate of chemical reaction is directly proportional to the
(a) equilibrium constant.
(b) volume of apparatus.
(c) properties of reactants.
(d) concentration of reactants.

4. In the chemical reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at equilibrium point, state whether
(a) Equal volumes of N_2 and H_2 are reacting
(b) Equal masses of N_2 and H_2 are reacting
(c) The reaction has stopped
(d) The same amount of ammonia is formed as is decomposed into N_2 and H_2

5. The partial pressures of CH_3OH, CO and H_2 in the equilibrium mixture for the reaction $CO + 2H_2 \rightleftharpoons CH_3OH$ at 427°C are 2.0, 1.0 and 0.1 atm, respectively. The value of K_P for the decomposition of CH_3OH to CO and H_2 is
(a) 1×10^2 atm (b) 4×10^2 atm
(c) 5×10^{-3} atm (d) 5×10^3 atm

6. The formation of SO_3 takes place according to the following reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$, $\Delta H = -45.2$ kcal. The formation of SO_3 is favoured by
(a) increase of volume.
(b) increase of pressure.
(c) increase in temperature.
(d) removal of oxygen.

7. The reaction $CaCO_3 \rightleftharpoons CaO + CO_2(g)$ goes to completion in lime kiln because
(a) Of the high temperature
(b) CaO is more stable than $CaCO_3$
(c) CaO is not dissociated
(d) CO_2 escapes continuously

8. According to Le Chatelier's principle, if heat is given to solid- liquid system, then
(a) quantity of solid will reduce.
(b) quantity of liquid will reduce.
(c) temperature will increase.
(d) temperature will decrease.

9. For the reaction $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ the position of equilibrium can be shifted to the right by
(a) Increasing the temperature
(b) Doubling the volume
(c) Addition of Cl_2 at constant volume
(d) Addition of equimolar quantities of PCl_3 and PCl_5

10. Which of the following factors will favour the reverse reaction in a chemical equilibrium?
(a) Increase in the concentration of one of the reactants.
(b) Increase in the concentration of one or more products.
(c) Removal of at least one of the products at regular time intervals.
(d) None of these.

11. A weak acid is 0.1 % ionized in 0.1 M solutions. Its pH is
(a) 2 (b) 3
(c) 4 (d) 1

12. For the gaseous phase reaction
$2NO \rightleftharpoons N_2 + O_2 \quad \Delta H° = +43.5\ kcal\ mol^{-1}$
Which statement is correct
(a) K varies with addition of NO
(b) K decrease as temperature decreases
(c) K Increases as temperature decreases
(d) K is independent of temperature

13. A 0.1 M solution of a weak acid HA is 1% dissociated. The approximate value of dissociation constant is
(a) 1.0×10^{-4} mol L^{-1} (b) 0.1×10^{-2} mol L^{-1}
(c) 1×10^{-3} mol L^{-1} (d) 0.1×10^{-4} mol L^{-1}

14. Concentration CN^- in $0.1M\ HCN$ is $[K_a = 4 \times 10^{-10}]$

(a) $2.5\times10^{-6} M$ (b) $4.5\times10^{-6} M$
(c) $6.3\times10^{-6} M$ (d) $9.2\times10^{-6} M$

15. The conjugate base of NH_2^-
(a) NH_3 (b) NH^{2-}
(c) NH_4^+ (d) N_3^-

16. At 298 K, the solubility of $PbCI_2$ is 2×10^{-2} mol L^{-1}, then its K_{sp} will be
(a) 1×10^{-7} (b) 3.2×10^{-7}
(c) 1×10^{-5} (d) 3.2×10^{-5}

17. The solubility product of a salt having general formula MX_2, in water is : 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is
(a) $2.0\times10^{-6} M$ (b) $1.0\times10^{-4} M$
(c) $1.6\times10^{-4} M$ (d) $4.0\times10^{-10} M$

18. Which is the correct representation of the solubility product constant of Ag_2CrO_4?
(a) $[Ag^+]^2[CrO_4^{2-}]$ (b) $[Ag^+][CrO_4^{2-}]$
(c) $[2Ag^+][CrO_4^{2-}]$ (d) $[2Ag^+]^2[CrO_4^{2-}]$

19. If the solubility product K_{sp} of a sparingly soluble salt MX_2 at $25°C$ is 1.0×10^{-11}, the solubility of the salt in *mole litre*$^{-1}$ at this temperature will be
(a) 2.46×10^{14} (b) 1.36×10^{-4}
(c) 2.60×10^{-7} (d) 1.20×10^{-10}

20. Let the solubility of an aqueous solution of $Mg(OH)_2$ be S then its K_{sp} is
(a) $4S^3$ (b) $108S^5$
(c) $27S^4$ (d) $9S$

21. The pH of a buffer solution containing 25 mL of 1 M CH_3COONa and 25 mL of 1 M CH_3COOH will be appreciably affected by 5 mL of which solution?
(a) 1 M CH_3COOH (b) 5 M CH_3COOH
(c) 5 M HCI (d) 1 M NH_4OH

22. A white substance having alkaline nature in solution is
(a) $NaNO_3$ (b) NH_4Cl
(c) Na_2CO_3 (d) Fe_2O_3

23. Which of the following will not function as a buffer solution?
(a) CH_3COONa and CH_3COOH
(b) $NaOH$ and NH_4OH
(c) CH_3COONH_4 and HCI
(d) Borax and boric acid

24. A solution of sodium cyanide is
(a) Acidic (b) Amphoteric
(c) Basic (d) Netural

25. Which salt will give basic solution on hydrolysis?
(a) KCN (b) KCI
(c) NH_4CI (d) CH_3COONH_4

Answer Key

1. (b)	2. (c)	3. (d)
4. (d)	5. (c)	6. (b)
7. (d)	8. (a)	9. (c)
10. (b)	11. (c)	12. (b)
13. (d)	14. (c)	15. (b)
16. (d)	17. (b)	18. (a)
19. (b)	20. (a)	21. (b)
22. (c)	23. (b)	24. (c)
25. (a)		

Examplar Questions

1. We know that the relationship between K_c and K_p is

(i) 1 (ii) 0.5

(iii) 1.5 (iv) 2

2. For the reaction $H_2(g) + I_2(g)$ U 2HI (g), the standard free energy is$G^{v} > 0$. The equilibrium constant (K) would be ___________.

(i) $K = 0$ (ii) $K > 1$

(iii) $K = 1$ (iv) $K < 1$

3. Which of the following is **not** a general characteristic of equilibria involving physical processes?

(i) Equilibrium is possible only in a closed system at a given temperature.

(ii) All measurable properties of the system remain constant.

(iii) All the physical processes stop at equilibrium.

(iv) The opposing processes occur at the same rate and there is dynamic but stable condition.

4. PCl_5, PCl_3 and Cl_2 are at equilibrium at 500K in a closed container and their concentrations are 0.8×10^{-3} mol L^{-1}, 1.2×10^{-3} mol L^{-1} and 1.2×10^{-3} mol L^{-1} respectively. The value of K_c for the reaction PCl_5 (g) U PCl_3 (g) + Cl_2 (g) will be

(i) 1.8×10^{3} mol L^{-1} (ii) 1.8×10^{-3}

(iii) 1.8×10^{-3} L mol^{-1} (iv) 0.55×10^{4}

5. Which of the following statements is incorrect?

(i) In equilibrium mixture of ice and water kept in perfectly insulated flask mass of ice and water does not change with time.

(ii) The intensity of red colour increases when oxalic acid is added to a solution containing iron (III) nitrate and potassium thiocyanate.

(iii) On addition of catalyst the equilibrium constant value is not affected.

(iv) Equilibrium constant for a reaction with negative H value decreases as the temperature increases.

6. When hydrochloric acid is added to cobalt nitrate solution at room temperature, the following reaction takes place and the reaction mixture becomes blue. On cooling the mixture it becomes pink. On the basis of this information mark the correct answer.

$$\underset{\text{(pink)}}{[Co(H_2O)_6]^{3+}(aq)} + 4Cl^-(aq) \rightleftharpoons \underset{\text{(blue)}}{[CoCl_4]^{2-}(aq)} + 6H_2O(l)$$

(i) $H > 0$ for the reaction

(ii) $H < 0$ for the reaction

(iii) $H = 0$ for the reaction

(iv) The sign of H cannot be predicted on the basis of this information.

7. The pH of neutral water at 25°C is 7.0. As the temperature increases, ionisation of water increases, however, the concentration of H^+ ions and OH^- ions are equal. What will be the pH of pure water at 60°C?

(i) Equal to 7.0 (ii) Greater than 7.0

(iii) Less than 7.0 (iv) Equal to zero

8. The ionisation constant of an acid, K_a, is the measure of strength of an acid. The K_a values of acetic acid, hypochlorous acid and formic acid are 1.74×10^{-5}, 3.0×10^{-8} and 1.8×10^{-4} respectively. Which of the following orders of pH of 0.1 mol dm^{-3} solutions of these acids is correct?

(i) acetic acid > hypochlorous acid > formic acid

(ii) hypochlorous acid > acetic acid > formic acid

(iii) formic acid > hypochlorous acid > acetic acid

(iv) formic acid > acetic acid > hypochlorous acid

9. K_{a_1}, K_{a_2} and K_{a_3} are the respective ionisation constants for the following reactions.

$$H_2S \rightleftharpoons H^+ + HS^-$$

$HS^- \rightleftharpoons H^+ + S^{2-}$

$H_2S \rightleftharpoons 2H^+ + S^{2-}$

The correct relationship between K_{a_1}, K_{a_2} and K_{a_3} is

(i) $K_{a_3} = K_{a_1} \times K_{a_2}$ (ii) $K_{a_3} = K_{a_1} + K_{a_2}$

(iii) $K_{a_3} = K_{a_1} - K_{a_2}$ (iv) $K_{a_3} = K_{a_1} / K_{a_2}$

10. Acidity of BF_3 can be explained on the basis of which of the following concepts?

(i) Arrhenius concept (ii) Bronsted Lowry concept

(iii) Lewis concept (iv) Bronsted Lowry as well as Lewis concept.

11. Which of the following will produce a buffer solution when mixed in equal volumes?

(i) 0.1 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl

(ii) 0.05 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl

(iii) 0.1 mol dm^{-3} NH_4OH and 0.05 mol dm^{-3} HCl

(iv) 0.1 mol dm^{-3} CH_4COONa and 0.1 mol dm^{-3} NaOH

12. In which of the following solvents is silver chloride most soluble?

(i) 0.1 mol dm^{-3} $AgNO_3$ solution (ii) 0.1 mol dm^{-3} HCl solution

(iii) H_2O (iv) Aqueous ammonia

13. What will be the value of pH of 0.01 mol dm^{-3} CH_3COOH ($K_a = 1.74 \times 10^{-5}$)?

(i) 3.4 (ii) 3.6

(iii) 3.9 (iv) 3.0

14. K_a for CH_3COOH is 1.8×10^{-5} and K_b for NH_4OH is 1.8×10^{-5}. The pH of ammonium acetate will be

(i) 7.005 (ii) 4.75

(iii) 7.0 (iv) Between 6 and 7

15. Which of the following options will be correct for the stage of half completion of the reaction A U B.

(i) $G^V = 0$ (ii) $G^V > 0$

(iii) $G^V < 0$ (iv) $G^V = -RT \ln 2$

16. On increasing the pressure, in which direction will the gas phase reaction proceed to re-establish equilibrium, is predicted by applying the Le Chatelier's principle. Consider the reaction.

$N_2 (g) + 3H_2 (g)$ U $2NH_3 (g)$

Which of the following is correct, if the total pressure at which the equilibrium is established, is increased without changing the temperature?

(i) K will remain same

(ii) K will decrease

(iii) K will increase

(iv) K will increase initially and decrease when pressure is very high

17. What will be the correct order of vapour pressure of water, acetone and ether at 30°C. Given that among these compounds, water has maximum boiling point and ether has minimum boiling point?

(i) Water < ether < acetone (ii) Water < acetone < ether

(iii) Ether < acetone < water (iv) Acetone < ether < water

18. At 500 K, equilibrium constant, K_c, for the following reaction is 5.

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

What would be the equilibrium constant K_c for the reaction

$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

(i) 0.04 (ii) 0.4

(iii) 25 (iv) 2.5

Examplar Solutions

1. (iv)
2. (iv)
3. (iii)
4. (ii)
5. (ii)
6. (i)
7. (iii)
8. (iv)
9. (i)
10. (iii)
11. (iii)
12. (iv)
13. (i)
14. (iii)
15. (i) $\Delta G^0 V = 0$
    Justification : $\Delta G^0 V = -RT \ln K$
    At the stage of half completion of reaction [A] = [B], Therefore, K = 1.
    Thus, $\Delta G^0 V = 0$
16. (i), Justification: According to Le-Chatelier's principle, at constant temperature, the equilibrium composition will change but K will remain same.
17. (ii)
18. (i)

JEE and NEET Previous Year

Jee Previous Year

Q.1. An aqueous solution contains 0.10M H_2S and 0.20 M HCl. If the equilibrium constants for the formation of HS^- from H_2S is 1.0×10^{-7} and that of S^{2-} from HS^- ions is 1.2×10^{-13} then the concentration of S^{2-} ions in aqueous solution is **[2018 Mains]**

(a) 5×10^{-8} (b) 3×10^{-20}
(c) 6×10^{-21} (d) 5×10^{-19}

Q.2. An aqueous solution contains an unknown concentration of Ba^{2+}. When 50 mL of a 1 M solution of Na_2SO_4 is added, $BaSO_4$ just begins to precipitate. The final volume is 500 mL. The solubility product of $BaSO_4$ is 1×10^{-10}. What is the original concentration of Ba^{2+}? **[2018 Mains]**

(a) 5×10^{-9} M (b) 2×10^{-9} M
(c) 1.1×10^{-9} M (d) 1.0×10^{-10} M

Q.3. PK_a of a week acid (HA) and PK_b of a weak base (BOH) are 3.2 and 3.4 and 3.4, respectively. The pH of their sals (AB) solution is **[2017 Mains]**

(a) 7.2 (b) 6.9
(c) 7.0 (d) 1.0

Q.4. The equilibrium constant at 298 K for a reaction $A+B \rightleftharpoons C+I$ is 100 . If the initial concentration of all the four species were I. M. each, then equilibrium concentration of D $(in\,mol^{-1})$ will be **[2016 Mains]**

(a) 0.818 (b) 1.818
(c) 1.182 (d) 0.182

Q.5. The equilibrium constant K_p for this reaction at 298 K, in term of $\beta_{equilibrium}$ is **[2016 Jee Adv.]**

(a) $\dfrac{8\beta^2_{equilibrium}}{2-\beta_{equilibrium}}$ (b) $\dfrac{8\beta^2_{equilibrium}}{4-\beta^2_{equilibrium}}$

(c) $\dfrac{4\beta^2_{equilibrium}}{2-\beta_{equilibrium}}$ (d) $\dfrac{4\beta^2_{equilibrium}}{2-\beta^2_{equilibrium}}$

Q.6. The incorrect statement among the following for the is reaction is **[2016 Jee Adv.]**

(a) Decrease in the total pressure will result in the formation of more moles of gaseous X
(b) At the start of the reaction, dissociation of gaeous X_2 takes place spontaneously
(c) $\beta_{equilibirium} = 0.7$
(d) $K_C < 1$

Q.7. The standard Gibbs energy change at 300 K for the reaction $2A \rightleftharpoons A+I$ is 2494 2J At a given time , the composition of the reaction mixture is $(A)=\frac{1}{2}(B)=2\,and\,[C]=\frac{1}{2}$. The reaction processed in the (R = 8.314 JK/mol. e = 2.781) **[2015 Mains]**

(a) forward direction because Q > K
(b) reverse direction because Q > K
(c) forward direction because Q < K
(d) reverse direction because Q < K

Q.8. For the reaction, $SO(g)+\frac{1}{2}O_3(g) \rightleftharpoons SO_3(g)$ $if\,K_r = K_c(RT)^2$ where the symbols have usual meaning them the value of x is (meaning ideality) **[2014 Mains]**

(a) –1 (b) $-\frac{1}{2}$
(c) $\frac{1}{2}$ (d) 1

Q.9. How many litres of water must be added to 1 L of a aqueous solution of HCI with a pH of 1 to create a aqueous solution with pH of 2? **[2013 Mains]**

(a) 0.1 L (b) 0.9 L
(c) 2.0 L (d) 9.0 L

Q.10. The thermal dissociation of equilibrium of $CaCO_3(x)$ is studies under different conditions. **[2013 Jee Adv.]**

$CaCO_3(s) \rightleftharpoons CaO(s)+CO_2(g)$

For this equilibrium, the correct statement(s) is are

(a) ΔH is dependent on I
(b) K is independent of the initial amount of $CaCO_3$
(c) K is dependent on the pressure of CO_2 at a given T
(d) ΔH is independent of the catalyst, if any

Q.11. The initial rate of hydrolysis of methyl acetate (1 M) by a weak acid (HA, 1M) is 1/100th of that of a strong acid (HX, 1M), at $25^{\circ}C$ The K_a (HA) is **[2013 Jee Adv.]**

(a) 1×10^{-4} (b) 1×10^{-5}
(c) 1×10^{-6} (d) 1×10^{-3}

Q.12. Total number of diprotic acids among the following is]

H_3PO_4 H_2SO_4 H_3PO_3
H_2CO_3 $H_2S_2O_7$ H_2BO_3
H_3PO_2 H_2CrO_4 H_2SO_3

[2011]

Q.13. The equilibrium $2Cu^+ \rightleftharpoons Cu^{2+}$ in aqueous medium at $25^\circ C$ shifts towards the left in the presence of **[2011 Mains]**

(a) NO_3^- (b) Cl^-
(c) SCN^- (d) CN^-

Q.14. Aqueous solutions of $HNO_3, KOH, CH_3COOH\ and\ CH_3COONa$ of identical concentrations are provided. The pair (s) of solutions which from a buffer upon mixing is (are) **[2010]**

(a) $HNO_3\ and\ CH_3COOH$
(b) $KOH\ and\ CH_3COONa$
(c) $HNO_3\ and\ CH_3COONa$
(d) $CH_3COOH\ and\ CH_3COONa$

Q.15. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is

KCN K_2SO_4 $(NH_4)_2C_2O_4$ $NaCl$
$Zn(NO_3)_2$ $FeCl_3$ K_2CO_3 NH_4NO_3
$LiCN$ **[2010 Mains]**

Q.16. Solubility product constant (K_{sp}) of salt of types MX, MX_2 and M_3X at temperature 'T' are 4.0×10^{-8} , 3.2×10^{-14} and 2.7×10^{-15}, respectively. Solubilities (mol dm^{-3}) of the salts at temperature 'T' are in the order **[2008 Mains]**

(a) $MX > MX_2 > M_3X$
(b) $M_3X > MX_2 > MX$
(c) $MX_2 > M_3X > MX$
(d) $MX > M_3X > MX_2$

Q.17. 2.5 mL of $\frac{2}{5}$M weak monoacidic base $(K_b = 1\times10^{-12}\ 25^0C)$ at is titrated with $\frac{2}{15}$M HCI in water at 25^0C The concentration of H^+ at equilvalance point is $(K_{w)} = 1\times10^{14}\ at\ 25^0C)$ **[2008 Mains]**

(a) $3.7 \times 10^{-13} M$ (b) $3.2\times10^{-7} M$
(c) $3.2\times10^{-2} M$ (d) $2.7\times10^{-2} M$

Q.18. $CH_3NH_2\,(0.1 mole, K_b = 5\times10^{-4})$ is added to 0.08 mole of HCI and the solution is diluted to one lite, resulting hydrogen ion concentration is **[2008 Mains]**

(a) 1.6×10^{-11} (b) 8×10^{-11}
(c) 5×10^{-5} (d) 5×10^{-5}

Q.19. $N_2 + 3H_2 \rightleftharpoons 2NH_3$ Which is correct statement if N_2 is added equlibrium condition? **[2006 Mains]**

(a) The equilibrium will shift to forward direction because according to IInd law of thermodynamics the entropy most increases in the direction of spontanious reaction.
(b) The condition for equilibrium is $G(N_2) + 3G(H_2) = 2G(NH_4)$
where G is Gibbs free energy per mole of the gaseous species measured at that partial pressure.
The conditions of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward reaction to the same extent
(c) catalyst will increases the rate of forward reaction by α and that of backward reaction by β.
(d) Catalyst will not after the rate of either of the reaction.

Q.20. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^2; K_1 = 3.5\times10^{-3}$

$\left[AG(NH_3)\right]^+ + NH_3 \rightleftharpoons \left[Ag(NH_3)_2\right]^4; K_2 = 1.7\times10^{-3}$

three the formation constant of $[Ag(NH_3)_2]^+$ **[2006 Mains]**

(a) 6.08×10^{-6} (b) 6.08×10^{4}
(c) 6.08×10^{-4} (d) None of these

Q.21. Consider the following equilibrium in a closed container

$N_2O_4(g) \rightleftharpoons 2NO(g)$

At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements hold true regarding the equilibrium constant and degree of dissection (K_p) and degree of dissocation (α) **[2005 Mains]**

(a) Neither K_r nor α changes
(b) Both K_r and α change
(c) K_r changes but α does not change
(d) K_r does not change but α changes

Q.22. HX is a weak acid $(K_a = 10^{-5})$. It forms a salt NaX (0.1 M) on reaction with caustic soda. The degree of hydrolysis of NaX is. **[2004 Mains]**

(a) 0.01 % (b) 0.0001%
(c) 0.1% (d) 0.5%

Q.23. A solution which is 10^{-3} M each in $Mn^{2+}, Fe^{2+}, Zn^{2+} and\ Hg^{2+}$ is treated with 10^{-16} M sulphide ion. If K_{sp} of MnS, FeS, ZnS and HgS are $10^{-15}, 10-23, 10^{-20}\ and\ 10^{-54}$ respectively, which one will precipitate first? **[2003 Mains]**

(a) FeS (b) MgS
(c) HgS (d) ZnS

Q.24. For a sparingly soluble Salt A_pB_q, the relationship of its solubility product (L_S) with solubility (S) is **[2001]**
(a) $L_S = S^{p+q}.p^p.q^q$ (b) $L_S = S^{p+q}.p^q.q^p$
(c) $L_S = S^{pq}.p^p.q^q$ (d) $L_S = S^{pq}.(p.q)^{(p+q)}$

Q.25. At constant temperature, the equilibrium constant (K_r) for the decomposition reaction $N_2O_4 \rightleftharpoons 2NO_2$ is expressed by $K_r = \frac{4x^2p}{(1-x^2)}$, where = pressure x= extent of decomposition. Which one of the following statement is true? **[2001]**
(a) increases with increases of p
(b) increases with increases of x
(c) increases with decrease of x
(d) remains constant with change in p and x

Q.26. When two reaction, A and B are mixed to give produce, C and D the reactions required, (Q) at the initial stage of the reaction **[2000]**
(a) is Zero
(b) decreases with time
(c) is independent of time
(d) increases with time

Q.27. For the reversible reactions,
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH(g)$
At the $500^\circ C$ value of K_r is 1.44×10^{-1} when partial pressure measured in atmosphere. The corresponding value of K_r with concentration in mol/L is **[2000]**
(a) $\frac{1.44\times10^{-5}}{(0.082\times500)^{-2}}$ (b) $\frac{1.44\times10^{-5}}{(8.314\times773)^{-2}}$
(c) $\frac{1.44\times10^{-5}}{(0.082\times773)^{2}}$ (d) $\frac{1.44\times10^{-5}}{(0.082\times773)^{-2}}$

NEET Previous Year

Q.28. For the chemical reaction **[2019]**
$N_2(g) + 3H_2(g)_2 \rightleftharpoons NH_3(g)$
The correct option is:
(a) $-\frac{d[N_2]}{dt} = \frac{1}{2}\frac{d[N_3]}{dt}$
(b) $3\frac{d[H_2]}{dt} = 2\frac{d[NH_3]}{dt}$
(c) $-\frac{1}{3}\frac{d[H_2]}{dt} = -\frac{1}{2}\frac{d[NH_3]}{dt}$
(d) $-\frac{d[N_2]}{dt} = 2\frac{d[NH_3]}{dt}$

Q.29. Which will make basic buffer? **[2019]**
(a) 100 mL of 0.1 M HCI + 200 mL of 0.1 M NH_4OH
(b) 100 mL of 0.1 M HCI + 100 mL of 0.1 M NaOH
(c) 50 mL of 0.1 M NaOH + 25 mL of 0.1 M CH_3COOH
(d) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M NaOH

Q30. Which one of the following condition will favour maximum formation of the product in the reaction. **[2018]**
$A_2(g)+B_2(g) \rightleftharpoons X_2(g)$: $\Delta_rH = -XkJ$
(a) Low temperature and high pressure
(b) Low temperature and low pressure
(c) High temperature and low pressure
(d) High temperature and high pressure

Q.31. The solubility of $BaSO_4$ in water is $2.42\times10^{-3}\ gL^{-1}$ at 298 K. The value of its solubility product (Ksp) will be **[2018]**
(Given molar mass of $BaSO_4$ = 233 g mol^{-1})
(a) $1.08\times10^{-10}\ mol^2L^{-2}$
(b) $1.08\times10^{-12}\ mol^2L^{-2}$
(c) $1.08\times10^{-8}\ mol^2L^{-2}$
(d) $1.08\times10^{-14}\ mol^2L$

Q.32. Following solutions were prepared by mixing different volumes of NaOH and HCI of different concentrations: **[2018]**
(a) 60 mL $\frac{M}{10}$ HCI+40 mL $\frac{M}{10}$ NaOH
(b) 55 mL $\frac{M}{10}$ HCI+45 mL $\frac{M}{10}$ NaOH
(c) 75 mL $\frac{M}{10}$ HCI+25 mL $\frac{M}{10}$ NaOH
(d) 100 mL $\frac{M}{10}$ HCI+100 mL $\frac{M}{10}$ NaOH

Q.33. The equillibirum constants of the following are
$N_2 + 3H_2 \rightleftharpoons 2NH_3\ K_1$
$N_2 + O_2 \rightleftharpoons 2NO\ K_2$
$H_2 + {}^1\!/_2 O_2 \rightarrow H_2O\ K_3$
The equillibirum constant (K) of the reaction K
$2NH_3 + -O_2 \rightleftharpoons 2NO + 3H_2O$ will be **[2017]**
(a) $K_1\ K^3_3/K_2$ (b) $K_2K^3_3/K_1$
(c) K_2K_3/K_1 (d) $K^3_2K_3/K_1$

Q.34. A 20 litre container at 400 K contains $CO_2(g)$ at pressure 0.4 atm and an excess of SrO neglect the volume of solid SrO). The volume of the container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO_2 attains its maximum value, will be (Given that : $SrCO_3(s)$

$SrO(s) + CO_2(g)$, Kp = 1.6 atm) **[2017]**
(a) 5 litre (b) 10 litre
(c) 4 litre (d) 2 litre

Q.35. Consider the following liquid-vapour equilibrium. **[2016]**
Liquid $\rightleftarrows$ Vapour
Which of the following relations is correct?
(a) $\frac{d\ln G}{dT^2} = \frac{\Delta H_v}{RT^2}$ (b) $\frac{d\ln P}{dT} = \frac{-\Delta H_v}{RT}$
(c) $\frac{d\ln P}{dT^2} = \frac{-\Delta H_v}{T^2}$ (d) $\frac{d\ln P}{dT} = \frac{\Delta H_v}{RT^2}$

Q.36. MY and NY3, two nearly insoluble salts, have the same Ksp values of 6.2 × 10–13 at room temperature. Which statement would be true in regard to MY and NY3 ? **[2016]**
(a) The molar solubilities of MY and NY3 in water are identical
(b) The molar solubility of MY in water is less than that of NY3
(c) The salts MY and NY3 are more soluble in 0.5 M KY than in pure water.
(d) The addition of the salt of KY to solution of MY and NY3 will have no effect on their solubilities.

Q.37. The K_{sp} of Ag_2CrO_4, AgCl, AgBr and Agl are respectively, 1.1×10^{-12}, 1.8×10^{-10}, 5.0×10^{-13}, 8.3×10^{-17}. Which one of the following salts will precipitate last if $AgNO_3$ solution is added to the solution containing equal moles of NaCl, NaBr, Nal and Na_2CrO_4? **[2015]**
(a) Agl (b) AgCl
(c) AgBr (d) Ag_2CrO_4

Q.38. If the value of an equilibrium constant for a particular reaction is 1.6×10^{12}, then at equilibrium the system will contains **[2015]**
(a) all reactants.
(b) mostly reactants
(c) mostly products
(d) similar amount of reactants and products

Q.39. Which of the following salts will give highest pH in water? **[2014]**
(a) KCl (b) NaCL
(c) Na_2CO_3 (d) $CuSO_4$

Q.40. Which is the strongest acid in the following? **[2013]**
(a) H_2SO_4 (b) $HClO_3$
(c) $HClO_4$ (d) H_2SO_3

Q.41. Which of these is least likely to act as a Lewis base? **[2013]**
(a) CO (b) F^-
(c) BF_3 (d) PF_3

Q.42. pH of saturated solution of $Ba(OH)_2$ The value of solubility product K_{sp} of $Ba(OH)_2$ is **[2012]**
(a) 3.3×10^{-7} (b) 5.0×10^{-7}
(c) 4.0×10^{-6} (d) 5.0×10^{-6}

Q.43. Equimolar solutions of the following substances were prepared separately.Which one of these will record the highest pH value? **[2012]**
(a) $BaCl_2$ (b) $AlCl_3$
(c) LiCl (d) $BeCl_2$

Q.44. A buffer solutions prepared in which the concentration of NH_3 IS 0.30 M and the concentration of NH_4^+ is 0.20 M. If the equilibrium constant, Kb for NH_3 equals 1.8×10^{-5}, what is the pH of this solution? [log 2.7 = 0.43] **[2011]**
(a) 9.43 (b) 11.72
(c) 8.73 (d) 9.08

Q.45. What is the $[H^-]$ in the finale solution prepared by mixing 20.0 mL of 0.050 M HCl with 30.0 mL of 0.10 M $Ba(OH)_2$? **[2009]**
(a) 0.10 M (b) 0.40 M
(c) 0.0050 M (d) 0.12 M

Q.46. The ionization constant of ammonium hydrolysis is 1.77×10^{-5} at 298 K. Hydrolysis constant of ammonium chloride is **[2009]**
(a) 5.65×10^{-10} (b) 6.50×10^{-12}
(c) 5.65×10^{-13} (d) 5.65×10^{-12}

Q.47. Which of the following molecules acts as a Lewis acid ? **[2009]**
(a) $(CH_3)_3B$ (b) $(CH_3)_2O$
(c) $(CH_3)_3P$ (d) $(CH_3)_3N$

Q.48. The dissociation equilibrium of a gas AB_2 can be represented as
$2AB_2(g) \rightarrow 2AB(g) + B_2(g)$
The degree of dissociationis x and is small compared to 1. The expression relating the degree of dissociation (x) with equilibrium constant K_p and total pressure p is **[2008]**
(a) $2(K_p / p)$ (b) $(2K_p / p)^{1/3}$
(c) $(2K_p / p)^{1/2}$ (d) (K_p / p)

Q.49. Equal volumes of three and solutions of pH 3, 4 and 5 are mixed in a vessel. What will be the H^+ ion concentration in the mixture? **[2008]**
(a) 1.11×10^{-4} M (b) 3.7×10^{-4} M
(c) 3.7×10^{-3} M (d) 1.11×10^{-3} M

Q.50. Calculate the pOH of a solution at 25^0C that contains 1×10^{-10} M of hydronium ion. **[2007]**
(a) 7.00 (b) 4.00
(c) 9.00 (d) 1.00

Q.51. The hydrogen ion concentration of a 10^{-8} M

HCl aqueous solution at 298 K ($K_w = 10^{-14}$) is **[2006]**

(a) 1.0×10^{-6} M (b) 1.0525×10^{-7} M
(c) 9.525×10^{-8} M (d) 1.0×10^{-8} M

Q.52. What is the correct relationship between the pH of isomolar solutions of sodium oxide (pH_1) sodium sulphide (pH_2), sodium selenide (pH_3) and sodium telluride (pH_4) ? **[2005]**

(a) $pH_1 > pH_2 \approx pH_3 > pH_4$
(b) $pH_1 < pH_2 < pH_3 < pH_4$
(c) $pH_1 < pH_2 < pH_3 \approx pH_4$
(d) $pH_1 > pH_2 > pH_3 > pH_4$

Q.53. The rapid change of pH near the stoichiometric point of an acid base titration is the basis of indicator detection. pH of the solution is related to ration of concentrations of the conjugate acid (HIn) and base (In^-) forms of the indicator given by the expression **[2004]**

(a) $\log\frac{[In^-]}{[HIn]} = pK_{In} - pH$

(b) $\log\frac{[HIn]}{[In]} = pK_{In} - pH$

(c) $\log\frac{[HIn]}{[In]} = pH - pK_{In}$

(d) $\log\frac{[In^-]}{[HIn]} = pH - pK_{In}$

Q.54. The soloubility product of a sparingly soluble salt AX_2 is 3.2×10^{-11} . Its soluvility (in mol/L) is **[2004]**

(a) 5.6×10^{-6} (b) 3.1×10^{-4}
(c) 2×10^{-4} (d) 4×10^{-4}

Q.55. The soloubility product of AgI at 25^0C is 1.0×10^{-16} mol^2L^{-2} . The solubility of AgI in 10^{-4} N solution of KI at 25^0C is approximately (in mol L1) **[2003]**

(a) 1.0×10^{-10} (b) 1.0×10^{-8}
(c) 1.0×10^{-18} (d) 1.0×10^{-12}

Q.56. Which has highest pH ? **[2002]**

(a) CH_3COOK (b) Na_2CO_2
(c) NH_4Cl (d) $NaNO_3$

Q.57. The conjugate acid of NH_2^- is **[2000]**

(a) N_2H_4 (b) NH_4^+
(c) NH_2OH (d) NH_3

Answer Key

1. (b)	2. (c)	3. (b)	4. (b)	5. (b)	6. (d)
7. (b)	8. (b)	9. (d)	10. (a,b,c,d)	11. (a)	12. (6)
13. (b,c,d)	14. (c,d)	15. ()	16. (d)	17. (d)	18. (b)
19. (b)	20. (a)	21. (a)	22. (a)	23. (c)	24. (a)
25. (d)	26. (d)	27. (d)	28. (a)	29. (a)	30. (a)
31. (a)	32. (c)	33. (b)	34. (a)	35. (d)	36. (b)
37. (d)	38. (c)	39. (c)	40. (c)	41. (c)	42. (b)
43. (a)	44. (a)	45. (a)	46. (a)	47. (a)	48. (b)
49. (b)	50. (b)	51. (b)	52. (a)	53. (d)	54. (c)
55. (d)	56. (d)	57. (d)			