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Physical chemistry

1 Atoms, molecules and stoichiometry

This topic illustrates how quantitative relationships can be established when different substances react. (The term *relative formula mass* or M_r will be used for all compounds including ionic compounds.)

Learning outcomes

Candidates should be able to:

1.1 Relative masses of atoms and molecules	a) define and use the terms <i>relative atomic</i> , <i>isotopic</i> , <i>molecular</i> and <i>formula masses</i> , based on the ^{12}C scale
1.2 The mole and the Avogadro constant	a) define and use the term <i>mole</i> in terms of the Avogadro constant
1.3 The determination of relative atomic masses, A_r	a) analyse mass spectra in terms of isotopic abundances (knowledge of the working of the mass spectrometer is not required) b) calculate the relative atomic mass of an element given the relative abundances of its isotopes, or its mass spectrum
1.4 The calculation of empirical and molecular formulae	a) define and use the terms <i>empirical</i> and <i>molecular formula</i> b) calculate empirical and molecular formulae, using combustion data or composition by mass
1.5 Reacting masses and volumes (of solutions and gases)	a) write and construct balanced equations b) perform calculations, including use of the mole concept, involving: (i) reacting masses (from formulae and equations) (ii) volumes of gases (e.g. in the burning of hydrocarbons) (iii) volumes and concentrations of solutions When performing calculations, candidates' answers should reflect the number of significant figures given or asked for in the question. When rounding up or down, candidates should ensure that significant figures are neither lost unnecessarily nor used beyond what is justified (see also Practical Assessment, Paper 3, Display of calculation and reasoning on page 51). c) deduce stoichiometric relationships from calculations such as those in 1.5(b)

2 Atomic structure

This topic describes the type, number and distribution of the fundamental particles which make up an atom and the impact of this on some atomic properties.

Learning outcomes

Candidates should be able to:

- | | |
|---|--|
| 2.1 Particles in the atom | <ul style="list-style-type: none"> a) identify and describe protons, neutrons and electrons in terms of their relative charges and relative masses b) deduce the behaviour of beams of protons, neutrons and electrons in electric fields c) describe the distribution of mass and charge within an atom d) deduce the numbers of protons, neutrons and electrons present in both atoms and ions given proton and nucleon numbers (atomic and mass numbers) and charge |
| 2.2 The nucleus of the atom | <ul style="list-style-type: none"> a) describe the contribution of protons and neutrons to atomic nuclei in terms of proton (atomic) number and nucleon (mass) number b) distinguish between isotopes on the basis of different numbers of neutrons present c) recognise and use the symbolism ${}^x_z\text{A}$ for isotopes, where x is the nucleon (mass) number and z is the proton (atomic) number |
| 2.3 Electrons: energy levels, atomic orbitals, ionisation energy, electron affinity | <ul style="list-style-type: none"> a) describe the number and relative energies of the s, p and d orbitals for the principal quantum numbers 1, 2 and 3 and also the 4s and 4p orbitals b) describe and sketch the shapes of s and p orbitals c) state the electronic configuration of atoms and ions given the proton (atomic) number and charge, using the convention $1s^2 2s^2 2p^6$, etc. d) <ul style="list-style-type: none"> (i) explain and use the term <i>ionisation energy</i> (ii) explain the factors influencing the ionisation energies of elements (iii) explain the trends in ionisation energies across a period and down a group of the Periodic Table (see also Section 9.1) e) deduce the electronic configurations of elements from successive ionisation energy data f) interpret successive ionisation energy data of an element in terms of the position of that element within the Periodic Table g) explain and use the term <i>electron affinity</i> |

3 Chemical bonding

This topic introduces the different ways by which chemical bonding occurs and the effect this can have on physical properties.

Learning outcomes

Candidates should be able to:

- | | |
|--|--|
| 3.1 Ionic bonding | a) describe ionic bonding, using the examples of sodium chloride, magnesium oxide and calcium fluoride, including the use of 'dot-and-cross' diagrams |
| 3.2 Covalent bonding and co-ordinate (dative covalent) bonding including shapes of simple molecules | <p>a) describe, including the use of 'dot-and-cross' diagrams:</p> <ul style="list-style-type: none"> (i) covalent bonding, in molecules such as hydrogen, oxygen, chlorine, hydrogen chloride, carbon dioxide, methane, ethene (ii) co-ordinate (dative covalent) bonding, such as in the formation of the ammonium ion and in the Al_2Cl_6 molecule <p>b) describe covalent bonding in terms of orbital overlap, giving σ and π bonds, including the concept of hybridisation to form sp, sp^2 and sp^3 orbitals (see also Section 14.3)</p> <p>c) explain the shapes of, and bond angles in, molecules by using the qualitative model of electron-pair repulsion (including lone pairs), using as simple examples BF_3 (trigonal planar), CO_2 (linear), CH_4 (tetrahedral), NH_3 (pyramidal), H_2O (non-linear), SF_6 (octahedral), PF_5 (trigonal bipyramidal)</p> <p>d) predict the shapes of, and bond angles in, molecules and ions analogous to those specified in 3.2(c) (see also Section 14.3)</p> |
| 3.3 Intermolecular forces, electronegativity and bond properties | <p>a) describe hydrogen bonding, using ammonia and water as simple examples of molecules containing N–H and O–H groups</p> <p>b) understand, in simple terms, the concept of electronegativity and apply it to explain the properties of molecules such as bond polarity (see also Section 3.3(c)), the dipole moments of molecules (3.3(d)) and the behaviour of oxides with water (9.2(c))</p> <p>c) explain the terms <i>bond energy</i>, <i>bond length</i> and <i>bond polarity</i> and use them to compare the reactivities of covalent bonds (see also Section 5.1(b)(ii))</p> <p>d) describe intermolecular forces (van der Waals' forces), based on permanent and induced dipoles, as in, for example, $CHCl_3(l)$; $Br_2(l)$ and the liquid Group 18 elements</p> |
| 3.4 Metallic bonding | a) describe metallic bonding in terms of a lattice of positive ions surrounded by delocalised electrons |
| 3.5 Bonding and physical properties | <p>a) describe, interpret and predict the effect of different types of bonding (ionic bonding, covalent bonding, hydrogen bonding, other intermolecular interactions, metallic bonding) on the physical properties of substances</p> <p>b) deduce the type of bonding present from given information</p> <p>c) show understanding of chemical reactions in terms of energy transfers associated with the breaking and making of chemical bonds</p> |

4 States of matter

The study of the particles in solids, liquids and gases and the interactions between them is important in understanding the physical properties of substances.

Learning outcomes

Candidates should be able to:

- | | |
|--|--|
| 4.1 The gaseous state:
ideal and real gases
and $pV = nRT$ | <ul style="list-style-type: none"> a) state the basic assumptions of the kinetic theory as applied to an ideal gas b) explain qualitatively in terms of intermolecular forces and molecular size: <ul style="list-style-type: none"> (i) the conditions necessary for a gas to approach ideal behaviour (ii) the limitations of ideality at very high pressures and very low temperatures c) state and use the general gas equation $pV = nRT$ in calculations, including the determination of M_r |
| 4.2 The liquid state | <ul style="list-style-type: none"> a) describe, using a kinetic-molecular model, the liquid state, melting, vaporisation and vapour pressure |
| 4.3 The solid state:
lattice structures | <ul style="list-style-type: none"> a) describe, in simple terms, the lattice structure of a crystalline solid which is: <ul style="list-style-type: none"> (i) ionic, as in sodium chloride and magnesium oxide (ii) simple molecular, as in iodine and the fullerene allotropes of carbon (C_{60} and nanotubes only) (iii) giant molecular, as in silicon(IV) oxide and the graphite, diamond and graphene allotropes of carbon (iv) hydrogen-bonded, as in ice (v) metallic, as in copper b) discuss the finite nature of materials as a resource and the importance of recycling processes c) outline the importance of hydrogen bonding to the physical properties of substances, including ice and water (for example, boiling and melting points, viscosity and surface tension) d) suggest from quoted physical data the type of structure and bonding present in a substance |

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5 Chemical energetics

Enthalpy changes and entropy changes accompany chemical reactions. This topic demonstrates why some reactions and processes are spontaneous and others are not.

Learning outcomes

Candidates should be able to:

- 5.1 Enthalpy change, ΔH**
- explain that chemical reactions are accompanied by energy changes, principally in the form of heat energy; the energy changes can be exothermic (ΔH is negative) or endothermic (ΔH is positive)
 - explain and use the terms:
 - enthalpy change of reaction and standard conditions*, with particular reference to: formation, combustion, hydration, solution, neutralisation, atomisation
 - bond energy* (ΔH positive, i.e. bond breaking)
 - lattice energy* (ΔH negative, i.e. gaseous ions to solid lattice)**
 - calculate enthalpy changes from appropriate experimental results, including the use of the relationship $\Delta H = -mc\Delta T$
 - explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy**

- 5.2 Hess' Law, including Born-Haber cycles**
- apply Hess' Law to construct simple energy cycles, and carry out calculations involving such cycles and relevant energy terms, with particular reference to:
 - determining enthalpy changes that cannot be found by direct experiment, e.g. an enthalpy change of formation from enthalpy changes of combustion
 - average bond energies
 - the formation of a simple ionic solid and of its aqueous solution**
 - Born-Haber cycles (including ionisation energy and electron affinity)**
 - construct and interpret a reaction pathway diagram, in terms of the enthalpy change of the reaction and of the activation energy

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- 5.3 Entropy change, ΔS**
- a) explain that entropy is a measure of the 'disorder' of a system, and that a system becomes more stable when its energy is spread out in a more disordered state
 - b) explain the entropy changes that occur:
 - (i) during a change in state e.g. (s) $\rightarrow$ (l); (l) $\rightarrow$ (g); (s) $\rightarrow$ (aq)
 - (ii) during a temperature change
 - (iii) during a reaction in which there is a change in the number of gaseous molecules
 - c) predict whether the entropy change for a given process is positive or negative
 - d) calculate the entropy change for a reaction, ΔS , given the standard entropies, S , of the reactants and products
-

- 5.4 Gibbs free energy change, ΔG**
- a) define the standard Gibbs free energy change of reaction by means of the equation $\Delta G = \Delta H - T\Delta S$
 - b) calculate ΔG for a reaction using the equation $\Delta G = \Delta H - T\Delta S$
 - c) state whether a reaction or process will be spontaneous/feasible by using the sign of ΔG
 - d) predict the effect of temperature change on the spontaneity/feasibility of a reaction, given standard enthalpy and entropy changes
-

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6 Electrochemistry

This topic illustrates the relationship between electricity and chemical changes. Chemical reactions can be investigated by looking at electrode potentials.

Learning outcomes

Candidates should be able to:

- | | |
|---|---|
| 6.1 Redox processes: electron transfer and changes in oxidation number (oxidation state) | <ul style="list-style-type: none"> a) calculate oxidation numbers of elements in compounds and ions b) describe and explain redox processes in terms of electron transfer and changes in oxidation number c) use changes in oxidation numbers to help balance chemical equations |
| 6.2 Electrolysis | <ul style="list-style-type: none"> a) state and apply the relationship $F = Le$ between the Faraday constant, the Avogadro constant and the charge on the electron b) predict the identity of the substance liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration c) calculate: <ul style="list-style-type: none"> (i) the quantity of charge passed during electrolysis (ii) the mass and/or volume of substance liberated during electrolysis, including those in the electrolysis of $\text{H}_2\text{SO}_4(\text{aq})$ and of $\text{Na}_2\text{SO}_4(\text{aq})$ d) describe the determination of a value of the Avogadro constant by an electrolytic method |

6.3 Standard electrode potentials $E^\ominus$; standard cell potentials $E^\ominus_{\text{cell}}$ and the Nernst equation	a) define the terms: (i) <i>standard electrode (reduction) potential</i> (ii) <i>standard cell potential</i> b) describe the standard hydrogen electrode c) describe methods used to measure the standard electrode potentials of: (i) metals or non-metals in contact with their ions in aqueous solution (ii) ions of the same element in different oxidation states d) calculate a standard cell potential by combining two standard electrode potentials e) use standard cell potentials to: (i) explain/deduce the direction of electron flow in a simple cell (ii) predict the spontaneity/feasibility of a reaction f) deduce from $E^\ominus$ values the relative reactivity of elements of Group 17 (the halogens) as oxidising agents g) construct redox equations using the relevant half-equations (see also Section 12.2(d)) h) predict qualitatively how the value of an electrode potential varies with the concentrations of the aqueous ions i) use the Nernst equation, e.g. $E = E^\ominus + (0.059/z) \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$ to predict quantitatively how the value of an electrode potential varies with the concentrations of the aqueous ions; examples include $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$, $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$, $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$
6.4 Batteries and fuel cells	a) state the possible advantages of developing other types of cell, e.g. the H_2/O_2 fuel cell and the nickel-metal hydride and lithium-ion rechargeable batteries

7 Equilibria

This topic illustrates that many chemical reactions are reversible and involve an equilibrium process. The consideration of the many factors that can affect an equilibrium is an important aspect of physical chemistry.

Learning outcomes

Candidates should be able to:

- | | |
|---|---|
| 7.1 Chemical equilibria: reversible reactions, dynamic equilibrium | <ul style="list-style-type: none">a) explain, in terms of rates of the forward and reverse reactions, what is meant by a <i>reversible reaction</i> and <i>dynamic equilibrium</i>b) state Le Chatelier's principle and apply it to deduce qualitatively (from appropriate information) the effects of changes in temperature, concentration or pressure on a system at equilibriumc) state whether changes in temperature, concentration or pressure or the presence of a catalyst affect the value of the equilibrium constant for a reactiond) deduce expressions for equilibrium constants in terms of concentrations, K_c, and partial pressures, K_p (treatment of the relationship between K_p and K_c is not required)e) calculate the values of equilibrium constants in terms of concentrations or partial pressures from appropriate dataf) calculate the quantities present at equilibrium, given appropriate data (such calculations will <i>not</i> require the solving of quadratic equations)g) describe and explain the conditions used in the Haber process and the Contact process, as examples of the importance of an understanding of chemical equilibrium in the chemical industry |
|---|---|

7.2 Ionic equilibria

- a) show understanding of, and use, the Brønsted-Lowry theory of acids and bases, including the use of the conjugate acid, conjugate base (acid-I base-I, acid-II base-II) concept
- b) explain qualitatively the differences in behaviour between strong and weak acids and bases and the pH values of their aqueous solutions in terms of the extent of dissociation
- c) **explain the terms pH, K_a , pK_a and K_w and use them in calculations**
- d) **calculate $[H^+(aq)]$ and pH values for strong and weak acids and strong bases**
- e) **explain the choice of suitable indicators for acid-base titrations, given appropriate data**
- f) **describe the changes in pH during acid-base titrations and explain these changes in terms of the strengths of the acids and bases**
- g) (i) **explain how buffer solutions control pH**
(ii) **describe and explain the uses of buffer solutions, including the role of HCO_3^- in controlling pH in blood**
- h) **calculate the pH of buffer solutions, given appropriate data**
- i) **show understanding of, and use, the concept of solubility product, K_{sp}**
- j) **calculate K_{sp} from concentrations and vice versa**
- k) **show understanding of the common ion effect**

7.3 Partition coefficients

- a) **state what is meant by a partition coefficient K_{pc} ; calculate and use a partition coefficient for a system in which the solute is in the same physical state in the two solvents**
-

8 Reaction kinetics

The investigation of the factors that affect the rate of a chemical reaction is important in the study of physical chemistry. The temperature and the addition of a catalyst can both affect the progression of a chemical reaction.

Learning outcomes

Candidates should be able to:

8.1 Simple rate equations, orders of reaction and rate constants

- a) explain and use the term *rate of reaction*
- b) explain qualitatively, in terms of collisions, the effect of concentration changes on the rate of a reaction
- c) **explain and use the terms *rate equation, order of reaction, rate constant, half-life of a reaction, rate-determining step***
- d) **construct and use rate equations of the form $\text{rate} = k[\text{A}]^m[\text{B}]^n$ (for which m and n are 0, 1 or 2), including:**
 - (i) **deducing the order of a reaction, or the rate equation for a reaction, from concentration-time graphs or from experimental data relating to the initial rates method and half-life method**
 - (ii) **interpreting experimental data in graphical form, including concentration-time and rate-concentration graphs**
 - (iii) **calculating an initial rate using concentration data****(integrated forms of rate equations are not required)**
- e) (i) **show understanding that the half-life of a first-order reaction is independent of concentration**
(ii) **use the half-life of a first-order reaction in calculations**
- f) **calculate the numerical value of a rate constant, for example by using the initial rates or half-life method**
- g) **for a multi-step reaction:**
 - (i) **suggest a reaction mechanism that is consistent with the rate equation and the equation for the overall reaction**
 - (ii) **predict the order that would result from a given reaction mechanism and vice versa**
- h) **devise a suitable experimental technique for studying the rate of a reaction, from given information**

8.2 Effect of temperature: on reaction rates and rate constants and the concept of activation energy

- a) explain and use the term *activation energy*, including reference to the Boltzmann distribution
- b) explain qualitatively, in terms both of the Boltzmann distribution and of collision frequency, the effect of temperature change on the rate of a reaction
- c) **explain qualitatively the effect of temperature change on the rate constant and hence the rate of a reaction**

Cambridge International AS & A Level Chemistry 9701 syllabus. Syllabus content
Syllabus for examination in 2019, 2020 and 2021.

8.3 Homogeneous and heterogeneous catalysts including enzymes

- a) explain and use the term *catalysis*
 - b) explain that catalysts can be homogeneous or heterogeneous
 - c) (i) explain that, in the presence of a catalyst, a reaction has a different mechanism, i.e. one of lower activation energy
(ii) interpret this catalytic effect in terms of the Boltzmann distribution
 - d) describe enzymes as biological catalysts (proteins) which may have specificity
 - e) **outline the different characteristics and modes of action of homogeneous, heterogeneous and enzyme catalysts, including:**
 - (i) the Haber process
 - (ii) the catalytic removal of oxides of nitrogen from the exhaust gases of car engines (see also Section 15.3(b)(i))
 - (iii) the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide (see also Section 13.1(f))
 - (iv) the catalytic role of Fe^{2+} or Fe^{3+} in the $\text{I}^-/\text{S}_2\text{O}_8^{2-}$ reaction
 - (v) the catalytic role of enzymes (including the explanation of specificity using a simple lock and key model but excluding inhibition)
-

Chapter 1 Atoms, molecules and Stoichiometry

Relative atomic mass (A_r) :-

It is the average mass of an atom of an element as compared to $\frac{1}{12}$ of the mass of an atom of Carbon which is taken as 12.

e.g. Bromine has two isotopes ^{79}Br and ^{81}Br , both has equal abundance

$$A_r \text{ of Bromine} = \frac{79 \times 50 + 81 \times 50}{100}$$

Similarly A_r of Chlorine can be calculated

by calculating the average no of the masses of its isotopes

^{35}Cl relative abundance 75%
 ^{37}Cl relative abundance 25%

$$A_r = \frac{35 \times 75 + 37 \times 25}{100} = 35.5$$

Relative molecular mass (M_r) :

It is the mass of one molecule of an element or compound as compared to $\frac{1}{12}$ of the mass of an atom which is taken as 12.

e.g. M_r of O_2 is 32

M_r of H_2 is 2

M_r of CO_2 is 44

Relative formula mass : This term is used for ionic compounds, it is the sum of

e.g. relative formula mass of MgO is $24 + 16 = 40$.
Relative formula mass can be defined as the mass of one formula unit of an ionic compound as compared to $\frac{1}{12}$ of the mass of an atom of C-12 .

Relative isotopic mass:- The mass of an isotope of an element as compared to $\frac{1}{12}$ of the mass of an atom of C-12 .

Relative ionic mass:- The mass of an ion of an element or a compound as compared to $\frac{1}{12}$ of the mass of an atom of C-12 .

Mole (Definition):- Mole is that amount of a substance which contains 6.02×10^{23} particles of that substance

OR

the amount of a substance containing as many particles as there are atoms in 12g of Carbon-12.

Isotopes:- Atoms of the same element which have same proton number but different mass number. Isotopes have same chemical but different physical properties.

Spectrometry and Ar
Mass spectrometer is used to measure the mass and relative abundance of each isotope.

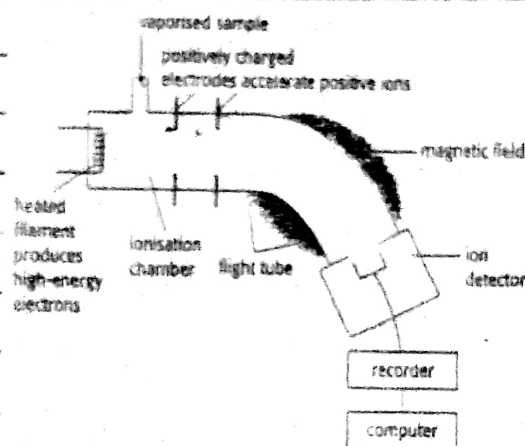
Working of mass spectrometer

- $\Rightarrow$ Atoms of the element become monovalent ion when a gaseous sample of an element is introduced in spectrometer.
- $\Rightarrow$ The stream of positive ions is brought to a detector.

Lighter ions (isotopes) are deflected more than heavier ions.

Deflected ions are brought to the detector, the detector is connected to a computer which displays the mass spectrum.

The mass spectrum produced shows the relative abundance on the vertical axis and the mass to charge ratio (m/z) on the horizontal axis.

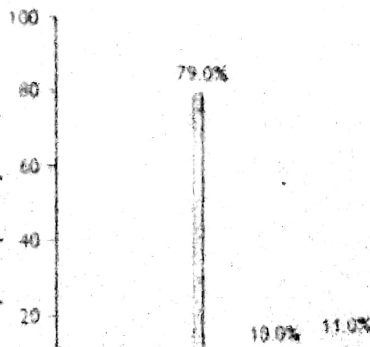


Determination of A_r from mass spectra

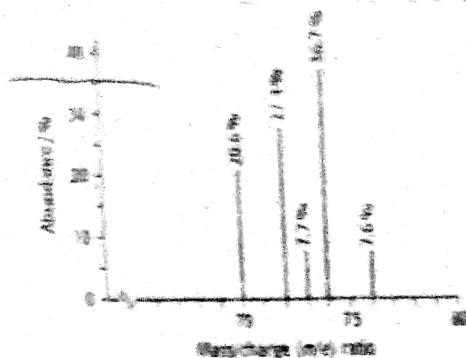
Calculate the A_r of Magnesium using mass spectra

$$A_r = \frac{24 \times 79 + 25 \times 10 + 26 \times 11}{100}$$

$$= 24.32$$



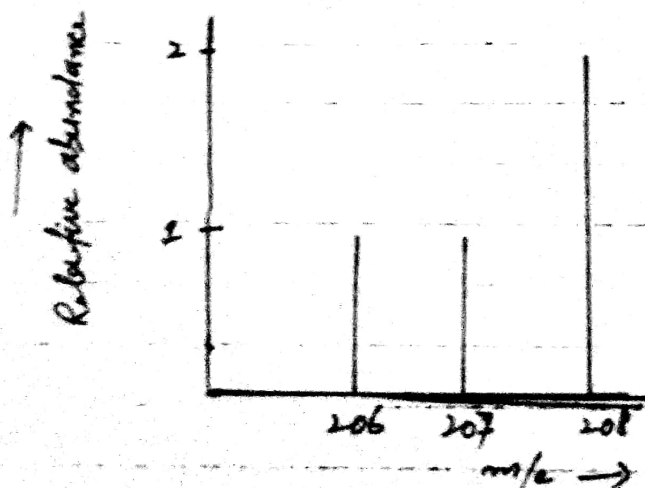
Mass spectrum of Germanium



$$A_r = \frac{70 \times 20.6 + 72 \times 27.4 + 73 \times 7.7 + 74 \times 36.7 + 76 \times 7.6}{100}$$

$$= 72.7$$

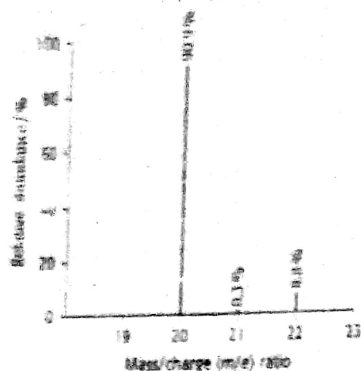
Mass spectrum of Lead



$$A_r = \frac{206 \times 1 + 207 \times 1 + 208 \times 2}{4}$$

$$= 207.25$$

Mass spectrum of Neon



$$A_r = \frac{20 \times 90.9 + 21 \times 0.3 + 22 \times 8.8}{100}$$

$$= 20.2$$

Determination of relative abundance of an isotope

The relative atomic mass of Boron, which consists of the isotopes ${}^{10}_5\text{B}$ and ${}^{11}_5\text{B}$ is 10.8. Calculate the relative abundance of each isotope of Boron.

Solution

$$A_r = 10.8$$

relative abundance of ${}^{10}_5\text{B} = x$

relative abundance of ${}^{11}_5\text{B} = 100 - x$

$$A_r = \frac{11 \times x + 10(100 - x)}{100}$$

$$10.8 = \frac{11x + 1000 - 10x}{100}$$

$$x = 80$$

Note: Relative abundance will be x for that isotope which is ${}^{10}_5\text{B}$.

Determination of relative isotopic abundance of the isotopes of Potassium

The relative atomic mass of Potassium is 39.1. The two main isotopes of Potassium are ^{39}K and ^{41}K . Calculate the relative isotopic abundance of each isotope.

Solution

$$A_r = 39.1$$

$$\text{Relative abundance of } ^{39}\text{K} = x$$

$$\text{Relative abundance of } ^{41}\text{K} = 100 - x$$

$$39.1 = \frac{39x + 41(100 - x)}{100}$$

$$x = 95\%$$

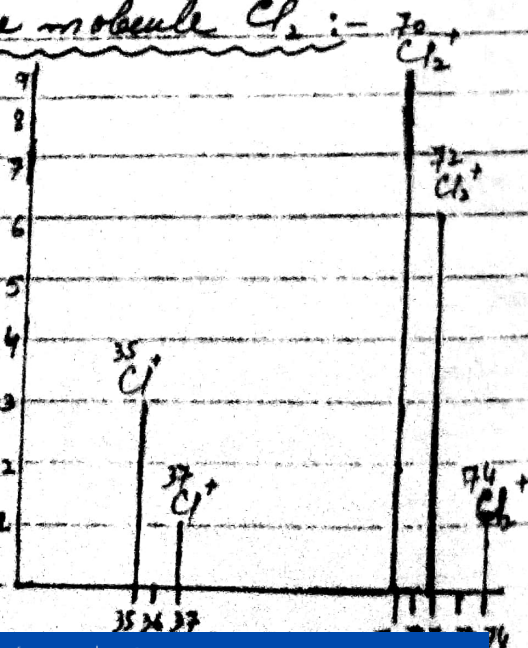
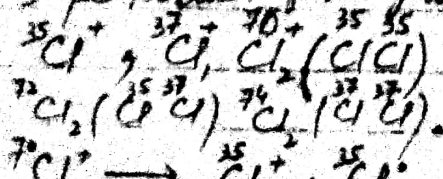
$$^{39}\text{K} = 95\%$$

$$^{41}\text{K} = 5\%$$

Mass spectrum of diatomic molecules

Mass spectrum of Chlorine molecule Cl_2 :-

When Chlorine gas is introduced in a mass spectrometer, a fraction of Chlorine molecules undergo fragmentation and produce 5 peaks due to following ions.



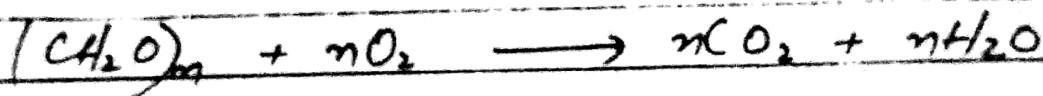
Stoichiometric calculations

The typical daily food requirement of a person can be considered to be 1.2 kg of carbohydrate. The person obtains energy by the oxidation of carbohydrate which can be represented by the formula $(CH_2O)_n$.

(a) Construct an equation for the complete combustion of carbohydrate.

(b) The empirical formula mass of the carbohydrate is 30, calculate the number of moles of oxygen required by the person each day.

Solution



$$\text{mass} = 1.2 \text{ kg} = 1200 \text{ g}$$

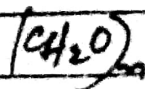
$$M_r = 30 \times n$$

Number of oxygen

$$\text{mole} = \frac{\text{Mass}}{M_r}$$

$$n = \frac{1200}{30n}$$

$$\text{moles} = \frac{40}{n}$$



1 mole

n moles

$$\frac{40}{n}$$

X

X

$$x = \frac{40}{n} \times n$$

40 moles of O_2 are required each day

0.144g of an aluminium compound x reacts with an excess of water, to produce a gas. This gas burns completely in O_2 to form H_2O and 72 cm³ of CO_2 only. The volume of CO_2 was measured at r.t.p.
 What could be the formula of x ?
 (A) Al_2C_3 (B) Al_2C_4 (C) Al_4C_3 (D) Al_5C_3

Solution

$$\begin{array}{r} \text{Mass of } CO_2 \\ 44 \text{ g mol}^{-1} \times 44 \text{ g} \\ 72 \text{ cm}^3 \times x \end{array}$$

$$0.132 \text{ g of } CO_2$$

$$\begin{array}{r} \text{Mass of C from } CO_2 \\ 12 \text{ g} \times 44 \text{ g} \\ x \times 0.132 \text{ g} \\ x = 0.036 \text{ g of C} \end{array} \quad \begin{array}{r} \text{moles of C} \\ \frac{0.036}{12} \\ = 0.003 \text{ mol of C} \end{array}$$

$$\begin{array}{r} \text{Mass of Al from unknown compound} \\ 0.144 - 0.036 = 0.108 \text{ g} \\ \frac{0.108}{27} \\ = 0.004 \text{ mol of Al} \end{array}$$

$$\begin{array}{r} \text{Mole ratio of C : Al} \\ 0.003 \quad 0.004 \\ 3 : 4 \\ Al_4C_3 \end{array}$$

When a sports metal with a total surface area of 150 cm² was evenly coated with silver, using electrolysis, its mass increased by 0.216 g.

How many atoms of Ag were deposited per cm² of the surface of metal?

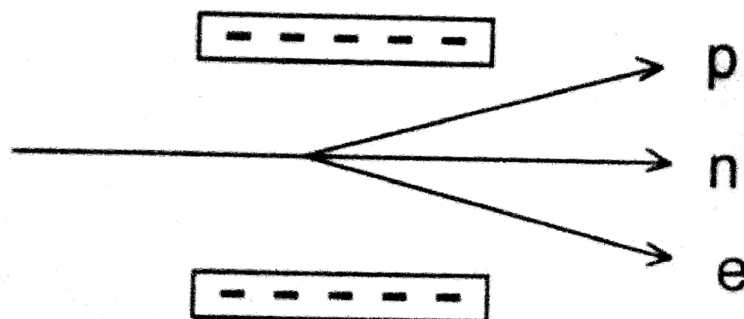
Solution: $150 \text{ cm}^2 \times 0.216 \text{ g} = 32.4 \text{ g}$

Atomic Structure

Sub atomic particles and their properties

Particles	Relative mass	Relative charge
Proton	1	+1
neutron	1	0
electron	$\frac{1}{1840}$	of the mass of proton -1

Behavior of proton electrons and of alpha particles in an electric field and magnetic field



In an electric or magnetic field electrons are deflected towards the positive pole while protons are deflected towards the negative pole while neutrons do not deflect as they carry no charge.

Electronic configuration

- The arrangement of electrons in different shells and sub shells is called electronic configuration.
- Electrons are arranged in different shells and sub shells adding

Shell or orbit or energy level (n)

- It is the path around the nucleus where electron revolves.
- Orbits are represented by English alphabets K, L, M, N, O, P, Q, ...
- The energy order of shells is $K < L < M < N < O < P < Q$

Principal quantum Number

Each orbit is also represented by a number called principal quantum number n ; Principal quantum number for K, L, M, N, O, P and Q is 1, 2, 3, 4, 5, 6 and 7 respectively

Sub shells: sub shells are the

sub division of shells.

- There are four sub shells represented by s, p, d and f
- Energy order of sub shells is $s < p < d < f$

Orbitals: orbitals are the

sub-division of sub shells.

- An orbital cannot accommodate more than 2 electrons.

<u>Sub shell</u>	<u>Orbitals</u>
s	one (s)
p	three (p_x, p_y, p_z)
d	Five ($d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{z^2}$)
f	

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<u>Shells</u>	<u>Sub shells</u>	<u>Number of electrons in each shell</u>
K	1s	2
L	2s 2p	8
M	3s 3p 3d	18
N	4s 4p 4d 4f	32
O	5s 5p 5d 5f	32
P	6s 6p 6d 6f	32
A	7s 7p 7d 7f	32

<u>Sub shells</u>	<u>Electrons</u>
s	2
p	6
d	10
f	14

Rules for electronic configuration

Auf Bau Principle :- According to this

principle, electrons are filled up in different shells and sub shells according to the increasing order of their energy.

4: 7, 19K

$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^2$ X wrong

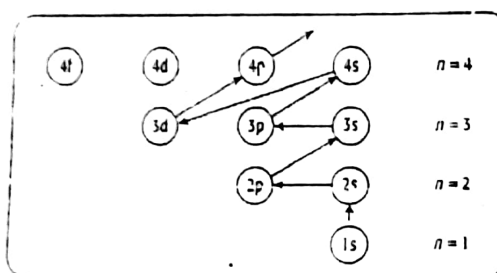
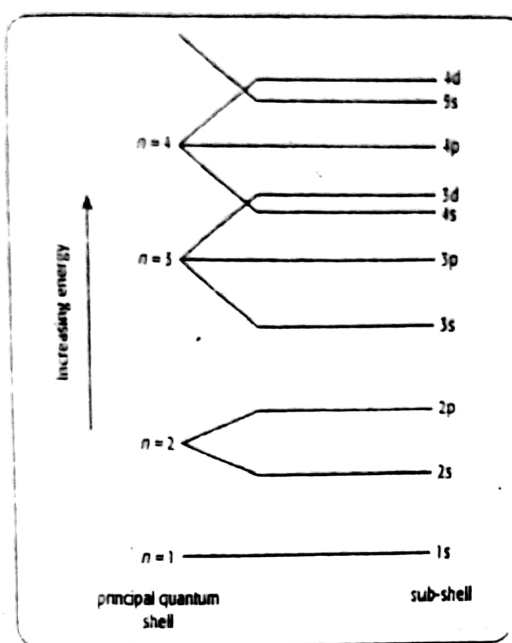
$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$ ✓ correct

E...

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Pauli's exclusion principle: A orbital

cannot accommodate more than 2 electrons.

Hund's rule: If degenerate orbitals

(orbitals of same energy) are available then electrons would like to go in separate orbitals rather than in a same orbital.

e.g. $6C = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$ X(wrong)

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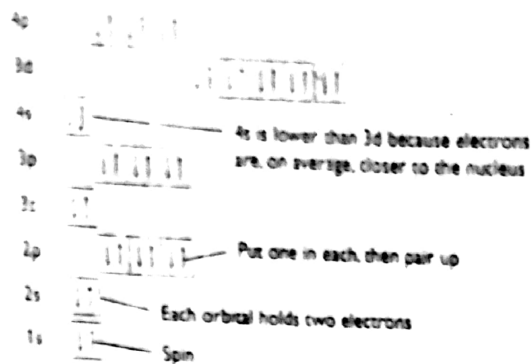
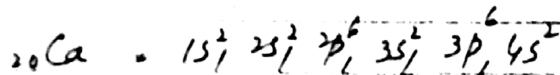
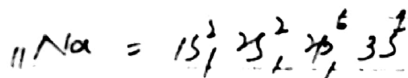
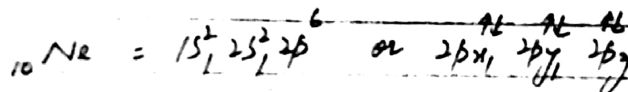
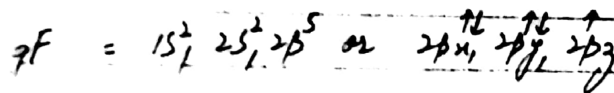
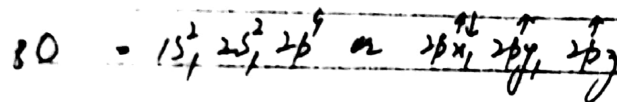
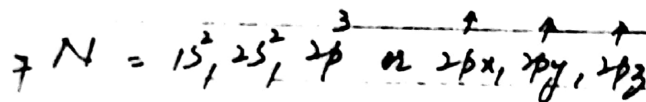
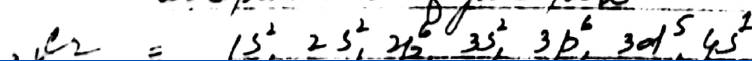
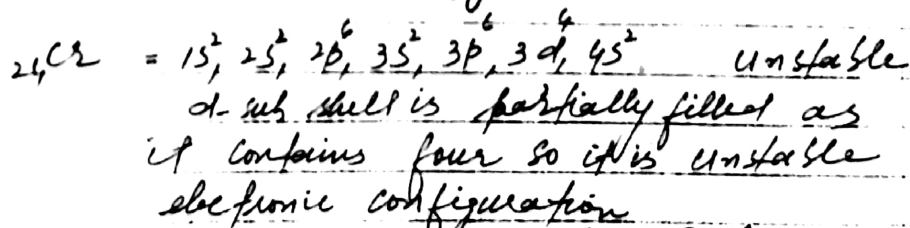


Figure 2.1 Sequence of filling orbitals with electrons

Examples of electronic configuration



Stable and unstable electronic configuration



Similarly, Cu

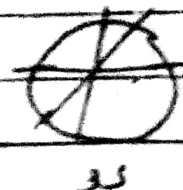
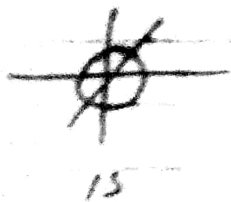
$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^9, 4s^1$ unstable

$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$ stable

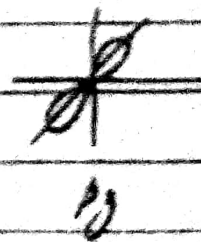
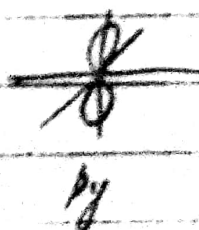
Shapes of orbital

s-orbitals - s-orbitals are

spherical in shape and the size of sphere increases with the increase in shell number.



p-orbital - p-orbitals are dumbbell or hourglass with two lobes.

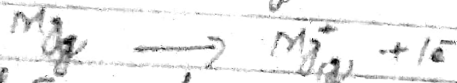


(7)

Ionization energy

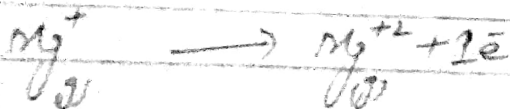
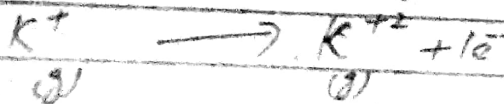
1st ionization energy: Amount of energy

which is required to remove one mole of electrons from one mole of a gaseous atom to form ^{one mole of} monovalent positive gaseous ions e.g;



2nd Ionization energy: Amount of energy

which is required to remove one mole of electrons from one mole of monovalent positive gaseous ions to form one mole of divalent positive gaseous ions, e.g;



Factors affecting ionization energy

(i) Shielding effect: Electrons present

between nucleus and valence shell protect valence electrons from nuclear attraction, this is called shielding effect.

⇒ Increase in shielding effect decreases the ionization energy.

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decreasing the attraction between nucleus and valence electrons

(2) Nuclear charge and effective nuclear charge

Nuclear charge :- Total number of protons present in the nucleus of an atom is called nuclear charge.

Effective nuclear charge :- Total

number of protons minus number of inner shell electrons is called effective nuclear charge

^{11}Na

$$11p - 10e = +1 \text{ (effective nuclear charge)}$$

^{12}Mg

$$12 - 10 = +2 \text{ effective nuclear charge}$$

^{13}Al

$$13 - 10 = +3 \text{ effective nuclear charge}$$

⇒ presence of inner shell electrons cancels the nuclear attraction for valence electrons but not completely.

⇒ Increase in nuclear charge or effective nuclear charge both increase the ionization energy by increasing attraction between nucleus and valence and by pulling valence shell

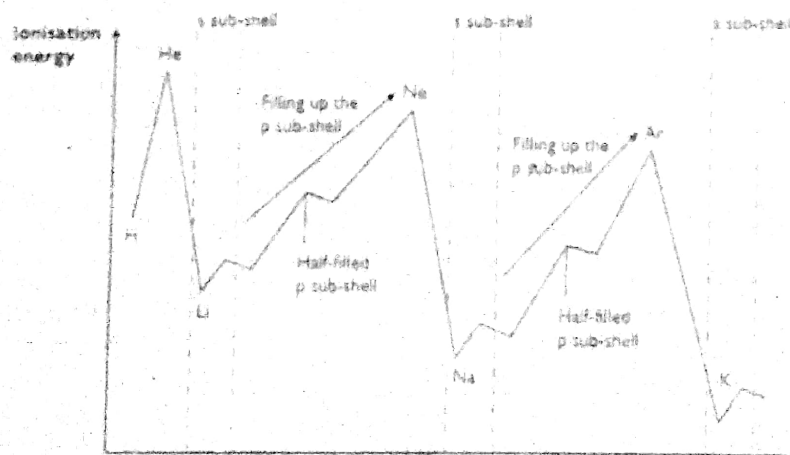
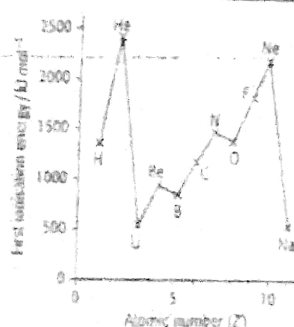
more towards the nucleus.

Trends in Ionization energy

Across the period: 1st ionization

energy increases from left to right across the period due to the following reasons.

- Effective nuclear charge increases from left to right across the period
- Shielding effect remains constant
- atomic size decreases
- due to this valence electron(s) get closer to the nucleus, hence more energy will be required to remove electrons.



Along the group

Unusual trends in ionization energy across the period

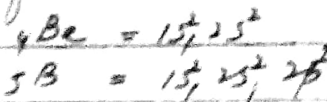
(i) From group II to III :- 1st ionization energy

decreases from group II to group III due to the difference in valence sub shell

⇒ group III elements have their valence electrons in p-sub shell while group II elements have valence electrons in s-sub shell

⇒ p-sub shell is at higher energy or electrons in p-sub shell are at higher energy

⇒ group II elements have completely filled s-sub shell, so more difficult to remove electron from s-sub shell of group II e.g.

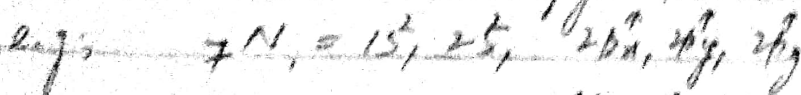


(ii) From group V to VI :- 1st ionization

energy of group V elements is greater than that of group VI due to the following reasons

(i) Group V elements have half filled p-sub shell which is more stable than partially filled p-sub shell of group VI

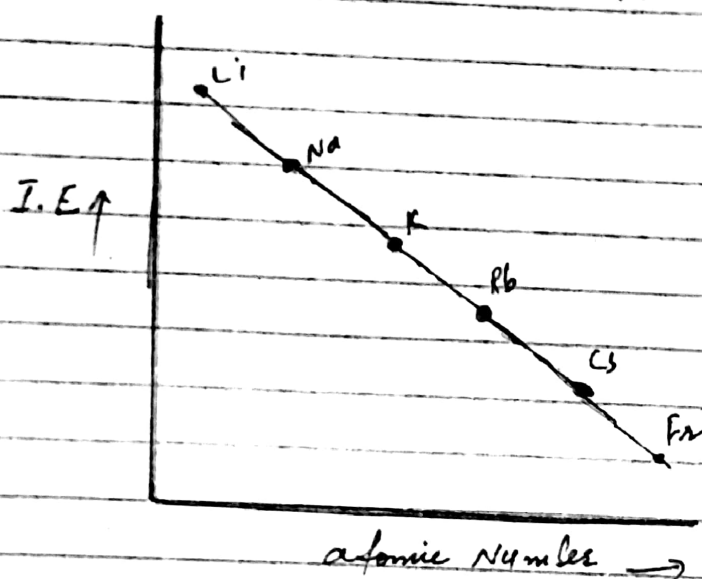
(ii) pair of electrons in p-sub shell of group VI repel each other and need lesser energy to remove



(2) Along the group

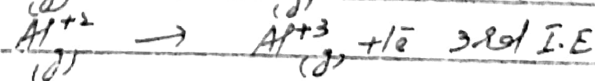
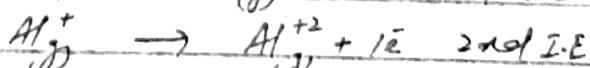
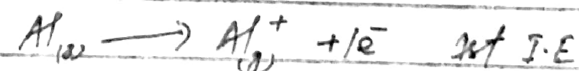
Ionization energy decreases down the group due to following reasons

- Increase in atomic size due to the increase in number of shells decreases the electrostatic attraction between nucleus and valence electrons.
- Increase in shielding effect



Successive Ionization energy

Successive ionization energy refers to the removal of 2nd and subsequent electrons e.g;



Prediction of group number

the group number of that element.

Successive ionization energies increase as the outer electrons are removed and biggest jump occurs when an electron is removed from a new inner orbital closer to the nucleus.

For example, the five successive ionization energies of an unknown element are given, predict the group number of that element

1st I.E	2nd I.E	3rd I.E	4th I.E	5th I.E
578	1817	2744	11577	14822

Biggest Increase

Biggest increase from 3rd to 4th I.E indicates the change in orbit, so element is present in group III and have three valence electrons.

Similarly

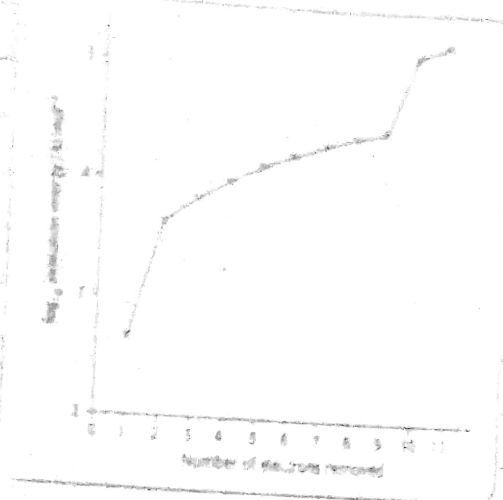
1st I.E	2nd I.E	3rd I.E	4th I.E	5th I.E
598	1145	4912	6491	853

Biggest increase

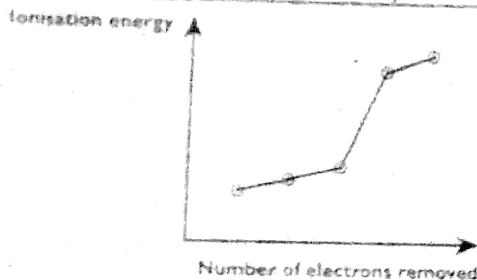
Biggest increase from 2nd to 3rd I.E indicates the presence of element in group II.

1st I.E	2nd I.E	3rd I.E	4th I.E	5th I.E
496	4562	6910	9543	13354

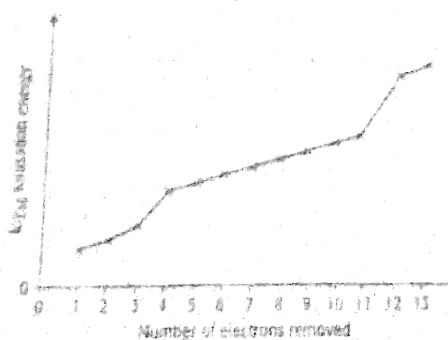
Graphical representation of successive ionization energies and prediction of group number



Biggest difference between 1st and 2nd ionization energy indicates the change in shell, so group 1, one valence electron



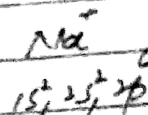
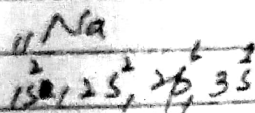
Biggest difference between 3rd and 4th, so third group



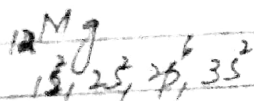
Biggest difference between 3rd and 4th, so third group

Why 2nd ionization energy is greater than 1st?

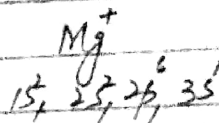
For group I elements, 1st electron is removed from the inner shell i.e. 2nd shell which is closer to the nucleus. Secondly after the removal of one electron effective nuclear charge increases which increases the electrostatic attraction between nucleus and valence electron.



⇒ For other elements removal of one electron increases effective nuclear charge, as a result nucleus have stronger hold over remaining electrons.



effective nuclear charge +2



effective nuclear charge +3

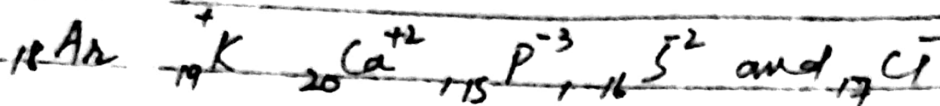
Important Note:

Increase in protons in the nucleus or removal of electron from the shell, both increase effective nuclear charge

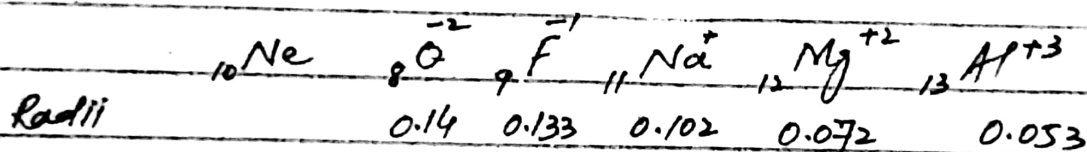
Radii of isoelectronic substances

ISOelectronic! substances with same number of electrons are called

(15)

For example

- ⇒ All have same number of electrons and are isoelectronic
- ⇒ Ca^{+2} has greatest effective nuclear charge and smaller radii
- ⇒ P^{-3} has lowest effective nuclear charge and has largest radii
- ⇒ So Ca^{+2} will have highest 1st I.E.

Another example

- ⇒ Al^{+3} has greatest effective nuclear charge and smallest radii, so highest 1st I.E.
- ⇒ O^{-2} has lowest effective nuclear charge and greatest radii, so have lowest 1st ionization energy.

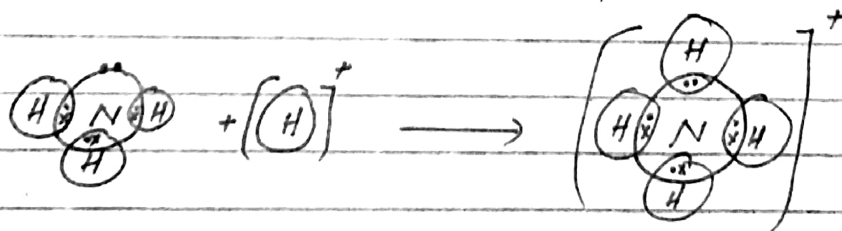
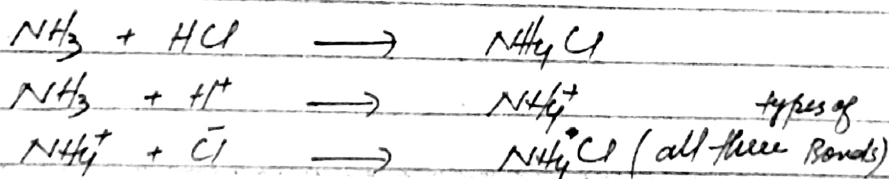
Chemical bonding

Ionic Bonding, covalent bonding, simple covalent molecules and giant covalent molecules and metallic bonding studied in O level are also included in A-level.

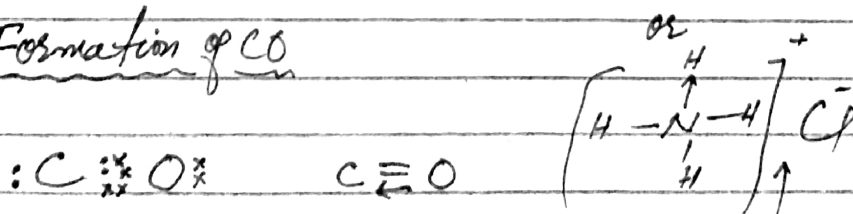
Coordinate covalent Bond or Dative Bond

- A dative Bond is a type of bond in which a pair of electron which is shared between two atoms is contributed by only one atom.
- An atom which contains a lone pair of electrons donates to an atom which is deficient of two electrons to complete its duplet or octet.

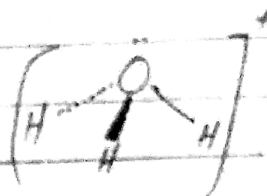
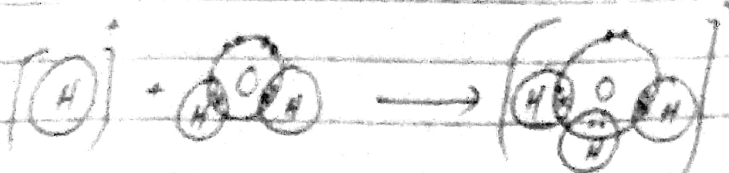
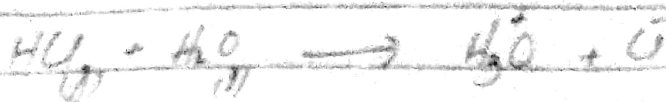
Formation of Ammonium ion



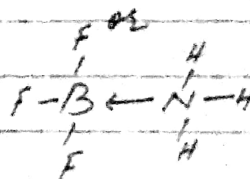
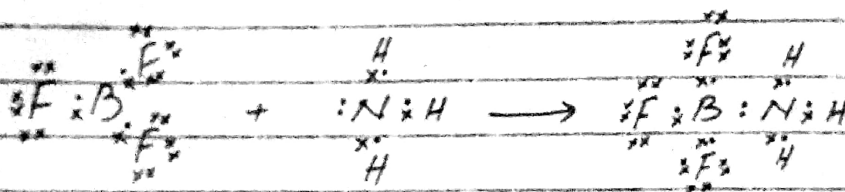
Formation of CO



Formation of hydronium ion

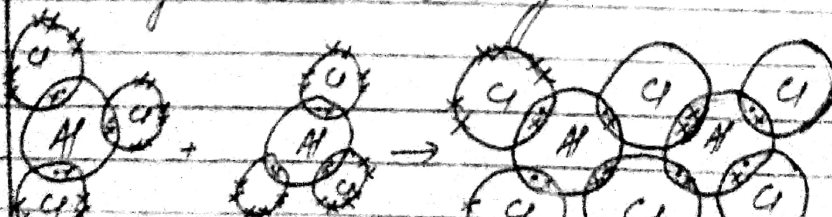


Formation of Boron trifluoride Amine BF_3NH_3



Dimerization of AlCl_3

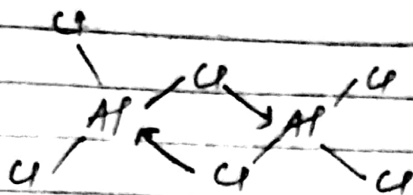
When two molecules of AlCl_3 (monomers) combine they form Al_2Cl_6 (dimer) through dative bonding.



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Each aluminium atom accepts a pair of electron from chlorine atom.

Shapes of molecules in the light of VSEPR theory (valence shell pair repulsion)

According to VSEPR theory shape of a covalent molecules depends upon the repulsion of electron pairs present in the valence shell of central atom.

Following are the points of VSEPR theory which helps predict the shapes of molecules

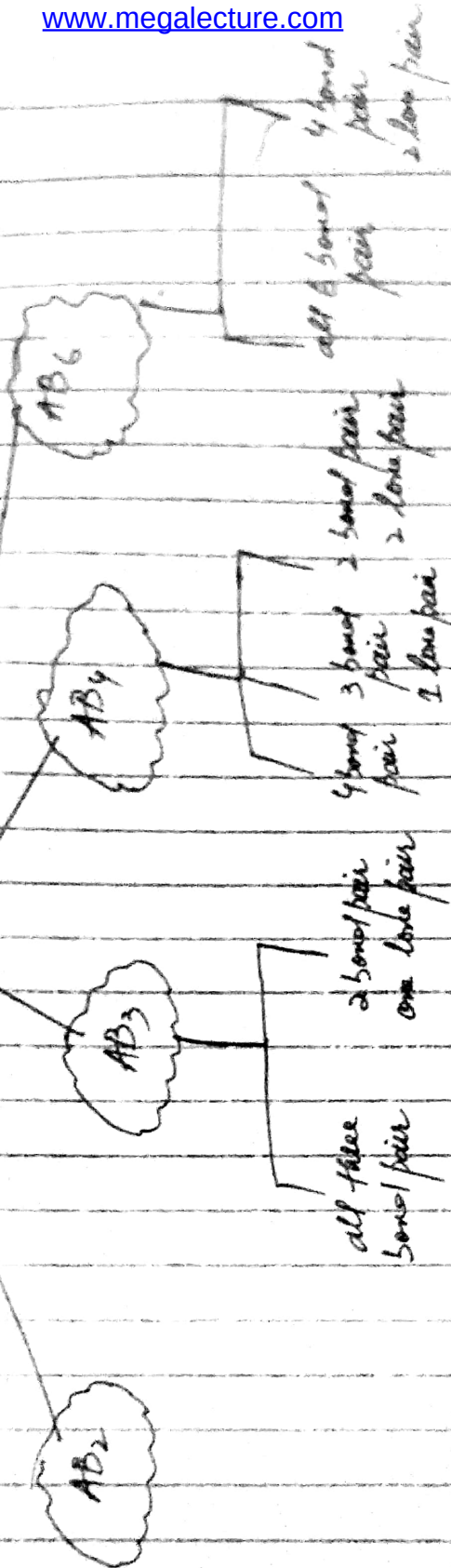
- ⇒ electron pairs around central atom try to keep themselves as far apart as possible
- ⇒ the order of repulsion between pairs of electrons is as follows

lone pair > lone pair > lone pair - bond pair > bond pair - bond pair

⇒ Single covalent bond, double covalent bond and triple covalent bond have equal repulsion.

Types of molecules

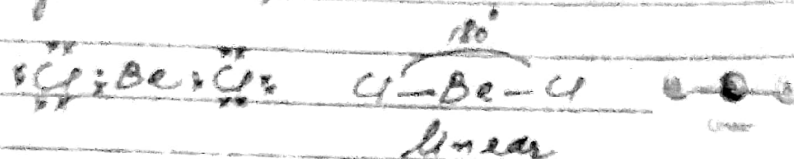
Central atom
 no. of electronic cloud in electronic region
 around central atom



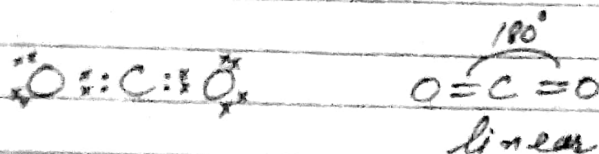
Shapes of AB₂ type molecules

All AB₂ type molecules are linear in shape with a bond angle of 180°

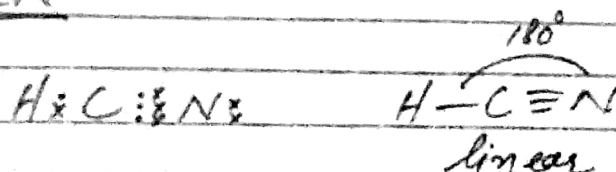
e.g. BeCl₂,



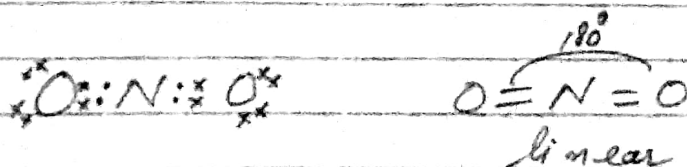
CO₂



HCN



NO₂ (Nitrogen is one electron deficient)



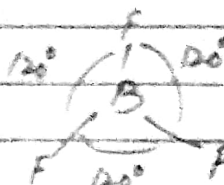
Shapes of molecules containing three electron pairs (AB₃ type)

ii) Molecules contain all three shared pairs

All AB₃ type molecules contain all three shared pairs of electrons are trigonal planar with bond angles of 120°

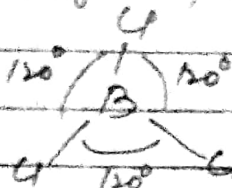
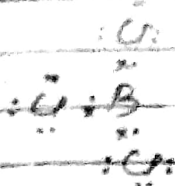
e.g. BF_3 , BCl_3 , SO_2 , CO_3^{2-}

BF_3



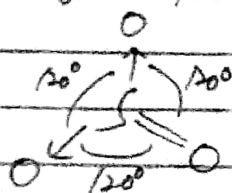
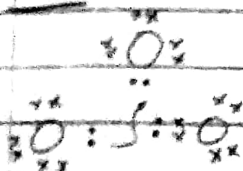
trigonal planar

AlCl_3



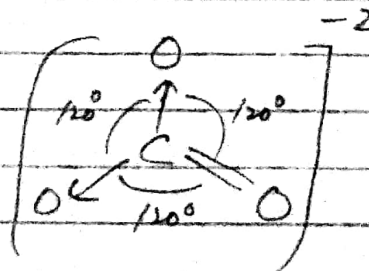
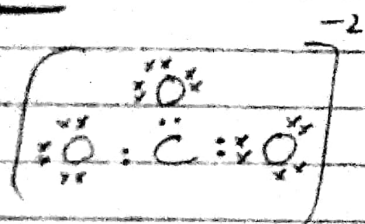
trigonal planar

SO_2



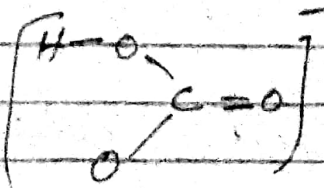
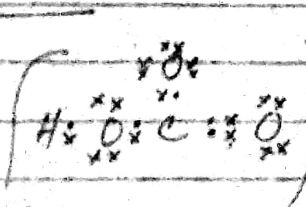
trigonal planar

CO_3^{2-}

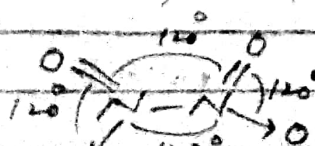


trigonal planar

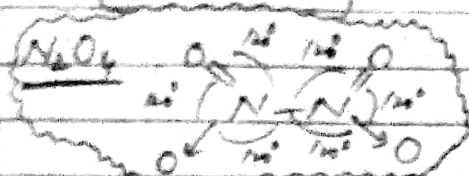
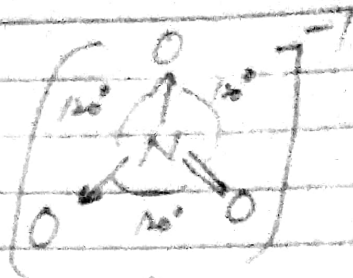
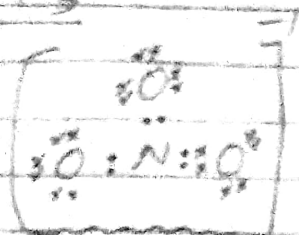
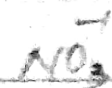
HCO_3^-



N_2O_4

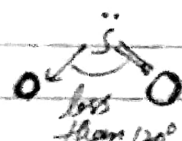
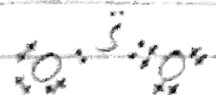
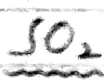


trigonal planar



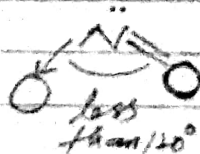
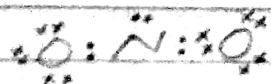
← trigonal planar

Shapes of AB_3 type molecules which
contain one lone pair and two bond pair

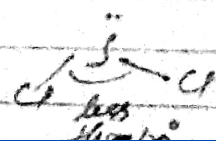
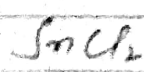


Bent or V-shaped

Lone pair of electron is under the influence of one nuclei, so is more free and occupies more space. Therefore it exerts greater repulsion.



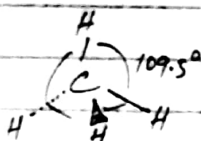
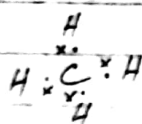
bent or angular shape



Shapes of AB_4 type molecules which contain all bond pair

All AB_4 type molecules in which all four pairs are bond pairs are tetrahedral in shape due to four faces and have bond angle of 109° , 109.2° or 109.5° .

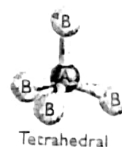
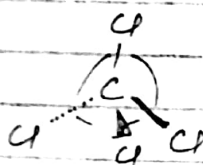
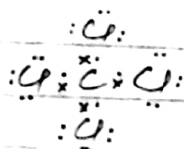
Shape of CH_4



tetrahedral

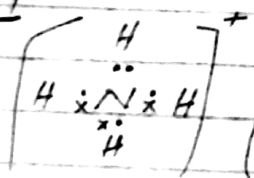


CCl_4

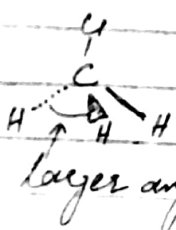
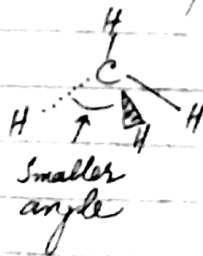


Tetrahedral

NH_4^+



Other examples are $SiCl_4$, SiH_4 , $PbCl_4$



Chlorine being more electronegative than carbon attracts pair of electrons itself so it exerts lesser repulsion.

Shapes of AB_3 molecules which contain
one lone pair and three bond pair

All such molecules are trigonal pyramidal
in shape and have bond angle of
 107° , 107.5° . e.g., NH_3 , H_2O , PH_3 , AsH_3

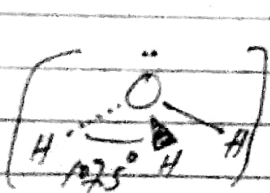
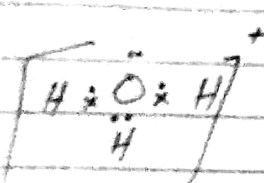
NH_3



trigonal pyramidal



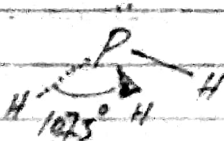
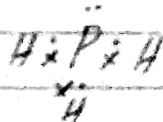
H_2O



Trigonal pyramidal

trigonal pyramidal

PH_3



trigonal pyramidal

$N_2 H_4$

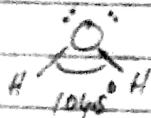
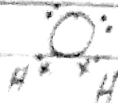


Shape of AB_2 type molecules which contain two lone pairs and two bond pairs

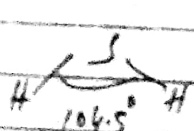
All such molecules are bent or V-shaped with angle of 104.5° .

Example of such molecules are H_2O , H_2S , F_2O etc.

H_2O

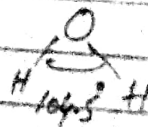
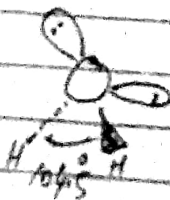
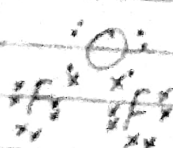


H_2S



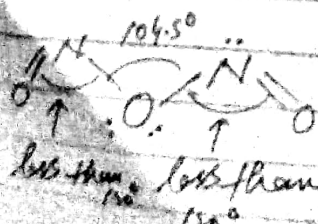
Bent or V-shaped

F_2O

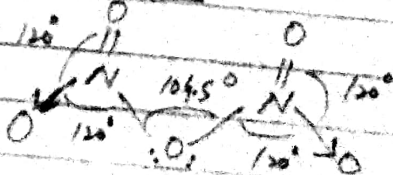


Some more examples

N_2O_3

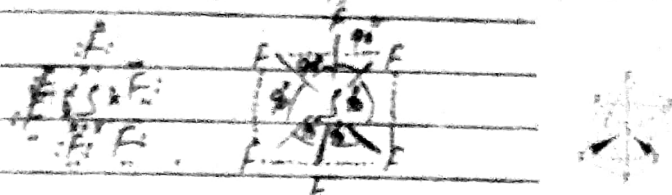


N_2O_5



Shapes of AB_6 type molecules which contain all bond pairs

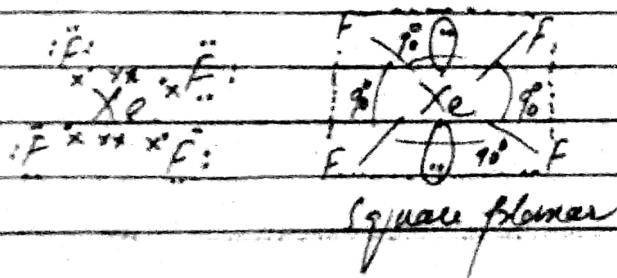
Such molecules are octahedral in shape with bond angles of 90° . e.g. SF_6



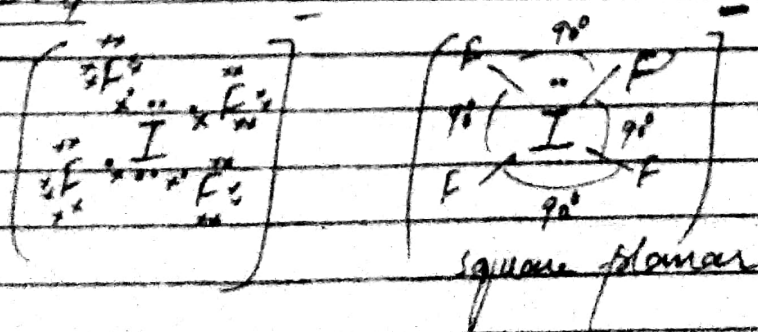
AB_6 type molecules which contain 2 lone pairs and 4 bond pairs

Such molecules are square planar in shape with all bond angles of 90° .

e.g. XeF_4

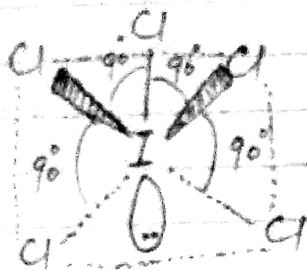


IF_4^-



AB_5 type molecules which contain one lone pair and 5 bond pair

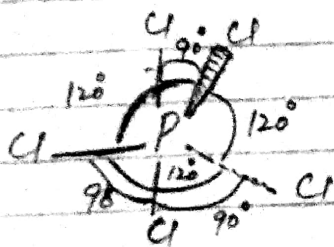
For example ICl_5 and IF_5



square bipyramidal

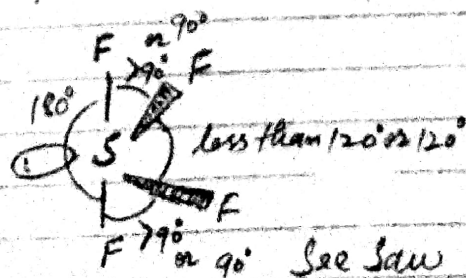
Shapes of AB_5 type molecules

(i) All bond pair e.g; PCl_5

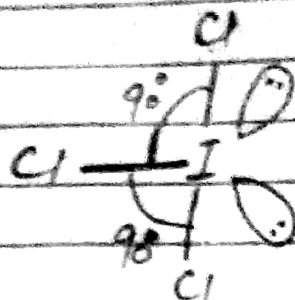


Trigonal bipyramidal

(ii) 4 bond pairs, one lone pair e.g; SF_6

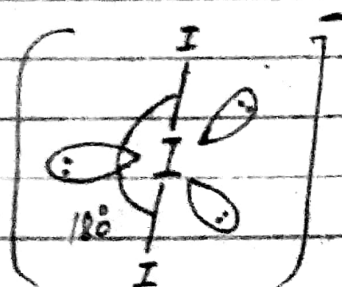


(iii) 2 lone pair and 3 bond pairs e.g. ICl_3



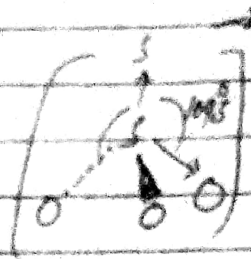
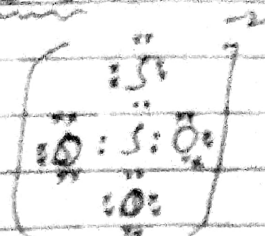
T-shaped

(iv) 3 lone pairs and 2 bond pairs e.g. I_3^-

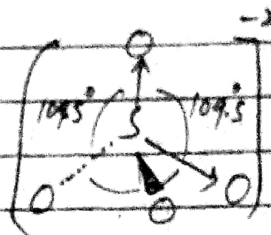
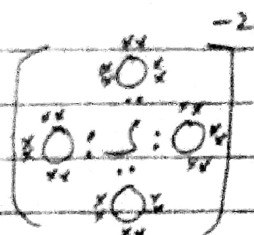


Linear

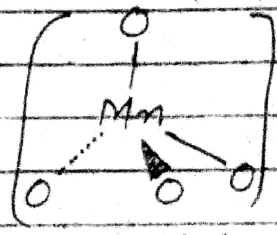
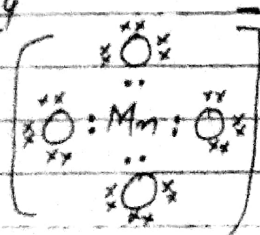
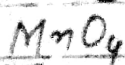
Some more examples



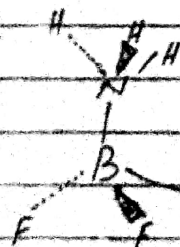
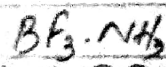
tetrahedral



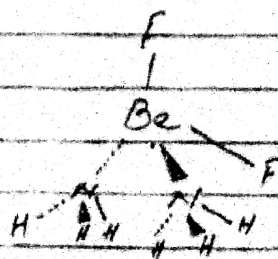
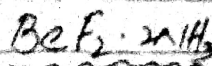
tetrahedral



tetrahedral



tetrahedral



tetrahedral

Atomic orbital hybridization

A process of mixing atomic orbitals of different energy and shape to form new set of equivalent orbitals of the same energy and same shape is called hybridization and orbitals obtained are called hybrid orbitals. The atomic orbital hybridization gives satisfactory explanation for the valency of the elements.

The electrons belonging to the ground state structure are promoted to the excited state as a result of which there is an increase in the number of unpaired electrons.

The electronic configuration of Be, B and C are shown in the table.

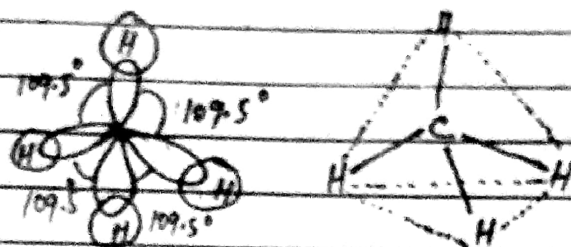
Element	Ground state Electronic Configuration	Excited state Configuration	Valency
4Be	$1s^2, 2s^2, 2p^0$	$1s^2, 2s^1, 2p^1$	2
5B	$1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$	$1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$	3
6C	$1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$	$1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$	4

After acquiring the excited state, the atomic orbitals undergo hybridization. The energy required for the excitation is compensated by the energy released during the process of bond formation with other atoms.

Hybridization holds significant importance in determining the shape and geometry of molecules.

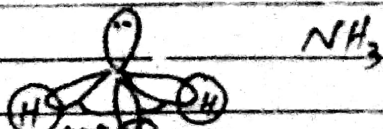
Depending upon the nature of atomic orbitals involved, there are many types of

Methane molecule is formed by the overlapping of partially filled hybrid orbitals of carbon and partially filled $1s$ orbital of hydrogen. Four hydrogen atoms form four sigma bonds with carbon.



Formation of NH_3 molecule

Electronic configuration of $N = 1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$. One s and three p orbitals of nitrogen atom hybridize to form four sp^3 hybrid atomic orbitals which are directed towards the four corners of a tetrahedron. One of the hybrid orbital is completely filled by a lone pair of electrons and the remaining three orbitals are half filled. The nitrogen atom undergoes three sp^3-s overlaps with three s -orbitals of hydrogen atoms. The three hydrogen atoms are located at 3 corners whereas the lone pair of electrons is at the fourth corner of a tetrahedron. This results in a pyramidal molecule.



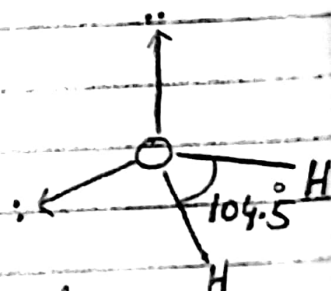
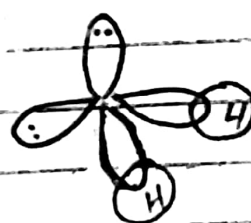
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www.megalecture.com

Formation of H_2O

Electronic configuration of $O = 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^0$
 In this case one $2s$ and three p -orbitals of oxygen hybridize to form four sp^3 hybridized orbitals which will have a tetrahedral arrangement. The two hybrid orbitals are completely filled by the two available lone pairs of electrons. The remaining two half-filled hybrid orbitals undergo sp^3-s overlapping with hydrogen atoms to form two sigma bonds. The two hydrogen atoms occupy the two corners of a tetrahedron and the remaining two corners are occupied by the two lone pairs of electrons. The bond angle in water is 104.5° .



V-shaped structure

sp^2 hybridization

Overlapping of $2s$ and two $2p$ atomic orbitals to form 3 new orbitals of same shape same energy is called sp^2 hybridization. Each newly formed orbital is called sp^2 hybridized orbital.

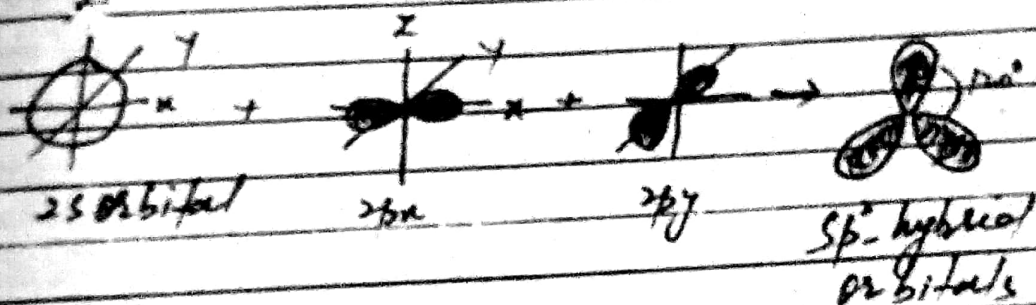
Each sp^2 hybrid orbital lie at an angle of 120° with trigonal planar geometry.

Formation of BF_3 molecule

Electronic configuration of B is $1s^2, 2s^2, 2p^1$
 one electron is promoted from
 $2s$ to $2p$.

So excited state electronic configuration
 of B is $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$

one s and $2p$ atomic orbitals intermixed
 to form three sp^2 hybrid orbitals.



BF_3 is formed by the overlapping of
 three half filled sp^2 hybrid orbitals
 of Boron with p -orbitals of fluorine
 atoms.



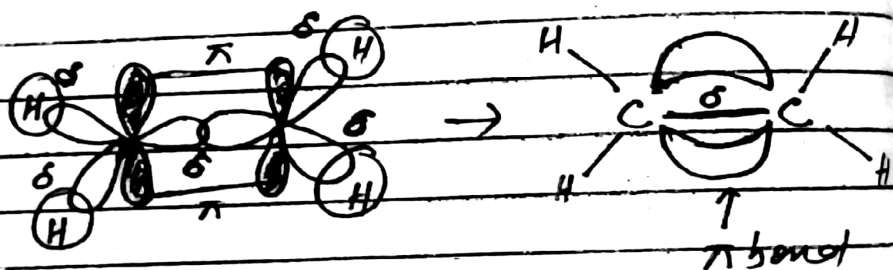
trigonal planar

Formation of ethane (C_2H_6)

$C = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$ Ground state

$H = 1s^1$

one s and two p orbitals intermix to form three sp^2 hybrid orbitals. Hybrid orbitals are trigonal planar and are oriented at an angle of 120° . Each atom is left with one half-filled p-orbital perpendicular to the planar sp^2 hybrid orbitals. Each carbon atom undergoes sp^2 -s overlap with two hydrogen atoms and sp^2 - sp^2 overlapping between themselves to form sigma bonds. The partially filled p-orbitals undergo sideways overlap to form a pi bond.



Sp-hybridization is the overlap of one 2s and one 2p atomic orbitals to form two new orbitals of same shape and energy each called sp hybrid orbitals.

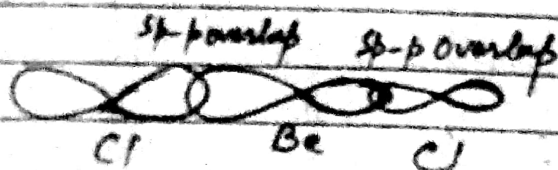
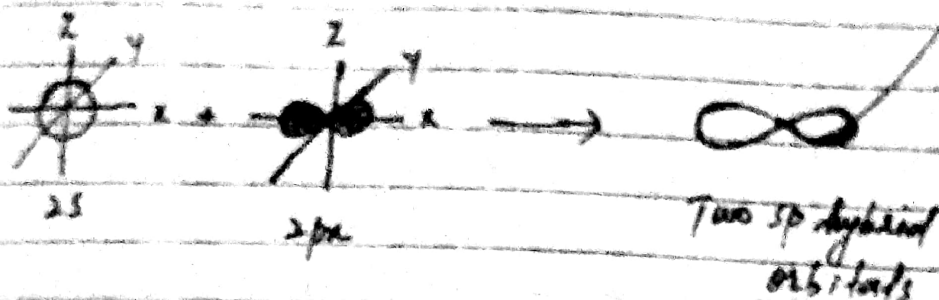
Formation of $BeCl_2$ molecule

Electronic configuration of $Be = 1s^2, 2s^2$

Excited state configuration = $1s^2, 2s^1, 2p^1$

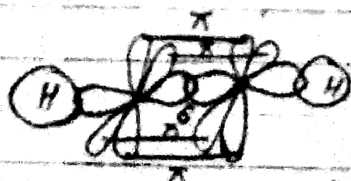
In Be one s and one p atomic orbitals intermix to form two hybrid orbitals. These hybrid orbitals are oriented at the angle of 180° . Each

hybrid orbital of Be overlap with half filled p orbital of Cl to form two sigma bonds.



Formation of ethyne (C_2H_2) molecule

In ethyne one s and one p orbital of carbon atom intermix to form two hybrid orbitals. Each carbon atom undergoes sp -s overlap with one hydrogen atom and sp - sp overlap with other carbon atom. Each carbon atom is left with two unhybridized p-orbitals perpendicular to the planar sp hybrid orbitals. These two unhybridized p-orbitals undergo parallel overlapping or side ways overlapping to form two π -bonds as shown below.



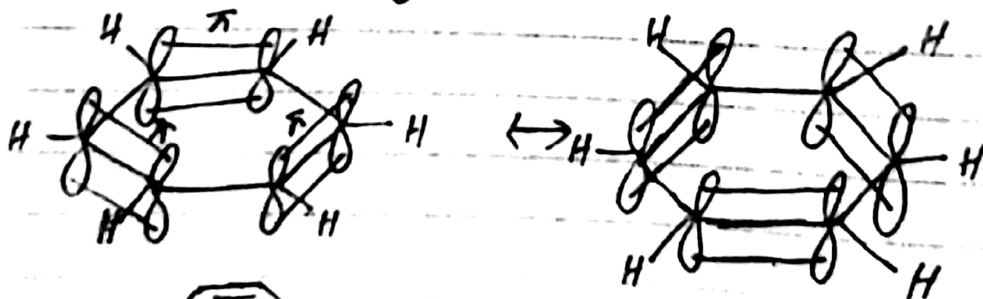
Ethyne (C_2H_2) molecule

Shape of Benzene (C₆H₆) an example of hybridized

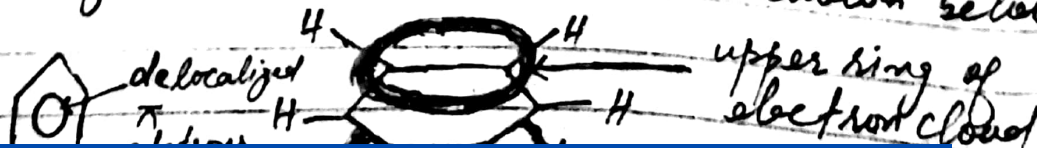
Benzene molecule consists of a hexagonal ring of six carbon atoms with one hydrogen atom bonded to each carbon. Each carbon uses three of its sp^2 hybridised orbitals in forming three sigma bonds, two of which are formed with two carbon atoms and one sigma bond is formed with hydrogen atoms.

The remaining unhybridized p-orbitals of each carbon are parallel to each other, which overlap to form pi-bonds which are perpendicular to the plane of the ring.

These π bonds are not localised between the pairs of carbon atoms as in alkenes instead they are spread over all six carbon atoms in the hexagonal ring. The six electrons in the π bonds are called delocalised electrons.



These π electrons quickly change their position therefore actual structure is shown below



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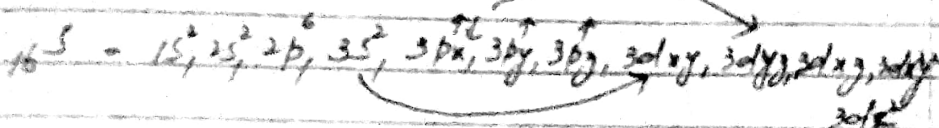
www.megalecture.com

Expansion of octet or shell

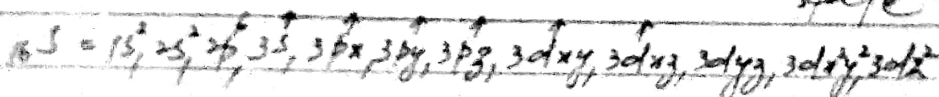
SF_6 exists while OF_6 does not exist, infers that sulphur and oxygen belong to the same group.

This is due to the presence of valence electrons of sulphur in 3rd shell which can expand but valence electron of oxygen is in 2nd period which can't further expand.

Let's see the electronic configuration of both oxygen and sulphur



Ground state



Excited state

Sulphur contains six unpaired electrons which need to be paired up during bonding, so sulphur attains 12 electrons in its valence shell.

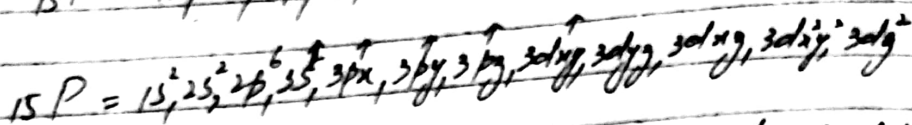
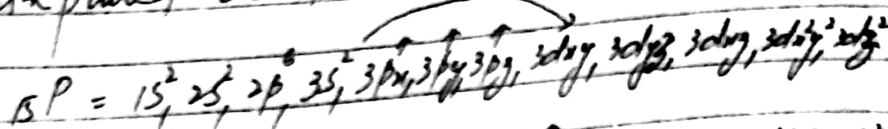
This all due to empty d-orbitals which is absent in oxygen.

Similarly phosphorus exists as PCl_3 and PCl_5 but nitrogen only exists as NCl_3 .

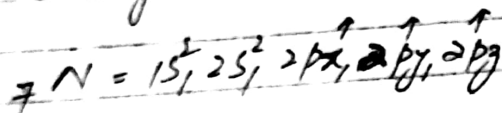
This is again due to the promotion of 3s electron to empty 3d orbital.

48

as a result fluorine has five unpaired electrons in its valence shell



Nitrogen does not have any empty d orbitals



SF_6 and PCl_5 are less stable as compared to SF_2 and PCl_3 respectively.

in

Overlapping of orbitals

A covalent bond is formed due to the overlapping of orbitals.
 orbitals overlap in two different ways.

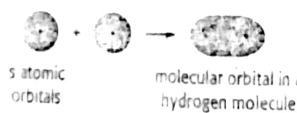
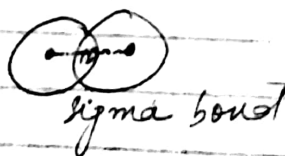
Linear overlapping of orbitals (sigma bond)

Bond formed by the linear overlapping of orbitals is called sigma bond.

→ sigma bond is formed when two orbitals of two atoms overlap to form a molecule

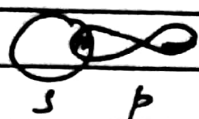
→ In sigma bond, electronic cloud is on the line joining the two nuclei.

e.g.



overlapping of s and p orbitals

Formation of HF



σ -bond (sigma bond)

OR



OR

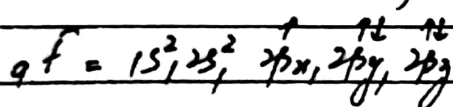


s atomic orbital, e.g. from hydrogen



overlapping of two p-orbitals

Formation of F₂



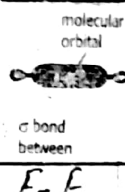
σ -bond



modified p orbital e.g. from F

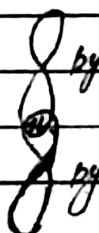
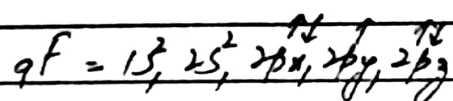


modified p orbital e.g. from F

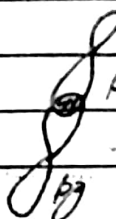


σ bond between F-F

2nd choice

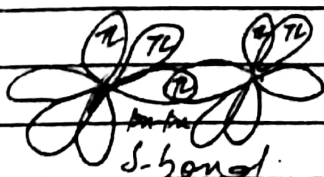


σ -bond



σ -bond

complete structure of F₂:



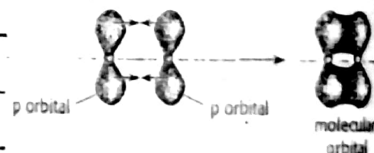
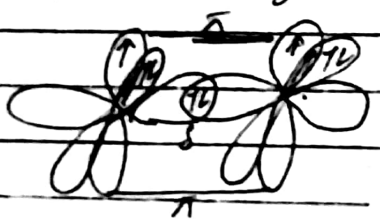
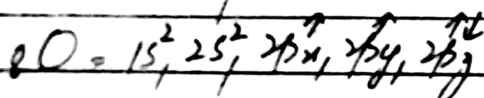
Parallel overlapping of orbitals (Pi Bond)

$\pi(\pi)$ bond is type of covalent bond which is formed by the parallel overlapping of two p orbitals either p_x-p_x or p_y-p_y .

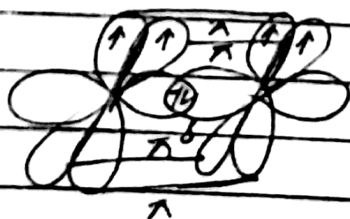
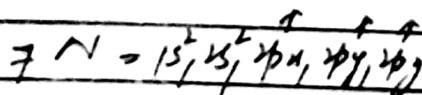
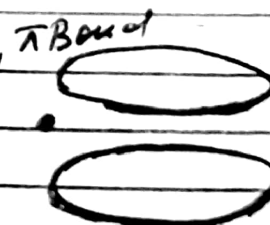
⇒ In π bond electronic cloud is perpendicular to the line joining the two nuclei, it is above and below the line joining the two nuclei.

⇒ π bond is always formed between those atoms which already have sigma bond i.e; π bond is responsible for the formation of double and triple covalent bond.

For example O_2

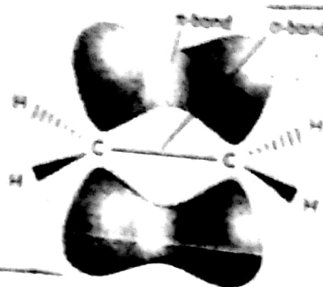
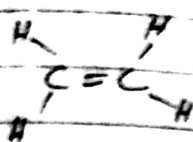
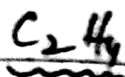


O_2 contains one sigma and one π bond.



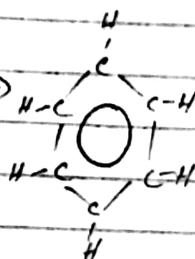
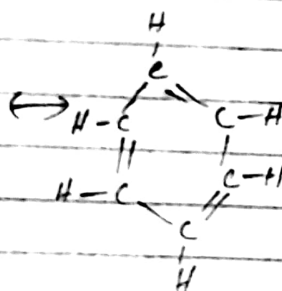
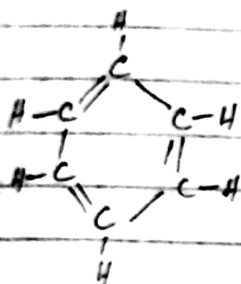
This is an acceptable way of writing the molecular orbital forming the π bond.

N_2 contains one sigma

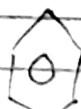


Shape of Benzene molecule (C_6H_6)

Benzene has ring structure which is hexagonal with alternate double covalent bond which keeps changing its position and appears as a circle between the ring.

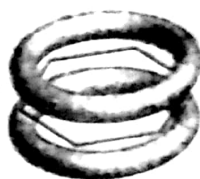
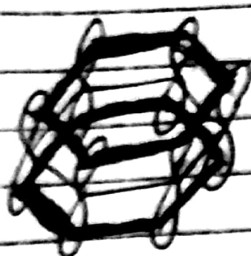


or



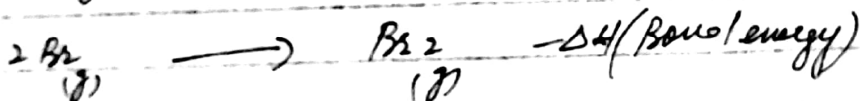
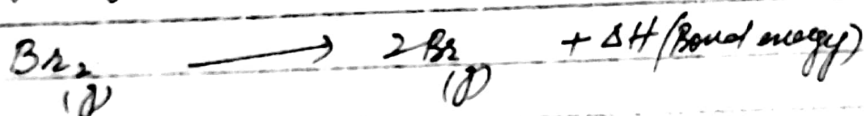
Benzene ring has 12 sigma bonds, 6 between carbon atoms and 6 between carbon and hydrogen atoms. Beside 12 sigma bonds each carbon atom also forms a pi-bond by overlapping its 2p orbital over and below the ring with its neighbouring carbon atoms. The electrons involved in π -bonding are said to be delocalised since they no longer belong to individual

Carbon atoms.



Bonding in Benzene

Bond energy:- It is defined as the enthalpy change for the breaking of one mole of bonds in a gaseous molecule to form gaseous atoms.



Bond energy depends upon the strength of covalent bond and strength of a covalent bond depends upon the number of pairs of electrons shared between the two atoms, greater the number of pairs of electrons greater will be the bond energy.

e.g.:

C - C	350 kJ/mole
C = C	610 kJ/mole
C ≡ C	840 kJ/mole

Bond length:- The distance between the centre of the nuclei of two covalently bonded atoms is called bond length.

Bond length depends upon the

Strength of a covalent bond e.g.:

C - C	154 pm
C = C	134 pm
C $\equiv$ C	120 pm

Electronegativity: Ability of an atom to attract shared pair of electrons towards itself is called electronegativity.

- Electronegativity increases from left to right across the period
 - It decreases from top to bottom along the group
 - Small atoms with many protons in the nucleus have high electronegativity
- order of electronegativity of some elements
 $F > O > N > Cl$

Polar and non polar covalent bond

Non polar covalent bond

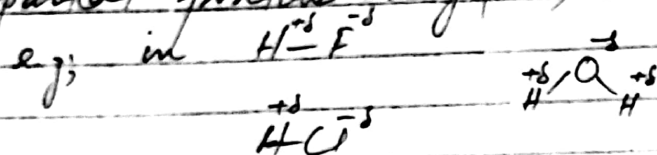
When a covalent bond is formed between the two same atoms, the pair of electrons is equally shared by the nuclei of two bonded atoms, so pair of electrons remains equally shared between the two atoms and is called non polar covalent bond
e.g. $H-H$, $O=O$, $N \equiv N$, $Cl-Cl$

Polar covalent bond

When a covalent bond is formed between the two different

atoms, different nuclei have a different attraction for the electrons, so electrons are pulled closer to one atom than the other. This unequal sharing of pairs of electrons leads to the polarity of covalent bond.

More electronegative elements attain partial negative charge (δ^-) while less electronegative element attains partial positive charge (δ^+).



Polarity of a covalent bond depends upon the difference of electronegativity between the bonded atom, greater the difference, more will be the polarity of a molecule. Polarity of a covalent bond is also called its ionic character.

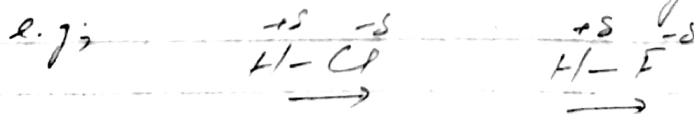
Dipole moment

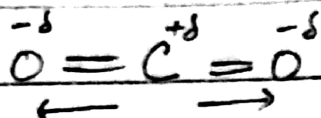
Dipole moment is a measure of the polarity of a molecule.

It is a vector quantity which has a direction and magnitude.

It is represented by a Greek letter (μ) called mu.

Its direction is from less electronegative element to more electronegative.

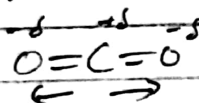




CO_2 has zero dipole moment because the two polar covalent bonds are opposite in direction and cancel each others effect, so CO_2 is a non polar molecule

Rules to decide polarity of molecules

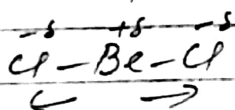
- (1) All triatomic molecules which are linear in shape and in which central atom is bonded with the same elements are non polar and have zero dipole moment
 e.g;



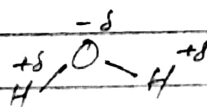
Non polar



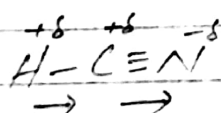
polar



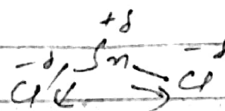
Non polar



polar

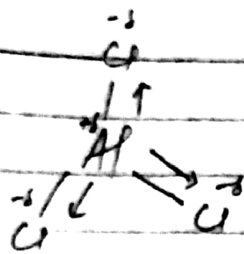


Polar

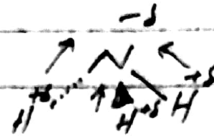


polar

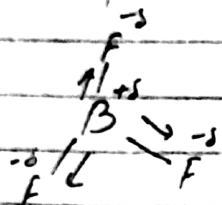
- (2) All tetra atomic molecules in which central atom is bonded with the same elements and are trigonal planar in shape are non polar while remaining are polar
 e.g; AlCl_3 , BF_3 , SO_3 are non polar



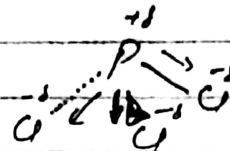
Non polar



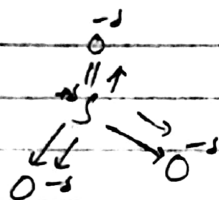
Polar



Non polar

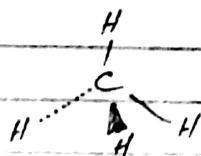


Polar



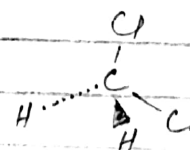
Non polar

(3) All pentatomic molecules which are tetrahedral in shape and in which central atom is bonded with same atoms are non polar and have zero dipole moment, remaining molecules are polar. e.g;

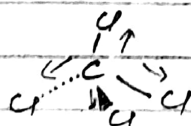


Non polar

$\mu = 0$



Polar



Non polar

Charge containing molecules are polar

e.g; IF_4 , ICl_4 , CF_4

COvalent character of Ionic compounds

Metals and non metals combine to form ionic compounds but few metals and non metals combine to form covalent compounds e.g; LiCl , MgCl_2 , BeCl_2 , AlCl_3 , MgBr_2 , MgI_2 , AlBr_3 , AlI_3 etc.

$\Rightarrow$ metals ^{ions} present at the top of their group have small size and has high density, so they can attract the electronic cloud of large size anion towards themselves when they form bond with them. This cause the distortion of anion. The ability of a cation to attract electron cloud of an anion towards itself and to distort an ion is called polarizability.



↑
Polarised electronic cloud of an anion

Why AlCl_3 is covalent but Al_2O_3 is ionic?

Al^{+3} with its high charge density can polarise large size Cl^- but cannot polarise O^{2-} due to its small size. Therefore AlCl_3 is soluble in organic solvents but Al_2O_3 is insoluble.

Types of Inter-molecular forces

There are three types of inter-molecular forces

- (i) Hydrogen Bonding
- (ii) Dipole-Dipole forces or Permanent dipole forces.
- (iii) Temporary dipole or London or Van der Waal's or instantaneous dipole induced-dipole forces

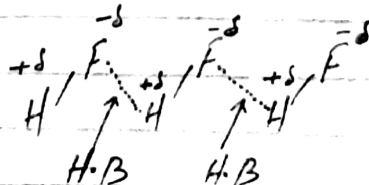
Hydrogen Bonding

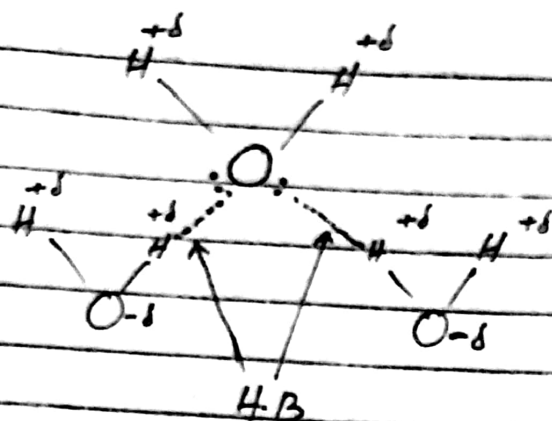
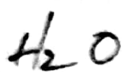
Hydrogen bonding is a weak electrostatic force of attraction between partial positively charged hydrogen ($H^{\delta+}$) and partial negatively charged $F^{\delta-}$, $O^{\delta-}$ or $N^{\delta-}$ of the same or different molecules.

Conditions required for Hydrogen Bonding

- $\Rightarrow$ One molecule having a hydrogen atom covalently bonded to F , O or N
- $\Rightarrow$ a second molecule having a F , O or N atom with an available lone pair of electrons.

e.g. In HF





Number of hydrogen Bonds formed per molecule

The number of hydrogen bonds formed per molecule depends upon

- ⇒ the number of hydrogen atoms attached to F, O or N in the molecule
- ⇒ the number of lone pairs present on the F, O or N.

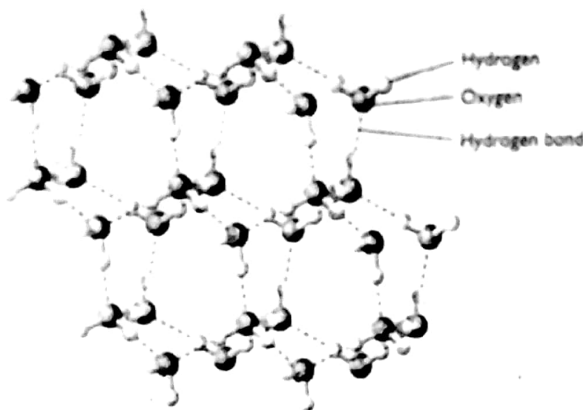
High Boiling point of water

Water has higher boiling point as compared to HF and NH_3 and is a liquid while HF and NH_3 are gases. This is because water has two hydrogen atoms and two lone pairs per molecule, so water is extensively hydrogen bonded with other water molecules because it has an average of two hydrogen bonds per molecule.

Ammonia is less extensively hydrogen bonded than water, it can form only one

62

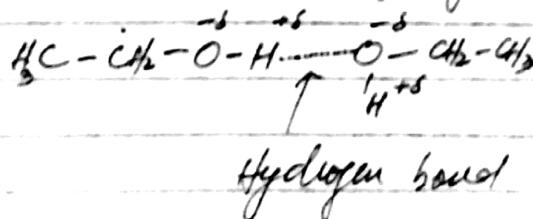
hydrogen atoms and two hydrogen bonds. This arrangement allows water molecules to be slightly further apart than in the liquid.



Structure of ice

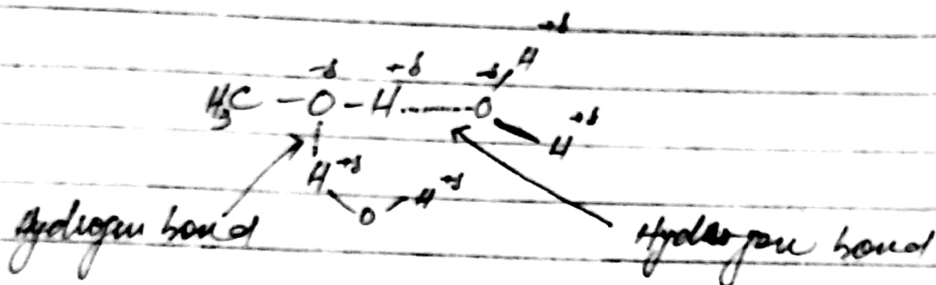
High boiling points of alcohols as compared to alkanes

Alkanes are non polar and have weak van der Waals forces but alcohols beside weak van der Waals forces also have hydrogen bonding which is stronger than van der Waals forces, hence more energy will be required to break hydrogen bonding



Solubility of alcohols in water

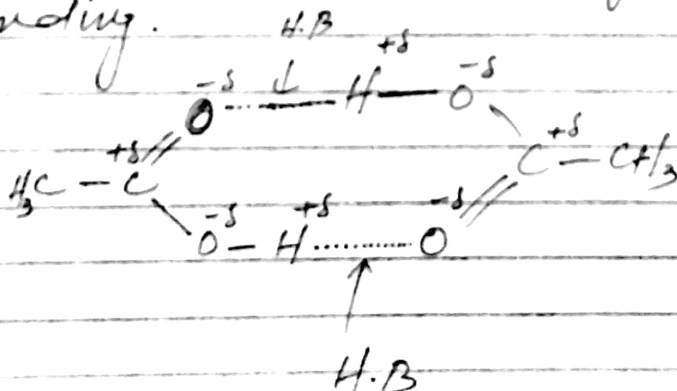
alcohols are miscible (soluble) in water due to formation of hydrogen bond between alcohol and water molecules.



Solubility of alcohols decreases down the series due to increase in the size of non polar alkyl group which is insoluble in water.

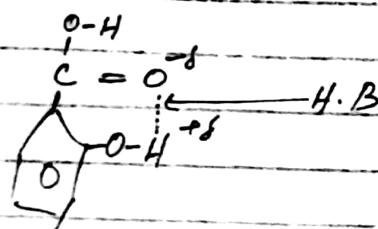
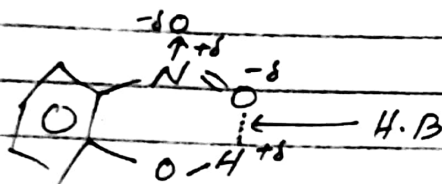
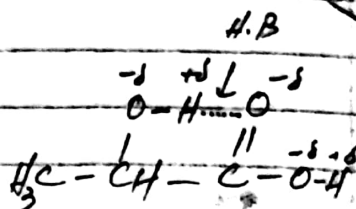
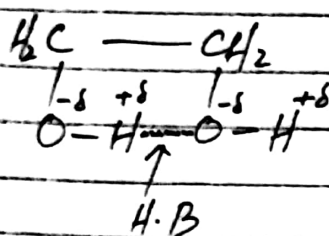
Dimerization of Carboxylic acids

Dimer means two units. M_r of ethanoic acid is 60 when it is present in water but when its vapours are collected over any non polar organic solvent then its M_r is 120. This is due to the dimerization of the molecules of ethanoic acid due to hydrogen bonding.



Intra molecular hydrogen Bonding

Hydrogen bonding between the different atoms of the same molecule is called intra molecular hydrogen bonding.



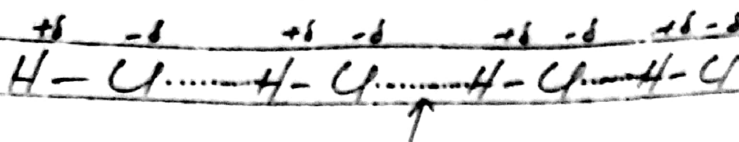
Dipole-Dipole forces

Permanent dipole-dipole forces

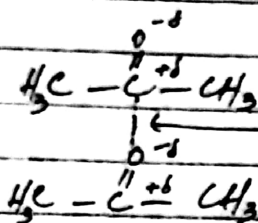
The forces of attractions between two molecules having permanent dipoles are called permanent dipole-dipole forces. The negative end of one molecule attracts the positive end of the other molecule.

These forces are weaker than Hydrogen bonding.

e.g;



dipole-dipole forces



dipole-dipole forces

Van der Waal's forces

or

Instantaneous dipole-induced dipole forces

or

London forces

or

Temporary dipole-dipole forces

These forces occur between non polar molecules e.g; in noble gases, halogens, alkanes and alkenes.

Generation of van der waal's forces

In non polar molecules electronic cloud is constantly moving around the nucleus and is symmetrical.

When two molecules collide with each other, it often happens that more of the electronic cloud is on

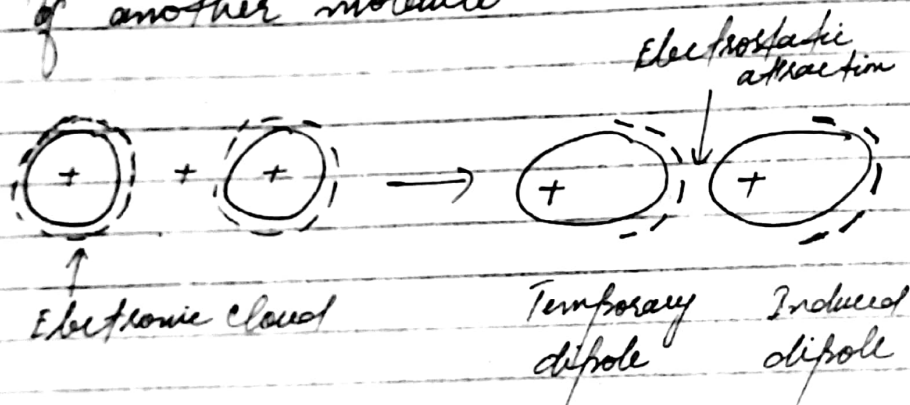
66

one side of the molecule than the other, this is due to the electron-electron repulsion.

As a result one side of the molecule has more negative charge and other side has more positive charge.

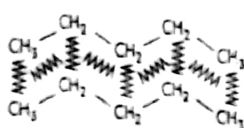
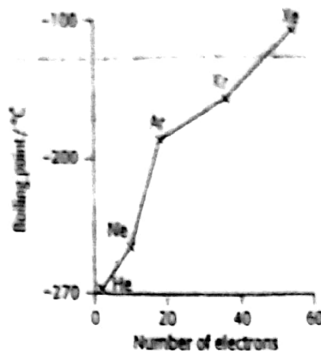
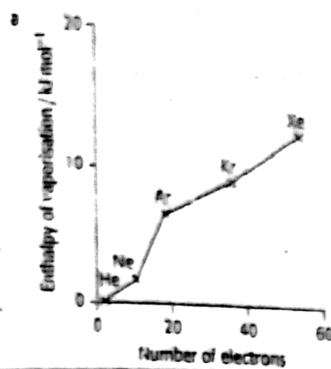
A temporary or instantaneous dipole is set up, this dipole can induce dipole on neighbouring molecules.

As a result of this there are forces of attraction between the positive end of one molecule and negative end of another molecule.

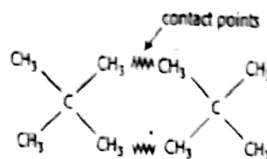


Factors affecting the strength of van der waal's forces

- van der waal's forces increase with
- ⇒ the increase in molecular size or with the increase in number of electrons in the molecule
- ⇒ the increase in the number of contact points between the molecules
- ⇒ Increase in the M_r of molecules

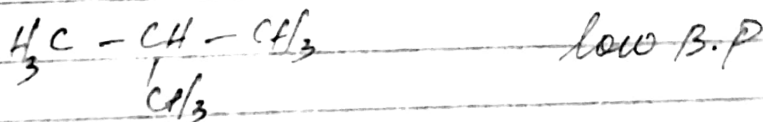
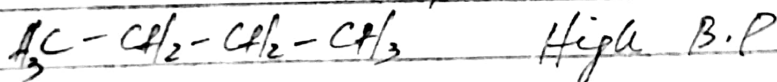


pentane,
boiling point 36 °C



2,2-dimethylpropane,
boiling point 10 °C

Straight chain molecules have large surface area as compared to branch chain molecules so have stronger ~~dipole~~ van der waal's forces and have high Boiling point e.g;



Van der waal's forces are weaker than dipole-dipole forces if two molecules have equal sizes (M_r)

e.g;



M_r

28

28

Polar

Non-polar

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But if the two molecules have different size (M_r) then the molecule with bigger size (M_r) have stronger forces of attraction e.g:

	CO_2	HCl
M_r	44	36.5
	non polar	polar
	high B.P	low B.P
	stronger forces	weaker forces

States of Matter

Kinetic theory of gases

The idea that molecules in gases are in constant movement is called kinetic theory of gases.

Following are the basic assumptions of kinetic theory of gases.

- (i) Gases are made up of small independent molecules which are in a constant random motion in all possible directions.
- (ii) Gas molecules collide with each other and with the walls of the container, the pressure exerted by the gas is due to these collisions.
- (iii) The collision of gaseous molecules are perfectly elastic i.e., the total energy of gaseous molecules remains equal before and after collisions.
- (iv) There are no forces of attractions or repulsions between gaseous molecules.
- (v) Actual volume of the gaseous molecules is negligible of the volume they occupy.
- (vi) Kinetic energy of the gaseous molecules is directly proportional to the temperature.

Common gas laws:

Boyle's law :: volume of a given mass of a gas is inversely proportional to the applied pressure under constant

70

$$V \propto \frac{1}{P}$$

$$V = K \cdot \frac{1}{P}$$

$$PV = K$$

If P_1 is the initial pressure and V_1 is the initial volume, so P_2 will be final pressure and V_2 will be the final volume.

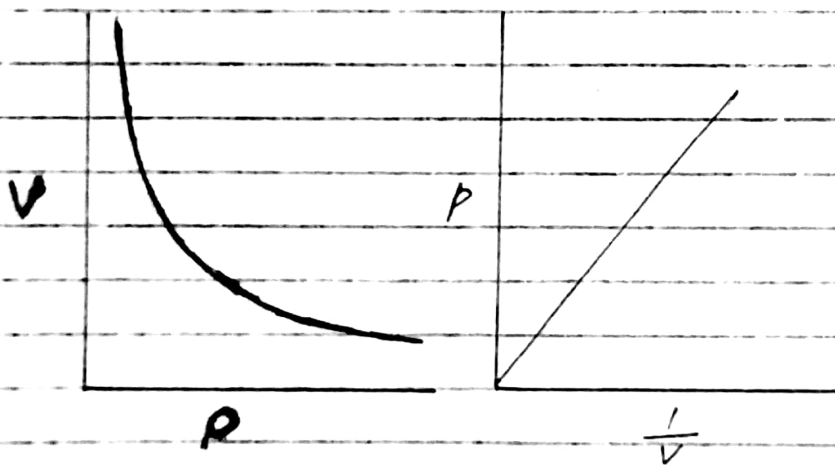
$$P_1 V_1 = K \quad \text{--- (1)}$$

$$P_2 V_2 = K \quad \text{--- (2)}$$

Putting the value of K in 2nd equation

$$P_1 V_1 = P_2 V_2$$

Graphical representation of Boyle's law



Boyle's law can also be defined as "the product of pressure and volume remains always constant".

Charles's law:- volume of a given mass of a gas is directly proportional to the temperature at constant pressure.

$$V \propto T$$

$$V = KT$$

$$\frac{V}{T} = K$$

If V_1 is initial volume and T_1 is initial temp then V_2 and T_2 will be the final volume and temperature respectively then

$$\frac{V_1}{T_1} = K \quad \text{--- (1)}$$

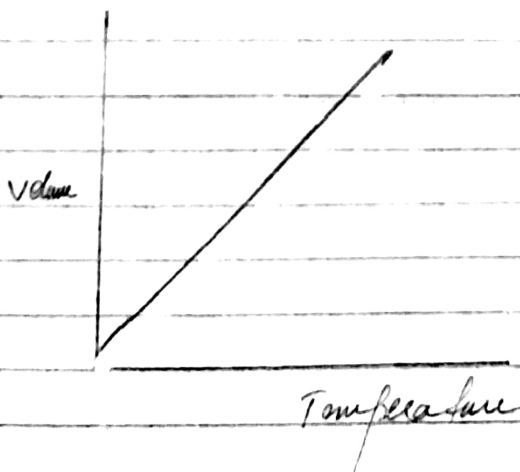
$$\frac{V_2}{T_2} = K \quad \text{--- (2)}$$

Putting the value of K in second equation

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

Ratio of the volume to temperature remains always constant

Graphical representation of
Charles's law



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Numerical questions based on Boyle's law

Flask A contains 3 dm^3 of helium at 2 kPa pressure and flask B contains 2 dm^3 of neon at 1 kPa pressure.

If the flasks are connected at constant temperature, what is the final pressure?

Solution

$p_1 = 2 \text{ kPa}$ (Higher pressure will be initial pressure)

$V_1 = 2 \text{ dm}^3$ (Higher volume)

$p_2 = ?$

$V_2 = 3 \text{ dm}^3$ (Sum of the volumes of two containers)

$$p_1 V_1 = p_2 V_2$$

$$p_2 = \frac{p_1 V_1}{V_2}$$

$$p_2 = \frac{2 \times 2}{3} = 1.33 \text{ kPa}$$

Flask X contains 5 dm^3 of helium at 12 kPa pressure and flask Y contains 10 dm^3 of neon at 6 kPa pressure.

If the flasks are connected at constant temperature, what is the final pressure?

Solution

$p_1 = 12 \text{ kPa}$

$V_1 = 10 \text{ dm}^3$

$p_2 = ?$

$V_2 = 15 \text{ dm}^3$

$$p_1 V_1 = p_2 V_2$$

$$p_2 = \frac{p_1 V_1}{V_2}$$

$$12 \times 10$$

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Avogadro's law: According to the

law, volume of a given mass of a gas is directly proportional to the number of moles or molecules under constant temperature and pressure.

$$V \propto n$$

$$V = kn$$

$$\frac{V}{n} = k$$

Dalton's law of partial pressure

According to the law, the total pressure exerted by the mixture of gases is equal to the sum of the partial pressures of all the gases present in a mixture at same temperature.

$$P_{\text{total}} = P_A + P_B + P_C + \dots \dots \dots P_n$$

Let's derive formula for calculating the partial pressure of a gas.

Partial pressure of a gas (A) depends upon its number of moles

$$P_A V = n_A RT$$

$$P_A V = n_A RT \quad \text{--- (1)}$$

$$\text{so } P_T V = n_T RT \quad \text{--- (2)}$$

Divide eq (1) by eq (2)

$$\frac{P_A V}{P_T V} = \frac{n_A RT}{n_T RT}$$

$$P_A = n_A$$

$$P_A = \frac{n_A}{n_T} \times P_T$$

General gas equation

By combining the gas laws we can derive general gas equation

$$V \propto \frac{1}{p}$$

Boyle's law

$$V \propto T$$

Charles's law

$$V \propto n$$

Avogadro's law

By combining the three laws

$$V \propto \frac{nT}{p}$$

$$V = \frac{RnT}{p}$$

Standard temperature and pressure

$$T = 0^\circ\text{C} \text{ or } 273\text{ K}$$

$$p = 101325\text{ N m}^{-2} \text{ or } 101325\text{ Pa}$$

$$V = 22.4\text{ dm}^3 \text{ or } 0.0224\text{ m}^3$$

$$n = 1 \text{ mole}$$

where R is a gas constant
Rearranging the equation

$$pV = nRT$$

p is the pressure in pascals or N m^{-2} ($1\text{ Pa} = 1\text{ N m}^{-2}$)
 V is the volume in cubic metres m^3

$$1\text{ m}^3 = 1000\text{ dm}^3$$

n is the number of moles of a gas

R is the gas constant and its value is $8.31\text{ J K}^{-1}\text{ mol}^{-1}$

T is the temp in kelvin

Determination of M_r using general gas equation

$$pV = nRT$$

$$n = \frac{m}{M_r}$$

$$pV = \frac{m}{M_r} RT$$

(8)

Determination of density using
general gas equation

$$PV = nRT$$

$$PV = \frac{m}{M_A} RT$$

$$PM_A = \frac{m}{V} RT \quad \text{where } \frac{m}{V} = D$$

$$PM_A = DRT$$

$$D = \frac{PM_A}{RT}$$

Combined gas law using general gas equation

For one mole of a gas, the general gas equation is

$$PV = RT \quad \text{or} \quad \frac{PV}{T} = R$$

$$\text{Hence } \frac{P_1 V_1}{T_1} = R \quad \text{--- (1)}$$

$$\frac{P_2 V_2}{T_2} = R \quad \text{--- (2)}$$

Putting the value of R in eq (1)

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Combined gas law or equation

Solved examples from the past papers
Calculate the volume occupied by 0.500 mol of carbon dioxide at a pressure of 150 kPa and a temperature of 19°C.

Solution

$$p = 150 \text{ kPa} = 150000 \text{ Pa}$$

$$T = 19^\circ\text{C} + 273 = 292 \text{ K}$$

$$V = \frac{nRT}{p}$$

$$V = \frac{0.500 \times 8.31 \times 292}{150000}$$

(18)

Q: A sample of nitrogen gas is enclosed in a vessel of volume 380 cm^3 at 120°C and pressure of 101325 N m^{-2} . This gas is transferred to a 10 dm^3 flask and cooled to 27°C . Calculate the pressure in N m^{-2} exerted by the gas at 27°C .

Solution

As all the three parameters of this gas have been changed, so we can solve this by using combined gas equation.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_1 = 380 \text{ cm}^3 = 0.00038 \text{ m}^3$$

$$T_1 = 120^\circ\text{C} + 273 = 393 \text{ K}$$

$$P_1 = 101325 \text{ N m}^{-2}$$

$$T_2 = 27^\circ\text{C} + 273 = 300 \text{ K}$$

$$V_2 = 10 \text{ dm}^3 = 0.01 \text{ m}^3$$

$$P_2 = ?$$

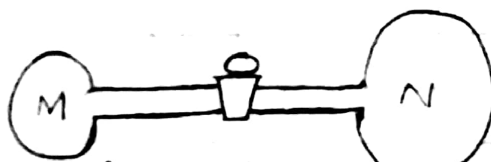
$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$P_2 = \frac{101325 \times 0.00038 \times 300}{393 \times 0.01}$$

$$\frac{11551.05}{3.93}$$

$$P_2 = 2939 \text{ N m}^{-2}$$

Two glass vessels M and N are connected by a closed valve



Q: M contains helium at a pressure of $1 \times 10^5 \text{ Pa}$. N has been evacuated, and has three times the volume of M. In an experiment the valve is opened and the temperature of the whole apparatus is raised to 100°C . What is the final pressure?

Solution

$$V_1 = 1$$

$$V_2 = 1 + 3 = 4$$

$$P_1 = 1 \times 10^5 \text{ Pa}$$

$$T_1 = 20 + 273 = 293 \text{ K}$$

$$T_2 = 100 + 273 = 373 \text{ K}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$P_2 = \frac{1 \times 10^5 \times 1 \times 373}{293 \times 4}$$

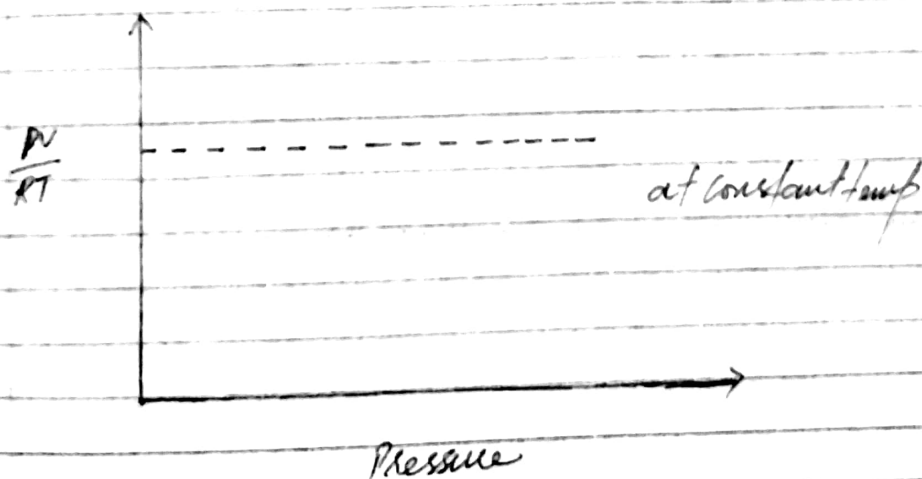
Ideal and non ideal gases

Ideal gases :- Gases which obey all postulates of kinetic particle theory under all conditions of temperature and pressure are called ideal gases.

In order to understand the behaviour of ideal gas we will have to plot a graph by taking pressure at x-axis and $\frac{PV}{RT}$ or $\frac{PV}{nRT}$ on y-axis.

The value of $\frac{PV}{RT}$ or $\frac{PV}{nRT} = 1$

If at constant temperature, we increase the pressure of a gas, the volume of gas will decrease in such a way that the product of $\frac{PV}{RT}$ will remain one and a straight line will be obtained.



Non ideal or real gases :- Those gases which do not obey all postulates of kinetic particle theory under all

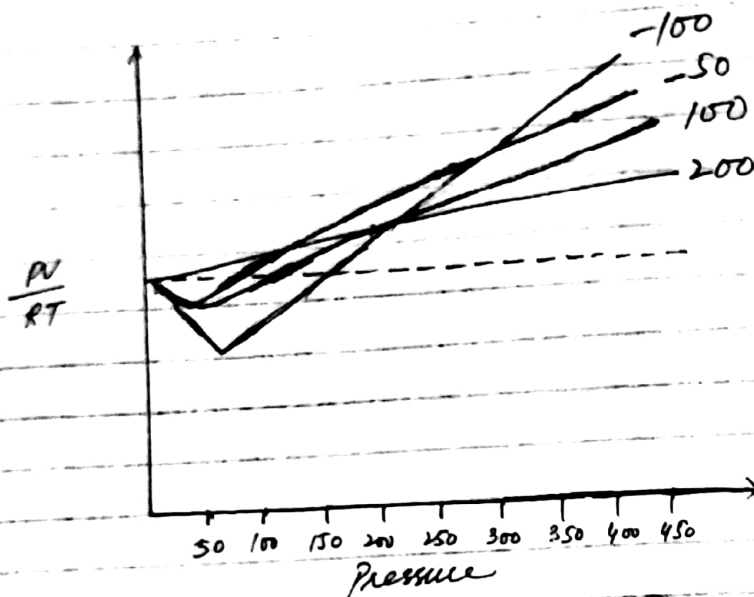
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conditions of temperature and pressure are called nonideal or real gases. All real gases are not ideal gases.



Graph shows that deviation of real gases from ideal behaviour increases with the increase in pressure and/or decrease in temperature.

Postulates of Kinetic particle theory which are not obeyed by real gases

- (i) There are no forces of attraction or repulsion among gaseous molecules.
- (ii) Volume of the gaseous molecules is negligible of the volume that they occupy.

Conditions at which real gases deviate from ideal behaviour

Low temperature : At low temperature

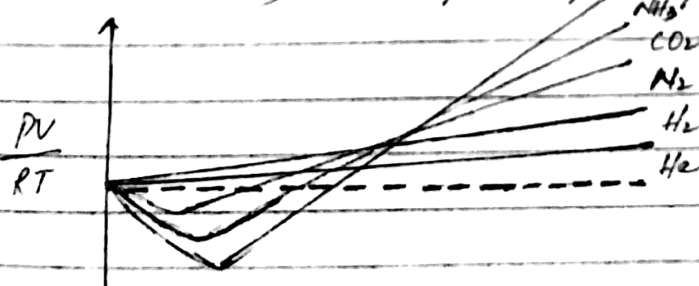
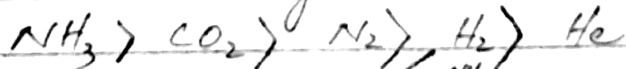
molecules of gas come closer together than there are enough attractive forces which cannot be ignored. Secondly, at low temp occupied volume of the gas is decreased and actual volume of the gas molecules does not remain negligible of the volume occupied by the gas.

High pressure :- At high pressure gas molecules come closer together and start attracting each other as well as occupied volume of the gas is also decreased, so the volume of gas molecules does not remain negligible of the volume occupied by the gas.

Nature of gas molecules :- Polar

molecules and large size non polar molecules have greater intermolecular forces and show more deviation from ideal behaviour.

The order of deviation of some gases is given below



In the beginning there is a greater decrease in volume with the increase in pressure.

8-

Conditions at which real gases behave ideally

High temperature:- At high temperature

kinetic energy of the particles is increased, particles get far from each other, so there are no attractive forces as well as occupied volume is also increased.

Low pressure:- At low pressure volume occupied by the gas is increased, therefore actual volume of the gas molecules becomes negligible, molecules get far from each other so no attractive forces between molecules.

Liquid

Common properties of liquids
vapour pressure

Solids

Properties of solid

Types of solids or crystals e.g;

Ionic crystal of NaCl, MgO
molecular crystals include Iodine,
sulphur, phosphorus

Giant molecular covalent solids
e.g; Diamond, graphite silica

Numerical problems based on Dalton's law of partial pressure

There is a mixture of hydrogen, helium and methane occupying a vessel at a pressure of 100 kPa. The masses of H_2 , He and methane are 0.8, 0.12 and 1.28 respectively. Calculate the partial pressure of each gas.

Solution

$$\text{number of moles of } H_2 = \frac{0.8}{2} = 0.4 \text{ mol}$$

$$\text{number of moles of He} = \frac{0.12}{4} = 0.03 \text{ mol}$$

$$\text{number of moles of } CH_4 = \frac{1.28}{16} = 0.08 \text{ mol}$$

$$\text{Total number of moles} = 0.4 + 0.03 + 0.08 = 0.51 \text{ mole}$$

According to Dalton's law

$$\frac{p_g}{p_t} = \frac{n_g}{n_t}$$

$$p_{H_2} = \frac{0.4}{0.51} \times 100 = 78.43 \text{ KPa}$$

$$p_{He} = \frac{0.03}{0.51} \times 100 = 5.88 \text{ KPa}$$

$$p_{CH_4} = \frac{0.08}{0.51} \times 100 = 15.68 \text{ KPa}$$

The sum of the partial pressures is almost equal to 100 KPa.

The solid state

There are two major types of solids.

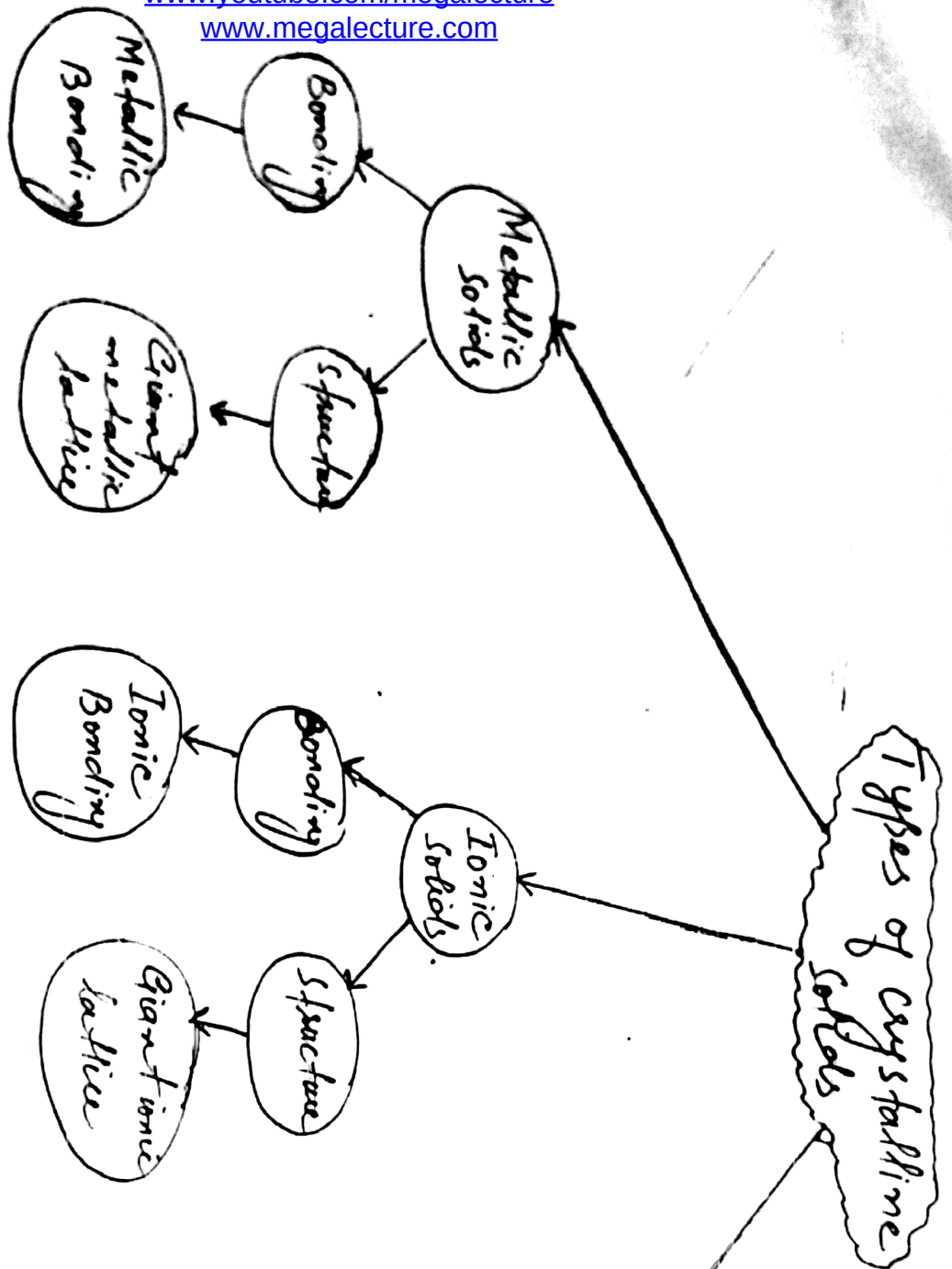
Non crystalline or Amorphous solids

In non crystalline solids, the particles are not arranged in a regular, repeating order. They are fixed in random positions, for example glass.

Crystalline solids

In crystalline solids, the particles are arranged in a regular three dimensional pattern, which is called lattice.
Common examples of crystalline solids

- (i) All solid metals
- (ii) Most ionic compounds
- (iii) Most covalent solids



For example
all solid metals

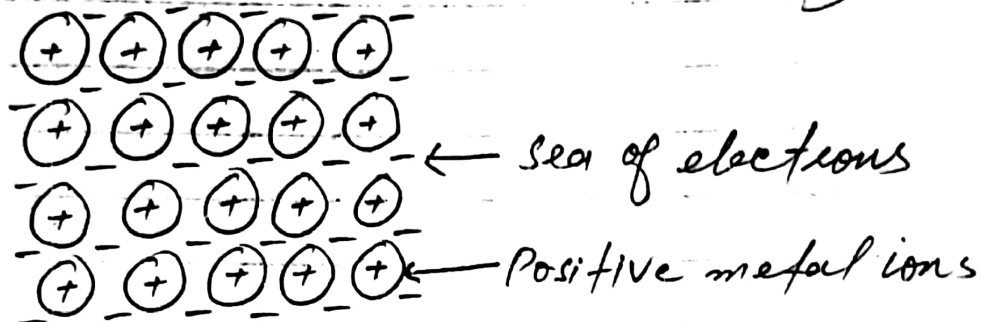
For example
Most ionic compounds
e.g., NaCl, MgO which
have giant cubic
crystal lattice.

Examples
Iodine (I_2)
Sulphur (S_8)
Phosphorus (P_4)
Bucky Balls (C_{60})
Carbon nanotubes

Examples
Diamond
Graphite
Silica
Crystalline

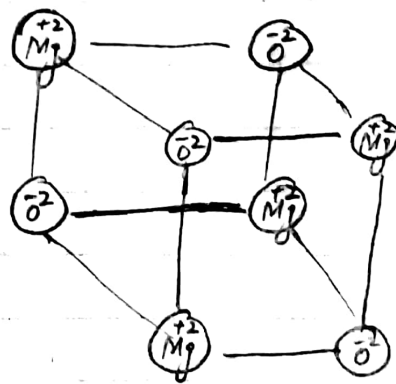
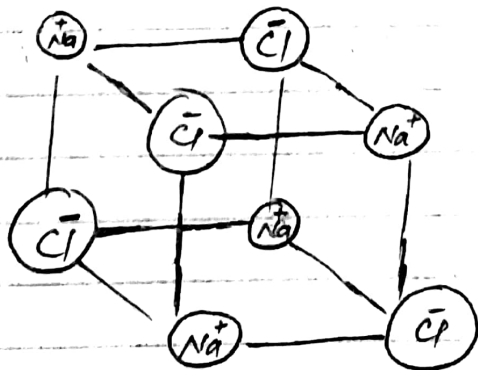
Metallic lattices

Metallic solids exist as metallic lattice which consists of positive ions surrounded by a sea of electrons.



Ionic lattices

Most ionic solids exist as ionic lattice which consists of three dimensional arrangement of alternating positive and negative ions to give giant ionic structure. For example NaCl and MgO which have giant cubic crystal lattice.



Structure of Bucky Balls & Carbon nanotubes

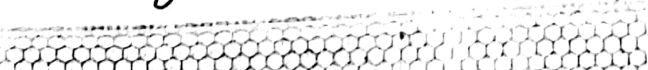
Bucky Ball is a third allotrope of carbon comprised of 60 carbon atoms in one molecule forming a sphere which contains pentagons and hexagons. Bucky Balls are also called Buckminsterfullerene. Bucky Balls have simple molecular lattice.



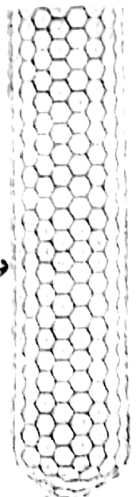
A 'buckyball'

Carbon nanotubes (simple molecular lattice)
Carbon nanotube is a single rolled up sheet of graphite which is cylindrical in structure.

If a nanotube is sealed at one end by a exactly half a buckyball molecule, it becomes a bucky test tube.

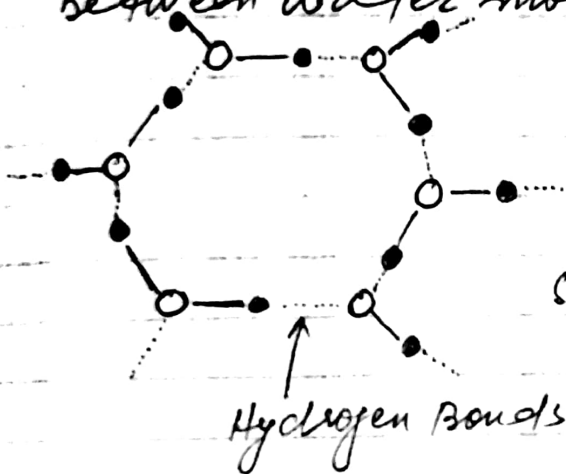


nano →
test
tube



Structure of Ice (H_2O)

Liquid water has a high surface tension due to hydrogen bonding between molecules to form a lattice across the surface of water, allowing objects to float over water. Ice is less dense than water. The hydrogen bonds between the water molecules in ice are positioned tetrahedrally around each oxygen atom, this produces empty spaces between water molecules.



Structure of Ice

Giant covalent molecular structure

Crystal lattice made up of big molecules in which large number of atoms are bonded together through a network of covalent bonds. They have high M.P & B.P due to large number of covalent bonds.

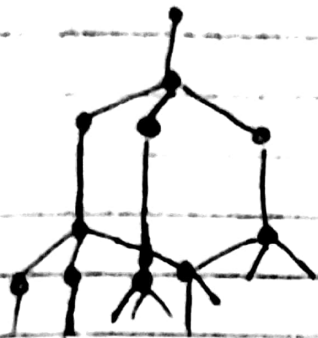
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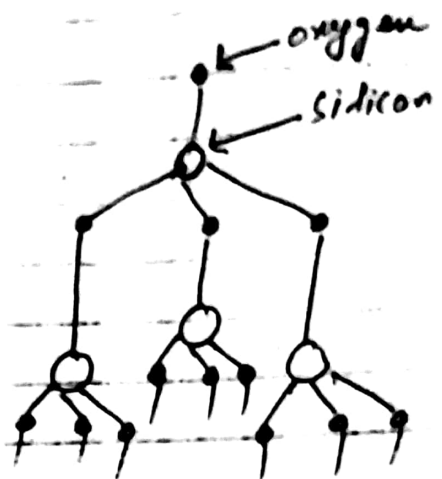
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Structure of Diamond

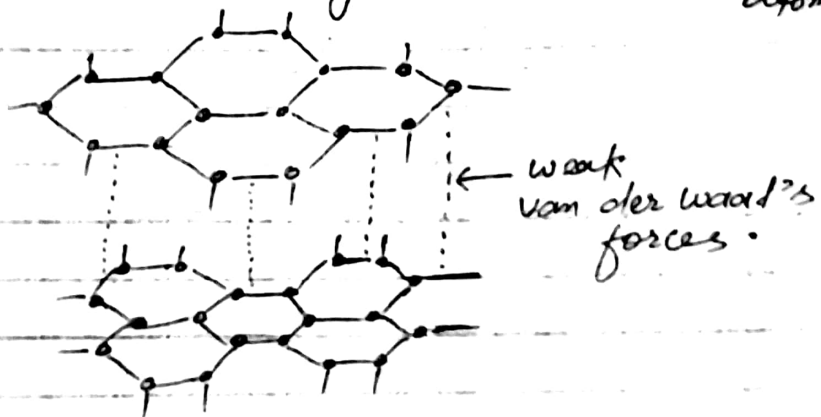


Structure of silica (SiO_2)



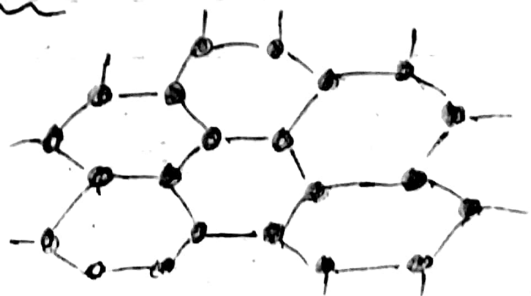
Structure of Graphite

In Graphite, Carbon atoms are present in layers. Within the layers carbon atoms are arranged in hexagon. Each carbon atom is joined with 3 carbon atoms.



Structure of Graphene

Graphene is a single sheet of carbon atoms isolated from graphite, it consists of a one-atom-thick



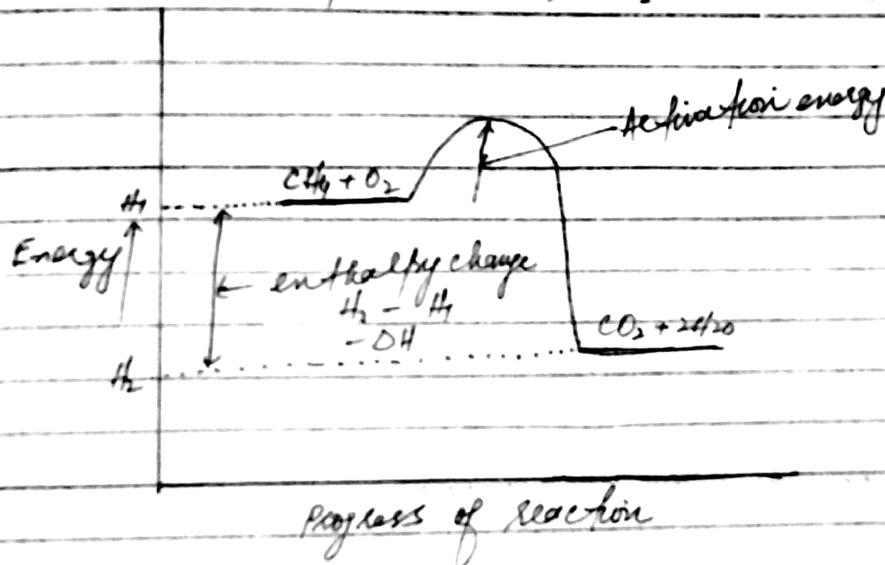
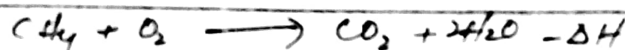
Chemical energetics

Most chemical reactions involve change in energy or enthalpy, i.e. energy is either released or absorbed during a chemical reaction.

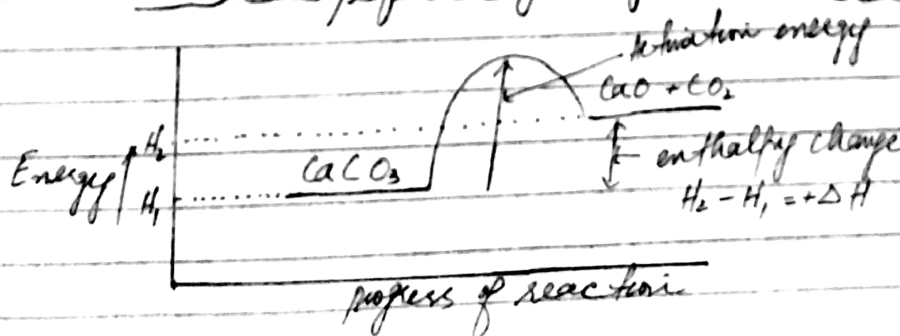
→ Those reactions in which energy is released to the surroundings are called exothermic reactions.

→ Those reactions in which energy is absorbed from the surroundings are called endothermic reactions.

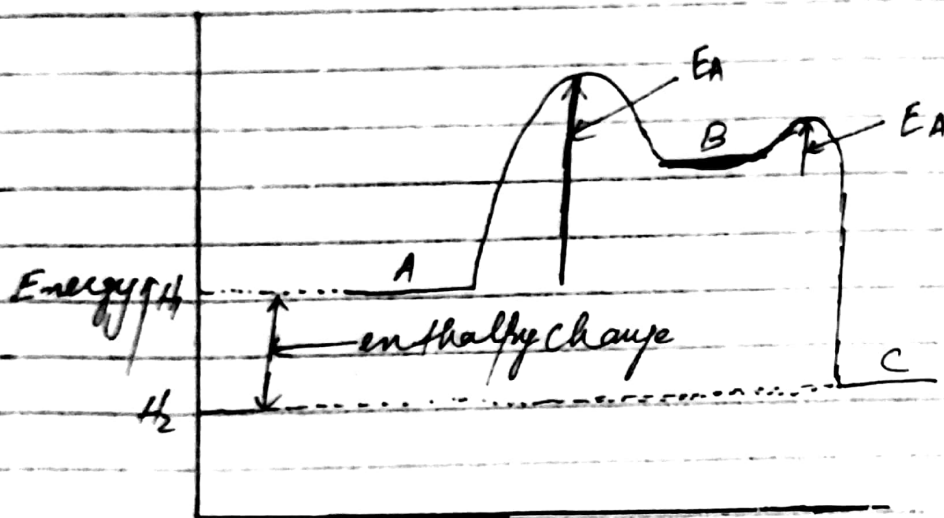
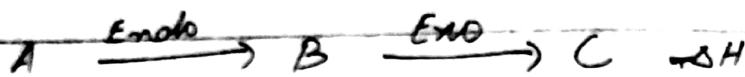
Energy profile diagram for exothermic reactions



Energy profile diagram for endothermic reactions



Energy profile diagram for those reactions take place in two steps in which first step is endothermic but overall reaction is exothermic.



Progress of reaction

Enthalpy and enthalpy change

Stored energy or internal energy of a substance is called its enthalpy which is represented by H .

Enthalpy of a substance cannot be measured, only the energy absorbed or released by a substance during a chemical reaction can be measured which is called enthalpy change represented by ΔH .

Standard conditions for measuring enthalpy change

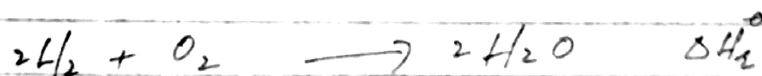
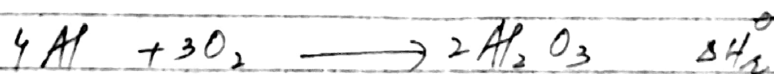
To make fair comparison of enthalpy changes, we must use the same conditions. These are called standard conditions, e.g.;

- ⇒ a pressure of 1 atm or 10^5 Pa or 100 kPa
- ⇒ a temperature of 25°C or 298 K
- ⇒ each substance involved in the reaction should have 1 mole
- ⇒ concentration of solutions should be 1 mol dm^{-3} .

Types of enthalpy changes

Standard enthalpy change of reaction ΔH_r°

Enthalpy change when any number of moles of reactants react to produce any number of moles of products under standard conditions.



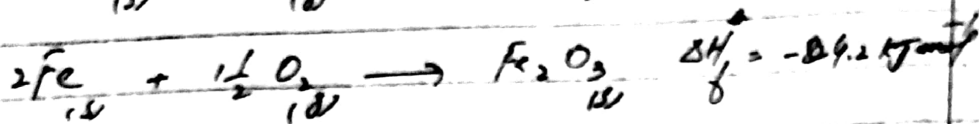
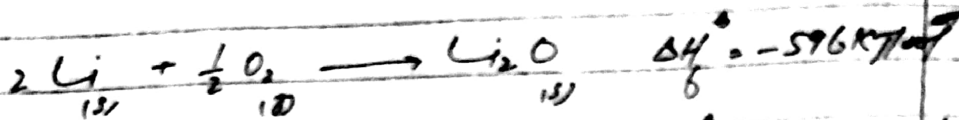
Standard enthalpy change of formation ΔH_f°

Enthalpy change when one mole of a compound is formed from its elements under standard

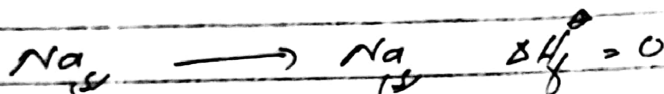
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(4)

conditions e.g.

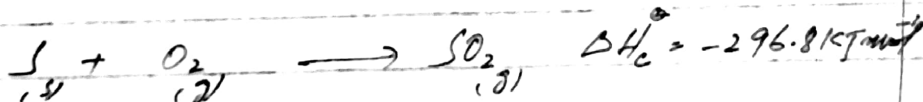
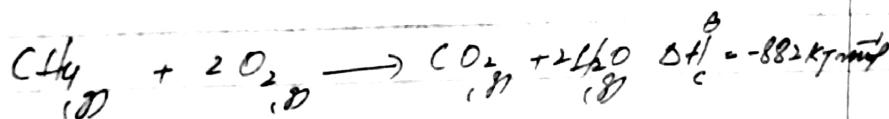


Note: Standard enthalpy change of formation of an element in its standard state is zero.



Standard enthalpy change of combustion ΔH_c°

Enthalpy change when one mole of a substance burns in excess of oxygen under standard conditions.



Standard enthalpy change of atomization ΔH_{atm}°

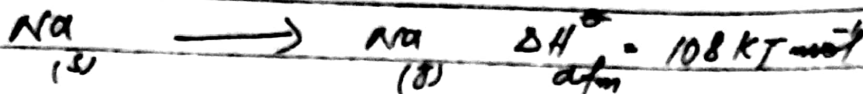
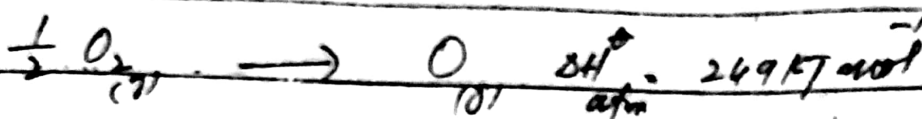
Enthalpy change when one mole of a gaseous atoms is formed from its element under standard conditions.

For example



(5)

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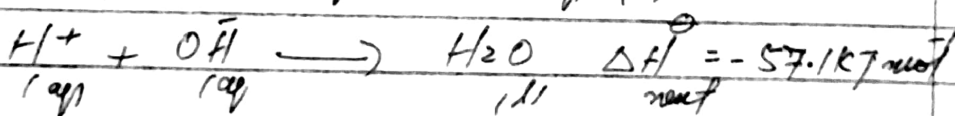
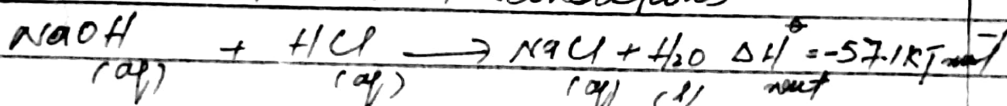


For diatomic molecules, enthalpy change of atomisation is equal to half of their bond energy.

For example bond energy of Cl-Cl bond is 242 kJ mol^{-1} while enthalpy change of atomisation of chlorine is 121 kJ mol^{-1}

Standard enthalpy change of neutralization
 $\Delta H^\circ_{\text{neut}}$

Enthalpy change when one mole of water is formed by the neutralization of an acid by an alkali under standard conditions

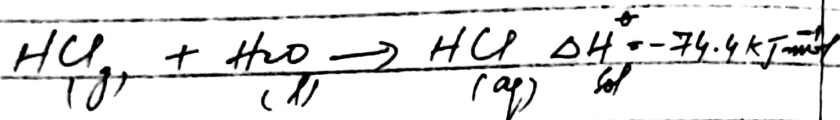


Process of neutralization becomes less exothermic as the strength of acid and alkali decreases.

For example,

Standard enthalpy change of solution ΔH_{sol}°

Enthalpy change when one mole of a substance is completely dissolved in a solvent to give an infinitely dilute solution under standard conditions.

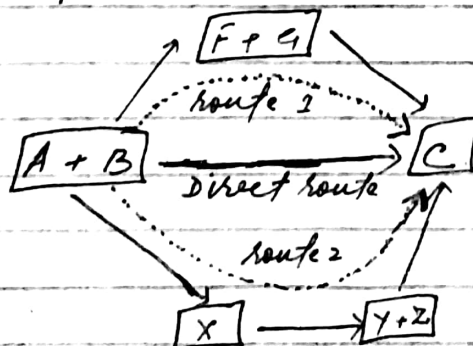


An infinitely dilute solution is one which does not produce any further enthalpy change when more solvent is added.

Hess's law

Hess's law states that 'the total enthalpy change in a chemical reaction is independent of the route by which the chemical reaction takes place as long as the initial and final conditions are the same.'

We can illustrate Hess's law by drawing enthalpy cycles.



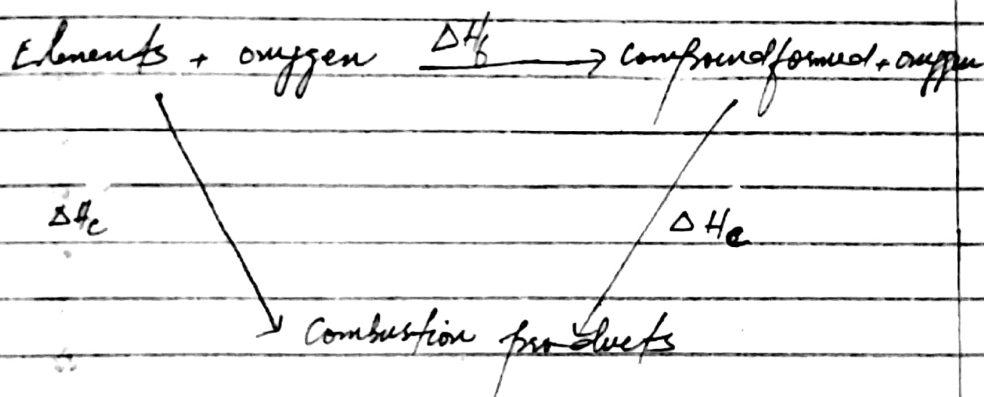
is same as for the indirect route.

Application of Hess's law

1st application

Calculation of enthalpy of formation from enthalpy change of combustion

Following cycle is used to calculate the enthalpy of formation using enthalpy of combustion.



Following steps are taken

- ⇒ Write the equation for enthalpy of formation at the top, add oxygen to both sides of the equation to balance the combustion reactions
- ⇒ Draw the cycles with the combustion products at the bottom
- ⇒ Draw in all arrows, making sure they go in the correct directions
- ⇒ Apply Hess's law

Solved examples

Calculate the enthalpy of formation of ethane using the following enthalpy changes

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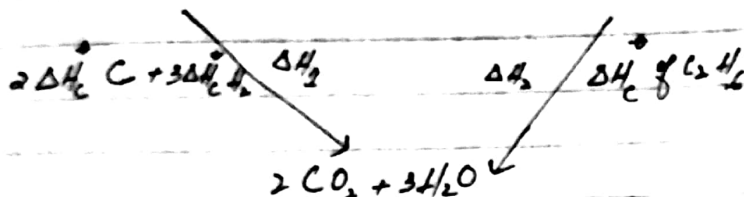
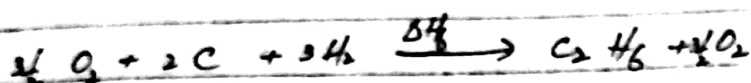
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$$\Delta H_c^\circ \text{ of Carbon} = -393.5 \text{ kJ mol}^{-1}$$

$$\Delta H_c^\circ \text{ of } H_2 = -285.8 \text{ kJ mol}^{-1}$$

$$\Delta H_c^\circ \text{ of } C_2H_6 = -1559.7 \text{ kJ mol}^{-1}$$

Solution



using Hess's law

$$\Delta H_f = \Delta H_c^\circ \text{ of reactants} - \Delta H_c^\circ \text{ of products}$$

$$\Delta H_f = \Delta H_c^\circ \text{ of reactants} - \Delta H_c^\circ \text{ of products}$$

$$\Delta H_f = \Delta H_c^\circ \text{ of reactants} - \Delta H_c^\circ \text{ of products}$$

$$\Delta H_f = 2(-393.5) + 3(-285.8) - (-1559.7)$$

$$= -84.7 \text{ kJ mol}^{-1}$$

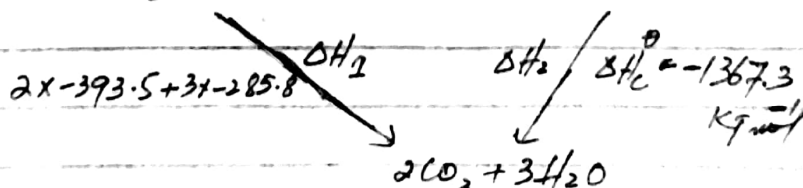
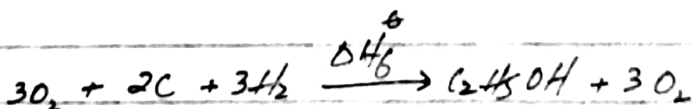
Calculate the enthalpy change of formation of ethanol using enthalpy changes of combustion.

$$\Delta H_c^\circ \text{ of Carbon} = -393.5 \text{ kJ mol}^{-1}$$

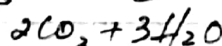
$$\Delta H_c^\circ \text{ of } H_2 = -285.8 \text{ kJ mol}^{-1}$$

$$\Delta H_c^\circ \text{ of } C_2H_5OH = -1367.3 \text{ kJ mol}^{-1}$$

Solution



$$\Delta H_c^\circ C_2H_5OH = -1367.3 \text{ kJ mol}^{-1}$$



$$\Delta H_f + \Delta H_2 = \Delta H_1$$

$$\Delta H_f = \Delta H_1 - \Delta H_2$$

$$2(-393.5) + 3(-285.8) - (-1367.3)$$

$$-787 - 857.4 + 1367$$

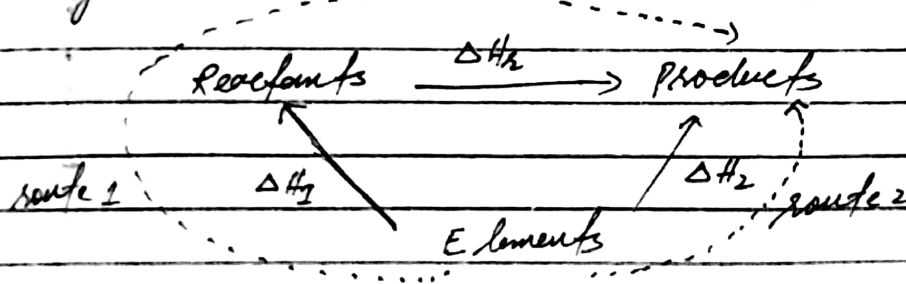
$$-1644.4 + 1367$$

$$-277.4 \text{ kJ/mole}$$

2nd application of Hess's law

Calculation of enthalpy of reaction using enthalpy of formation

We can calculate the enthalpy change of reaction by using the following enthalpy cycle.



$$\Delta H_r + \Delta H_f = \Delta H_f$$

$$\Delta H_r = \Delta H_f - \Delta H_f$$

$$\Delta H_r = \Delta H_f \text{ Products} - \Delta H_f \text{ Reactants}$$

Following steps are followed while calculating enthalpy of reaction

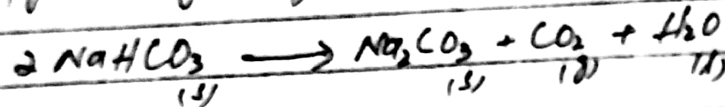
- ⇒ write the balanced equation at the top
- ⇒ Draw the cycles with elements at the bottom
- ⇒ Draw in arrows in correct directions
- ⇒ Apply Hess's law

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Solved examples

Calculate the standard enthalpy change for the reaction using the relevant enthalpy changes of formation

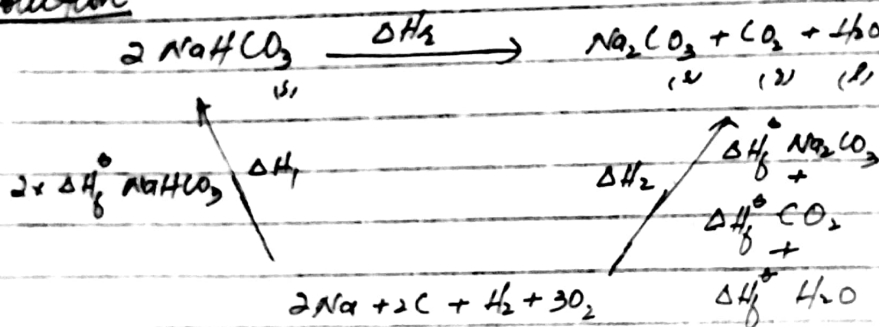


$$\Delta H_f^\circ \text{ of NaHCO}_3 = -950.8 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ \text{ of Na}_2\text{CO}_3 = -1130.7 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ \text{ of CO}_2 = -393.5 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ \text{ of H}_2\text{O} = -285.8 \text{ kJ mol}^{-1}$$

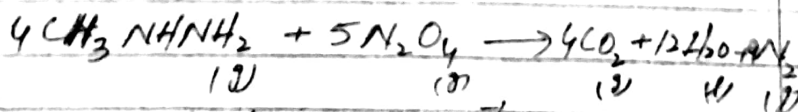
Solution

$$\Delta H_2 = \Delta H_2 - \Delta H_1$$

$$(-1130.7) + (-393.5) + (-285.8) - (-1901.6)$$

$$\Delta H_2 = +91.6 \text{ kJ mol}^{-1}$$

Calculate the enthalpy change for the following reaction using the standard enthalpy of formations



$$\Delta H_f^\circ \text{ of CH}_3\text{NHNH}_2 = 53 \text{ kJ mol}^{-1}$$

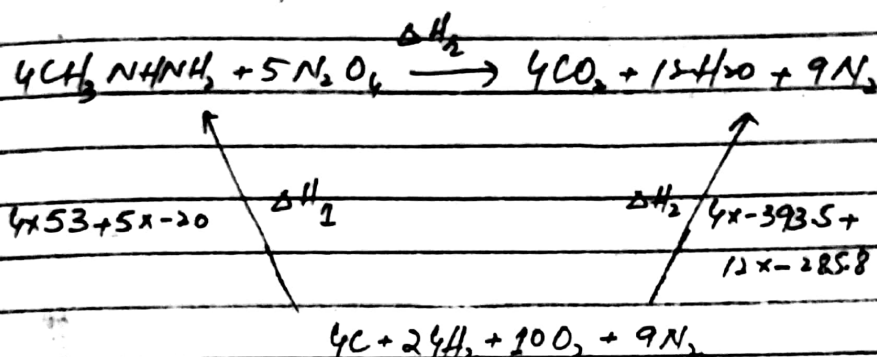
$$\Delta H_f^\circ \text{ of N}_2\text{O}_4 = -20 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ \text{ of } \text{CO}_2 = -393.5 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ \text{ of } \text{H}_2\text{O} = -285.8 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ \text{ of } \text{N}_2 = 0$$

Solution



$$\Delta H_2 = \Delta H_2 - \Delta H_1$$

$$(4 \times -393.5 + 12 \times -285.8) - (4 \times 53 + 5 \times -20)$$

$$-5003.6 - 112$$

$$-5115.6 \text{ kJ mol}^{-1}$$

3rd application of Hess's law

Calculation of enthalpy change
of combustion from enthalpy
of formation

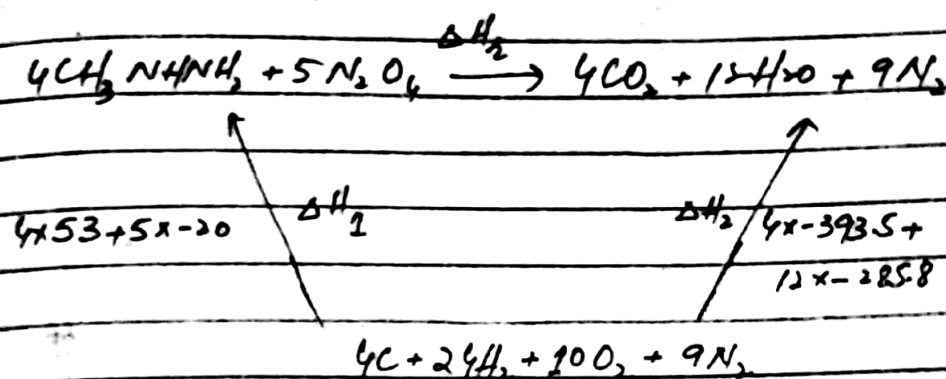
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$$\Delta H_f^\circ \text{ of } \text{CO}_2 = -393.5 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ \text{ of } \text{H}_2\text{O} = -285.8 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ \text{ of } \text{N}_2 = 0$$

Solution



$$\Delta H_2 = \Delta H_1 - \Delta H_f$$

$$(4 \times -393.5 + 12 \times -285.8) - (4 \times 53 + 5 \times -20)$$

$$-5003.6 - 112$$

$$-5115.6 \text{ kJ mol}^{-1}$$

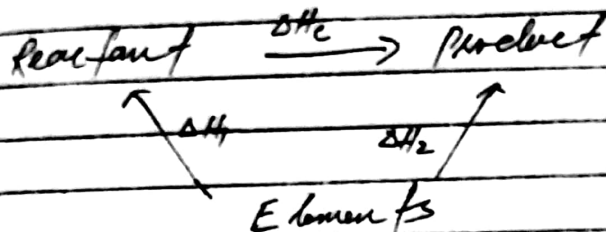
3rd application of Hess's law

Calculation of enthalpy change
of combustion from enthalpy
of formation

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Following cycle is used to measure enthalpy change of combustion using enthalpy change of formation



$$\Delta H_c = \Delta H_2 - \Delta H_1$$

$$\Delta H_c = \text{Enthalpy of formation of Products} - \text{enthalpy of formation of reactants}$$

Solved examples

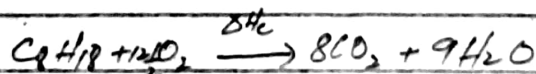
Calculate the enthalpy of combustion of octane C_8H_{18} using following enthalpy of formations

$$\Delta H_f^\circ \text{ of } C_8H_{18} = -250 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ \text{ of } CO_2 = -393 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ \text{ of } H_2O = -286 \text{ kJ mol}^{-1}$$

Solution



$$\begin{array}{ccc} & \swarrow \Delta H_f & \searrow \Delta H_f \\ -250 & & \begin{array}{l} 8 \times -393.5 \\ + \\ 9 \times -285.8 \end{array} \end{array}$$

$$\begin{aligned} \Delta H_c &= \Delta H_f \text{ Products} - \Delta H_f \text{ of reactants} \\ &= 8 \times -393.5 + 9 \times -285.8 - (-250) \\ &= -5470.2 \text{ kJ mol}^{-1} \end{aligned}$$

Calculating enthalpy changes using bond energies

We can use bond energies to calculate enthalpy change of a reaction that we cannot measure directly

Solved examples

Calculate enthalpy change for the Haber's process used for the manufacture of ammonia, using the bond energies which are given below

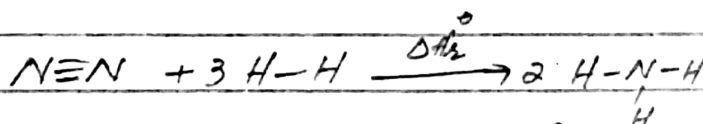


$$\text{N} \equiv \text{N} = 945 \text{ kJ mol}^{-1}$$

$$\text{H}-\text{H} = 436 \text{ kJ mol}^{-1}$$

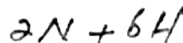
$$\text{N}-\text{H} = 391 \text{ kJ mol}^{-1}$$

Solution



$$\begin{array}{r} 945 \\ + \\ 3 \times 436 \end{array}$$

$$6 \times 391$$



$$\Delta H_r = \text{Bond energy of reactants} - \text{Bond energy of products}$$

$$(945 + 3 \times 436) - (6 \times 391)$$

$$2253 - 2346$$

$$= -93 \text{ kJ mol}^{-1}$$

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(14)

Example

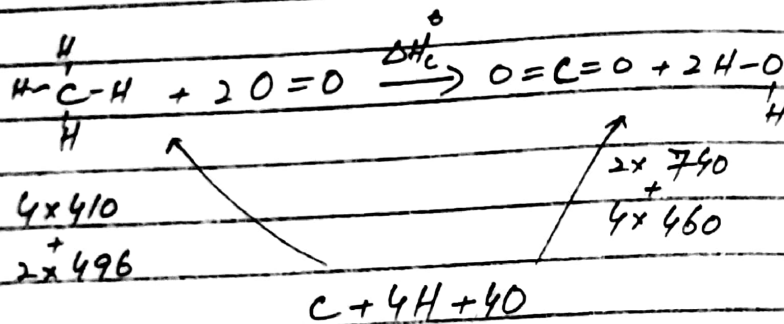
Calculate the enthalpy of combustion of methane using following bond energies.

$$C-H = 410 \text{ kJ mol}^{-1}$$

$$O=O = 496 \text{ kJ mol}^{-1}$$

$$C=O = 740 \text{ kJ mol}^{-1}$$

$$O-H = 460 \text{ kJ mol}^{-1}$$

Solution

$\Delta H_c^\circ =$ Bond energy of reactants - Bond energy of products

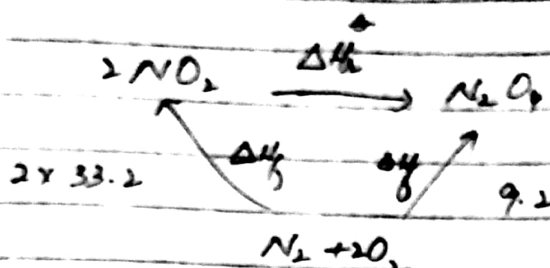
$$(4 \times 410 + 2 \times 496) - (2 \times 740 + 4 \times 460)$$

$$\Delta H_c^\circ = -688 \text{ kJ mol}^{-1}$$

Example

A molecule of N_2O_4 is formed by the dimerisation of NO_2 . Calculate the N-N single bond energy in N_2O_4 using the following enthalpy of formation.

$$\Delta H_f^\circ \text{ of } NO_2 = 33.2 \text{ kJ mol}^{-1}$$

Solution

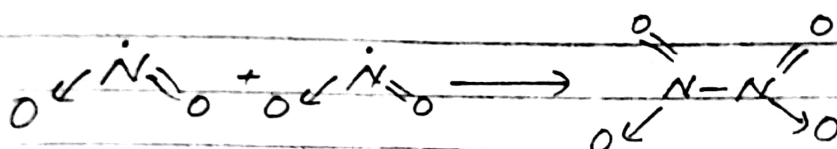
$$\Delta H_f^\circ = \Delta H_f^\circ \text{ of products} - \Delta H_f^\circ \text{ reactants}$$

$$9.2 - (2 \times 33.2)$$

$$9.2 - 66.4$$

$$-57.2 \text{ kJ mol}^{-1}$$

$-57.2 \text{ kJ mol}^{-1}$ is the bond energy of N-N in N_2O_4



The only change that comes during the reaction is the formation of N-N, so enthalpy change during the reaction is only due to the formation of this bond.

Solved example

Calculate the bond energy of S-F bond using the following reaction



$$\Delta H_f^\circ = -434 \text{ kJ mol}^{-1}$$

$$\text{F}-\text{F} = 158 \text{ kJ mol}^{-1}$$

Solution:

$$\Delta H_f^\circ = \text{Bond energy of reactants} - \text{Bond energy of products}$$

Measuring enthalpy changes

Calorimetry : We can measure the

enthalpy change of some reactions by a technique called calorimetry. The apparatus used is called a calorimeter.

A simple calorimeter can be a polystyrene cup or a styrofoam beaker or a metal can.

Calorimetry relies on the fact that it takes 4.18 J of energy to increase the temperature of 1 g of water by 1°C , which is called the specific heat capacity of water which is $4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$.

The energy transferred as heat is given by the relationship

$$q = mc \Delta T$$

where q = energy transferred in J

m = mass of water

c = specific heat capacity in $\text{J g}^{-1} \text{ }^\circ\text{C}^{-1}$

ΔT = change in temp in $^\circ\text{C}$

Since 1 cm^3 of water weighs 1 g we can substitute volume of water in cm^3 of water for mass of water in g in the equation.

Similarly aqueous solutions of acids, alkalis and salts are assumed to be largely water.

Solutions has same specific heat capacity as water.

Experimental measurement of enthalpy of neutralization

A typical procedure for neutralization reaction is as follows.

Place 50 cm³ of 1.0 mol dm⁻³ HCl in a polystyrene cup and record its temperature.

Add 50 cm³ of 1.0 mol dm⁻³ NaOH to the acid in the cup.

Stir the reaction mixture with the thermometer and record the highest temperature.

Calculations

$$\text{Initial temp} = 21.3^{\circ}\text{C}$$

$$\text{Final temp} = 27.8^{\circ}\text{C}$$

$$\text{Change in temp } \Delta T = 6.5^{\circ}\text{C}$$

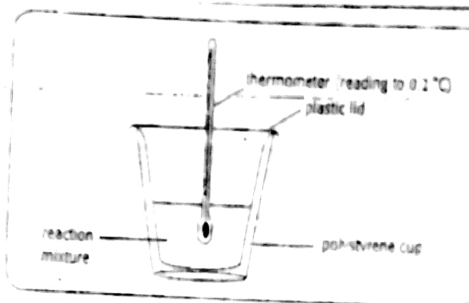
$$m = 50 + 50 = 100 \text{ cm}^3 = 100 \text{ g}$$

$$C = 4.2 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$$

$$q = m C \Delta T$$

$$100 \times 4.2 \times 6.5 = 2717 \text{ J}$$

$$\frac{2717}{1000} = 2.717 \text{ kJ}$$



We used 50 cm³ 1.0 mol dm⁻³ solution of HCl and NaOH, so number of mole of acid and alkali are

$$\text{moles} = C \times V$$

$$\frac{0.1 \times 50}{1000} = 0.050 \text{ mole}$$

When 0.050 mol of water formed energy released 2.717 kJ

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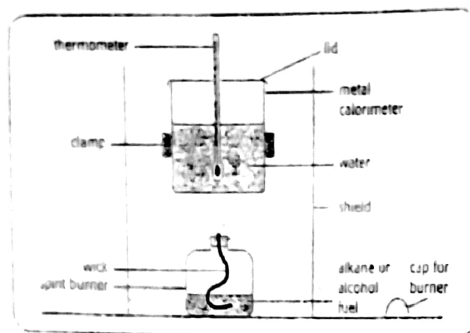
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Experimental measurement of enthalpy change of combustion using propan-2-ol

We can find the enthalpy change of combustion by burning a known mass of a substance and using the heat released to raise the temperature of known mass of water.

The apparatus used consists of a spirit burner and a metal calorimeter.



To find the standard enthalpy change of combustion we need to know

- the mass of fuel burnt
- the temp rise of the water
- the mass of water
- Mr of propan-2-ol

mass of water in calorimeter = 100 g
 mass of spirit burner + propan-2-ol = 86.27 g
 mass of spirit burner + propan-2-ol at the end = 86.06 g
 mass of propan-2-ol burnt = 0.21 g
 initial temp of water = 20.2 °C
 final temp of water = 30.9 °C
 rise in temp = 10.7 °C

(21)

using the relationship $q = mc\Delta T$

$$q = 100 \times 4.2 \times 10.7$$

$$4472.6 \text{ J}$$

$$\frac{4472.6}{1000} = 4.472 \text{ KJ}$$

Mr of propan-2-ol is 60g

So for 60g of propan-2-ol energy released is

$$\frac{4.472}{0.21} \times 60$$

$$= 1300 \text{ KJ mol}^{-1}$$

This is much less than the recorded value due to the heat losses to the surroundings.

Experimental measurement of enthalpy change of solution

The enthalpy change of solution of sodium hydroxide can be found by using a polystyrene cup as a calorimeter.

We use known amounts of solute and solvent with the solvent in excess to make sure that all the solute dissolves.

Calculations

$$\text{mass of polystyrene cup} = 23.00 \text{ g}$$

$$\text{mass of cup + water} = 123.45 \text{ g}$$

$$\text{mass of water} = 100.45 \text{ g}$$

$$\text{mass of cup + water + NaOH} = 124.95 \text{ g}$$

$$\text{mass of dissolved NaOH} = 1.50 \text{ g}$$

$$\text{Temperature rise} = 3.6^\circ \text{C}$$

$$q = 100.45 \times 4.2 \times 3.6 = 1511.57 \text{ J}$$

$$1.5 \text{ KJ} = \frac{1.5}{1.5} \times 40 = -40 \text{ KJ mol}^{-1}$$

Solved example

30 cm³ of 2.00 mol dm⁻³ HCl in excess was placed in a conical flask and the temperature recorded as 21°C.

When 0.0200 mol of K₂CO₃ was added to the acid and the mixture stirred with a thermometer, the maximum temperature recorded was 26.2°C.

Calculate the enthalpy change per mole of K₂CO₃ in kJ mol⁻¹.

Solution

$$q = mc\Delta T$$

$$30 \times 4.18 \times 5.2$$

$$652.08 \text{ J for } 0.02 \text{ mol of K}_2\text{CO}_3$$

$$0.020 \text{ mol of K}_2\text{CO}_3 = 652.08 \text{ J}$$

$$1 \text{ mol of K}_2\text{CO}_3 = \frac{652.08}{0.02} \text{ J}$$

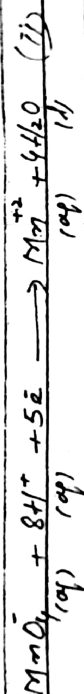
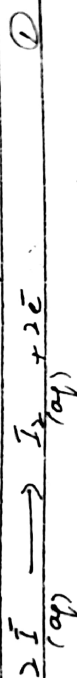
$$= 32604 \text{ J}$$

$$= -32.60 \text{ kJ mol}^{-1}$$

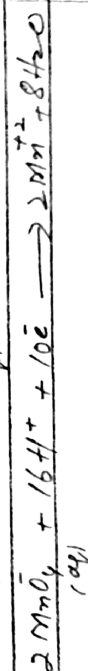
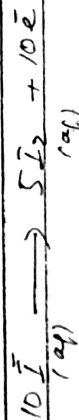
Redox reactions

Balancing of ionic equations :- A

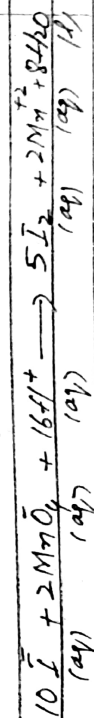
balanced ionic equation is the one which is balanced not only with respect to atoms but also with respect to charges. e.g. Constructed balanced ionic equation for the reaction of iodide ions (i) with manganate (VII) ions (MnO_4^-) in acidic medium using the two half equations



By multiplying equation (1) with 5 and equation (2) with 2 we can make number of electrons equal in both equations

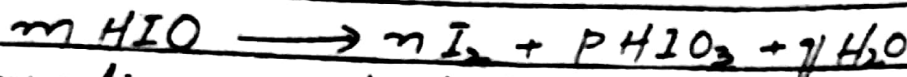


After cancelling electrons from each equation, the final ionic equation will be as follows



Redox reactions (solved examples)

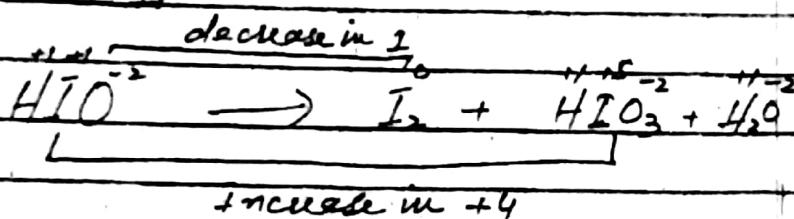
In aqueous solution, the acid HIO disproportionates according to the following equation where m , n , p and q are simple whole numbers in their lowest ratios.



This equation can be balanced by using oxidation numbers.

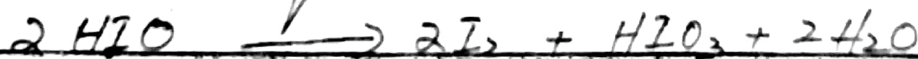
What are the values for n and p ?

	n	p
A	1	2
B	2	1
C	4	1
D	4	2

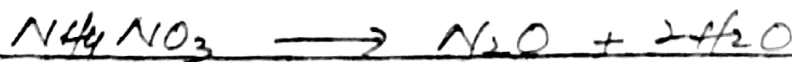


Increase and decrease should be equal, so there should be two I_2 at product side to make increase and decrease in oxidation number equal, so the value $m = 2$, $n = 2$, $p = 1$, $q = 2$

So balanced equation is

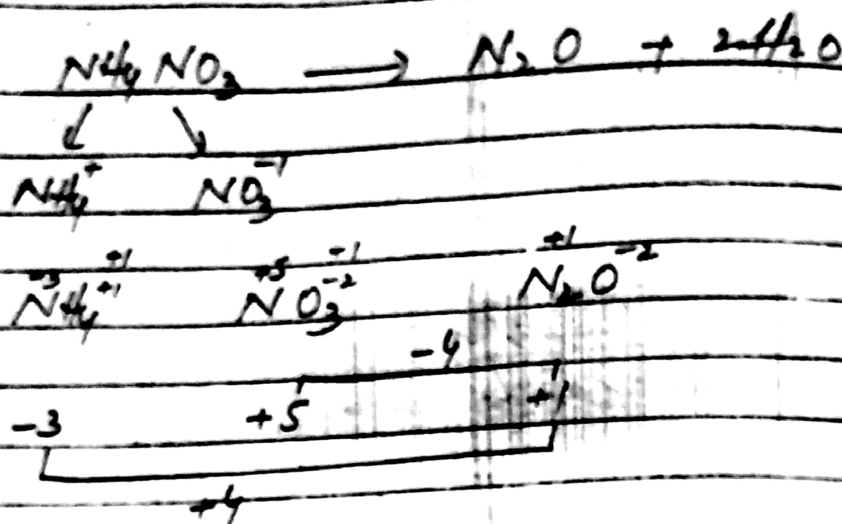


Ammonium nitrate NH_4NO_3 can decompose explosively when heated.



What is the change in oxidation numbers of the two nitrogen atoms in NH_4NO_3 as the reaction proceeds?

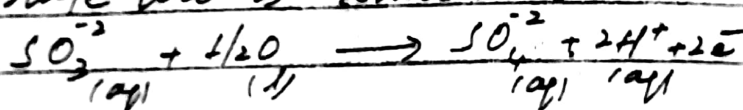
(A)



So correct answer is (D)

In an experiment 50cm^3 of a 0.10mol dm^{-3} solution of a metallic salt reacted exactly with 25.0cm^3 of 0.10mol dm^{-3} aqueous sodium sulphite.

The half equation for the oxidation of sulphite ion is shown below.



If the original oxidation number of the metal in the salt was +3, what would be the new oxidation number of the metal?

- (A) +1 (B) +2 (C) +4 (D) +5

Let's calculate the moles of two solutions

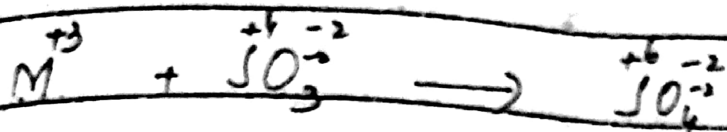
$$\text{moles of metallic salt} = \frac{50}{1000} \times 0.1 = 0.005 \text{ moles}$$

$$\text{moles of aq sodium sulphite} = \frac{25}{1000} \times 0.1 = 0.0025 \text{ moles}$$

Moles of metal salt

Moles of SO_3^{2-}

(18)



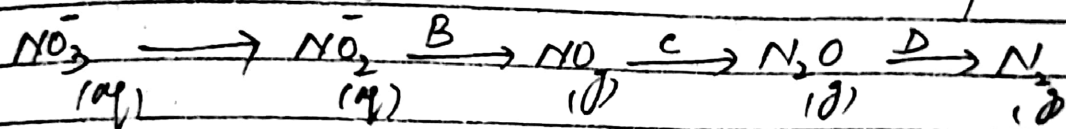
Loss of 2 moles of electrons

2 moles of M^{+3} react with one mole of SO_3^{+4-2}

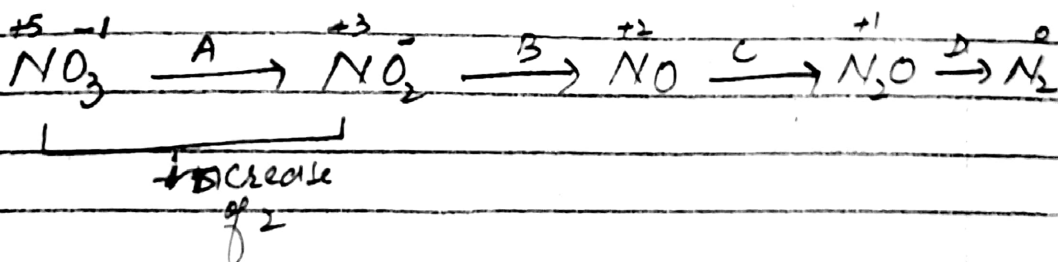
So when 2 moles of electrons will be gained by 2 moles of metal M^{+3} they will decrease its oxidation state from +3 to +2

So correct answer is (B)

14) In which step is the change in oxidation number of nitrogen different to the change in the other steps?



Solution

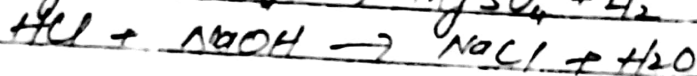
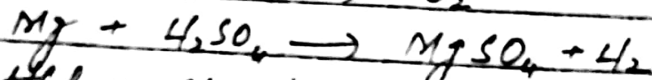
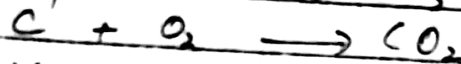
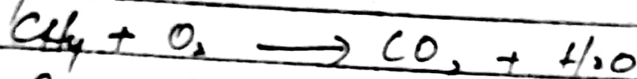


So (A) is the correct answer

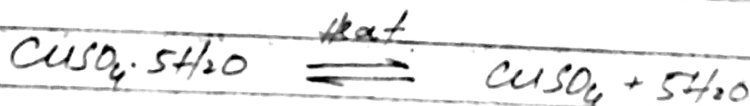
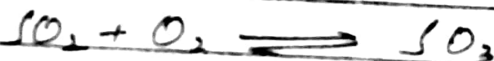
Equilibria

Irreversible and reversible reactions

Those reactions which proceed only in one direction i.e., in which only reactants are converted into products but products cannot turn back to reactants are called irreversible reactions.
For example



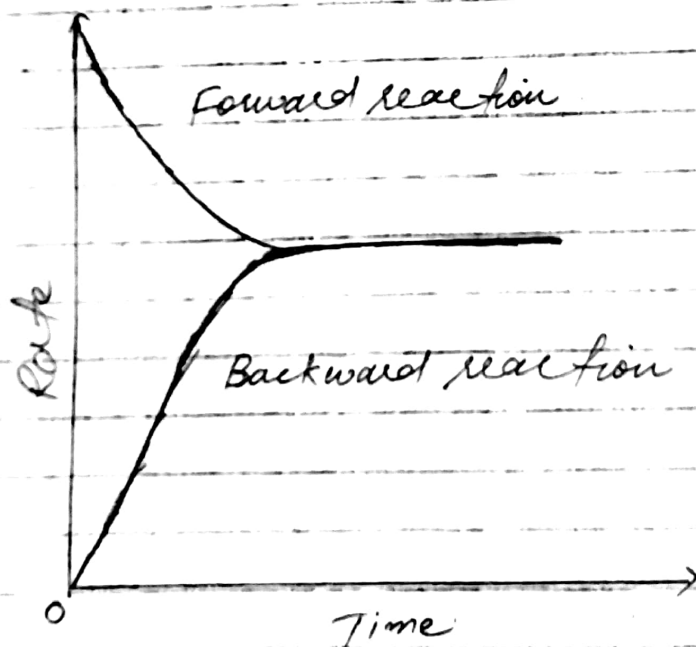
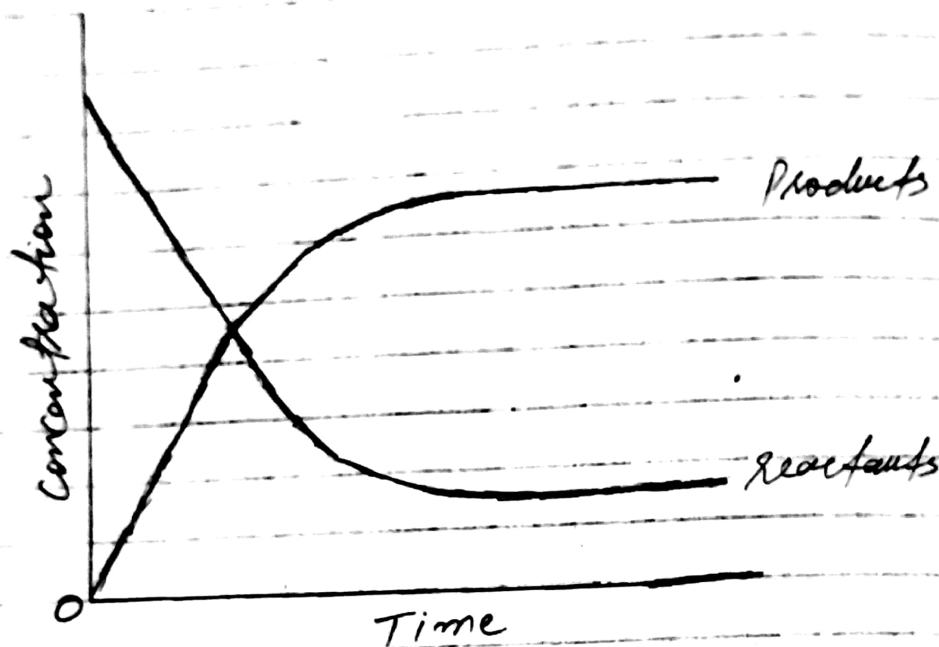
Those reactions which proceed in both directions i.e., in which reactants are converted to products and products are converted back to reactants simultaneously are called reversible reactions.
For example



Dynamic equilibrium:- During reversible reactions when the rate of forward reaction becomes equal to the rate of backward reaction, this state is called dynamic equilibrium.

At equilibrium the concentration of reactants and products become constant.

Graphical representation of reversible reactions



Equilibrium requires a closed system where none of the reactants or products escape.

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Changing the position of equilibrium

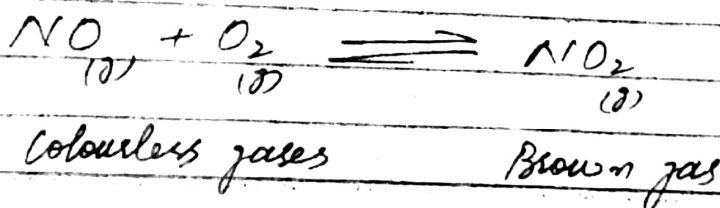
Le-Chatelier's principle - when a chemical reaction which is dynamic equilibrium is disturbed by making a change, the position of equilibrium moves in a direction which reduces or opposes the change.

Effect of concentration on the position of equilibrium

Increase in the concentration of reactants shifts equilibrium towards forward direction in order to decrease the concentration of reactants, similarly decrease in the concentration of products also shifts equilibrium towards forward direction.

Opposite occurs when the concentration of products is increased or any of the reactants is removed.

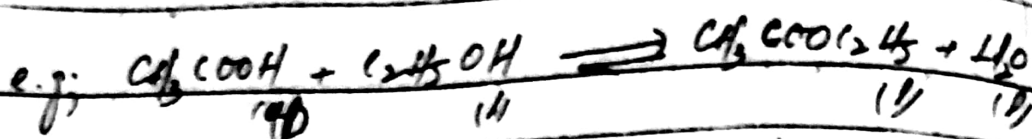
e.g;



addition of oxygen in reaction mixture will increase the darkness of the Brown colour of mixture as equilibrium will be shifted towards backward direction.

Effect of change in pressure:

only applicable to gaseous reactions because solids and liquids cannot be



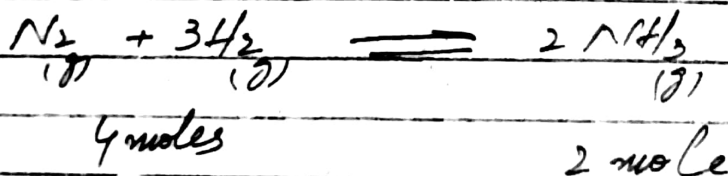
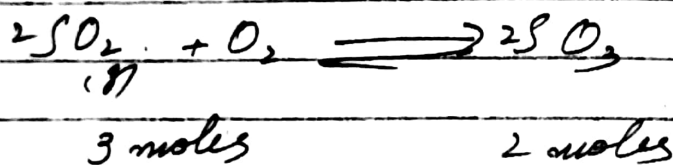
⇒ change in pressure does not affect those reactions in which number of moles of gases are equal at both sides of the equation

e.g;



But in those reactions where number of moles of gases are not equal at both sides of the equation, increase in pressure shifts dynamic towards the side where there are lesser number of moles and vice versa.

e.g;



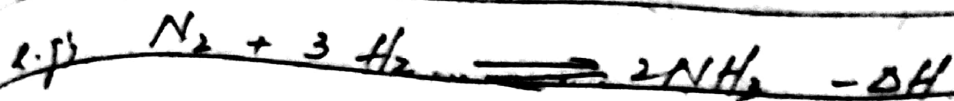
Effect of change in temperature

Increase in temperature favours endothermic reactions more than exothermic, so increase in temperature shifts dynamic equilibrium towards backward direction in exothermic reaction and shifts dynamic equilibrium towards forward direction in endothermic reactions.

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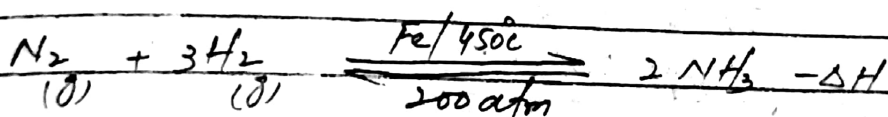
In these reactions yield of NH_3 and SO_3 will decrease with the increase in temperature and will increase with the decrease in temperature.

Effect of catalyst

Catalyst does not affect the position of dynamic equilibrium, it only helps dynamic equilibrium attained faster by equally increasing the rate of forward and backward reaction.

Manufacture of Ammonia by

Haber process



⇒ As the process is exothermic, so high temp of $450^\circ C$ is a compromise over yield as it will decrease the yield of NH_3 but keeps the reaction faster.

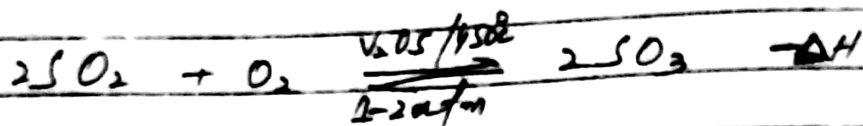
⇒ Al_2O_3 is also used with catalyst as promoter of catalyst and avoids poisoning of catalyst by reacting with impurities.

uses of Ammonia :- Ammonia is used in the manufacture of fertilizers.

Equilibrium and the Contact process

Contact process is used for the manufacture of sulphuric acid.

The most important step in the manufacture of sulphuric acid is given below



High temperature of 450°C will decrease the yield of SO_3 by shifting equilibrium towards backward direction but it will keep the reaction faster, so it is a compromise over yield. This is because forward reaction is exothermic.
 $\Rightarrow$ Very high pressure is avoided although high pressure shifts equilibrium towards forward direction, to keep the process economical.

Equilibrium constant K_c and equilibrium expression

Equilibrium constant is the ratio of the concentration of products to the concentration of reactants where each concentration raised to the power which is equal to the coefficient of the substances in the balanced equation.

For example, for a given reaction



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The equilibrium expression for this reaction

$$K_c = \frac{[C]^p [D]^q}{[A]^m [B]^n} \quad [] = \text{concentration in mol dm}^{-3}$$

This ratio of the concentration of products to the reactants will remain constant whatever the initial concentration of reactants or both reactants and products we take.

This constant is called equilibrium constant K_c where "c" represents the concentration.

Let's prove this by taking the following reaction as an example



This reaction is carried out by using different starting concentrations of H_2 and I_2 and then calculating the concentrations of reactants and products at equilibrium.

Concentration of H_2 at equilibrium in mol dm^{-3}	Concentration of I_2 at equilibrium	conc of HI at equilibrium	K_c
0.68×10^{-3}	0.68×10^{-3}	8.64×10^{-3}	161
0.50×10^{-3}	0.50×10^{-3}	6.30×10^{-3}	159
1.10×10^{-3}	2.00×10^{-3}	18.8×10^{-3}	161
2.50×10^{-3}	0.65×10^{-3}	16.1×10^{-3}	160

Results indicate that the ratio of the concentration of products to the reactant remains almost constant close to 160 whatever the starting concentrations of reactants we take. This constant is called equilibrium constant K_c .

K_p :- For reactions involving gases, the equilibrium constant is more convenient to express in terms of the partial pressures of gases, again the ratio of the partial pressures of products to the reactants remain always constant at constant temperature, this equilibrium constant is called K_p . It can be represented as

$$K_p = \frac{(p_C)^p (p_D)^q}{(p_A)^m (p_B)^n}$$

The units for K_p is atmosphere

Homogenous and Heterogenous equilibria

Chemical equilibrium in which all the components of the equilibrium mixture are in the same phase or same state is called homogenous equilibria e.g.





Chemical equilibrium in which all the components of the reaction mixture are not in the same phase is called heterogeneous equilibrium e.g.



Equilibrium expression for this reaction will be written in terms of partial pressure without including carbon which is a solid.

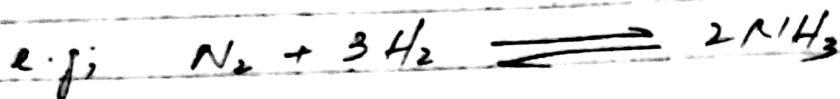
$$K_p = \frac{(p_{\text{CO}})(p_{\text{H}_2})}{(p_{\text{H}_2\text{O}})}$$

Where K_p is called modified equilibrium constant

Factors affecting the value of equilibrium constant

Concentration:- Change in concentration shifts the position of equilibrium in a way that the ratio of the concentration of products to reactants remain same, so change in concentration does not change the value of K_c .

Pressure :- overall increase in pressure will bring an increase in the partial pressures of reactants and products both, so the ratio of the partial pressures of reactants to products remain same, therefore the value of K_p remains constant.



4 mole

2 mole

If forward reaction gets double with the increase in pressure, some of its amount will also be converted back to reactant which will keep K_p constant.

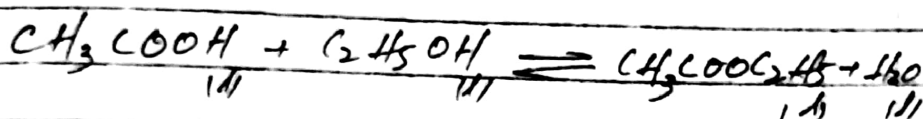
Catalyst :- Catalyst does not shift the position of equilibrium so it does not affect the value of K_c .

Temperature :- Increase in temperature increases the value of K_c for endothermic reaction because high temperature shifts dynamic equilibrium towards forward direction, this increases the concentration of products and decreases the concentration of reactants. Increase in temperature decreases the value of K_c for exothermic

Le Chatelier's backward direction, this increases the concentration of reactants and decreases the concentration of products.

Solved examples

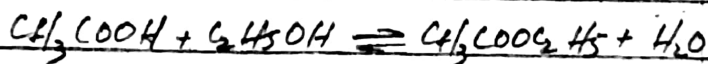
① Ethanol reacts with ethanoic acid to form ethyl ethanoate and water



500 cm³ of the reaction mixture at equilibrium contained 0.235 mol of ethanoic acid and 0.0350 mol of ethanol together with 0.182 mol of ethyl ethanoate and 0.182 mol of water.

Use this data to calculate a value of K_c for this reaction.

Solution :-



Convert moles	0.235	0.0350	0.182	0.182
into concentration	$\frac{500}{1000}$	$\frac{500}{1000}$	$\frac{500}{1000}$	$\frac{500}{1000}$

$$0.470 \text{ mol dm}^{-3} \quad 0.070 \text{ mol dm}^{-3} \quad 0.364 \text{ mol dm}^{-3} \quad 0.364 \text{ mol dm}^{-3}$$

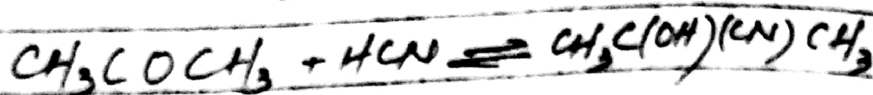
$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

$$K_c = \frac{[0.364][0.364]}{[0.470][0.070]}$$

$$K_c = 4.03$$

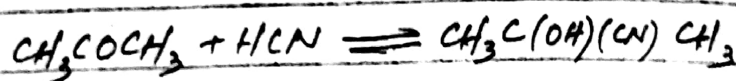
no unit

(2) Propanone reacts with hydrogen cyanide as follows:



A mixture of $0.0500 \text{ mol dm}^{-3}$ propanone and $0.0500 \text{ mol dm}^{-3}$ hydrogen cyanide is left to reach at equilibrium. At equilibrium the concentration of the product is $0.0233 \text{ mol dm}^{-3}$. Calculate K_c for this reaction.

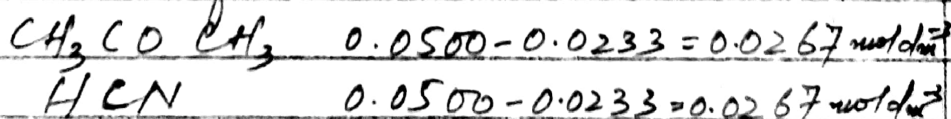
Solution



Initial concentration $0.0500 \text{ mol dm}^{-3}$ $0.0500 \text{ mol dm}^{-3}$ 0

Equilibrium concentration Not known Not known $0.0233 \text{ mol dm}^{-3}$

Chemical equation shows that for every one mole of product formed one mole of CH_3COCH_3 and 2 mole of HCN are consumed, so the equilibrium concentration of reactants are as follows



$$K_c = \frac{[\text{CH}_3\text{C(OH)(CN)CH}_3]}{[\text{CH}_3\text{COCH}_3][\text{HCN}]}$$

$$K_c = \frac{[0.0233]}{[0.0267][0.0034]}$$

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(13)

(3) Nitrogen and hydrogen at a partial pressure of 1 atm and 3 atm respectively are allowed to reach equilibrium at a certain temperature, where ammonia at a partial pressure of 0.4 atm is formed. Calculate the value of K_p under these conditions.

Solution

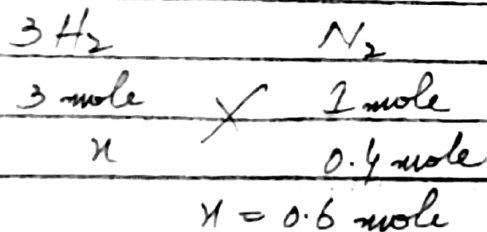


initial partial pressure 1 atm 3 atm 0 atm

Equilibrium partial pressures not known not known 0.4 atm

as partial pressure is directly proportional to the number of moles, so 0.4 atm can be taken as 0.4 moles of NH_3 .

so 0.4 moles of NH_3 are formed by 0.2 moles of N_2
left over moles of $N_2 = 0.8 \text{ mol} = 0.8 \text{ atm}$



so at equilibrium $3 - 0.6 = 2.4 \text{ moles} = 2.4 \text{ atm}$

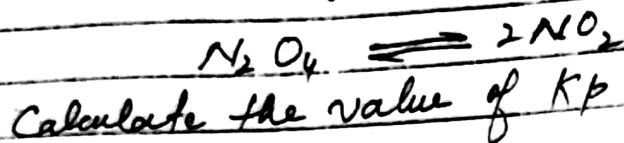


Equilibrium partial pressures 0.8 atm 2.4 atm 0.4 atm

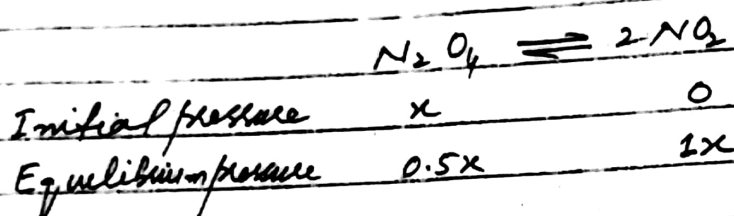
$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3} = \frac{(0.4)^2}{(0.8)(2.4)^3}$$

(14)

At 60°C and a total pressure of 1 atm
 N_2O_4 is 60% dissociated according to
 the following equation



Solution



Let's calculate value of x

$$0.5x + x = 1$$

$$1.5x = 1$$

$$x = \frac{1}{1.5} = 0.67$$

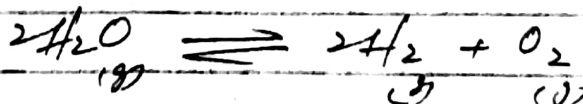
$$0.5 \times 0.67 = 0.335$$

$$1 \times 0.67 = 0.67$$

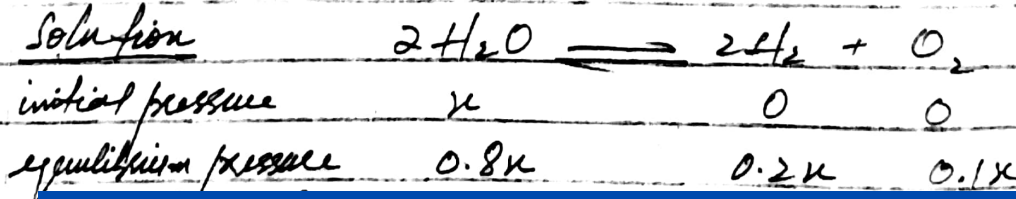
$$K_p = \frac{(0.67)^2}{(0.335)}$$

1.34 atm

At a certain temperature and a total
 pressure of 1 atm , steam is 20% dissociated
 according to the following equation.



Solution



OR

$$1.1x = 1$$

$$x = \frac{1}{1.1} = 0.909$$

$$0.8 \times 0.909 = 0.727$$

$$0.2 \times 0.909 = 0.1818$$

$$0.1 \times 0.909 = 0.09$$

$$0.8x + 0.2x = 1$$

$$0.1x = 1$$

$$p_{H_2O} = \frac{0.8}{1.1} \times 1 = 0.727$$

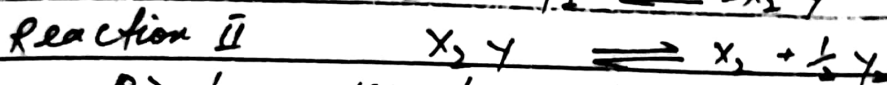
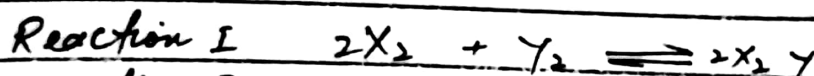
$$p_{H_2} = \frac{0.2}{1.1} \times 1 = 0.1818$$

$$p_{O_2} = \frac{0.1}{1.1} \times 1 = 0.09$$

$$K_p = \frac{(0.1818)(0.09)}{(0.727)^2}$$

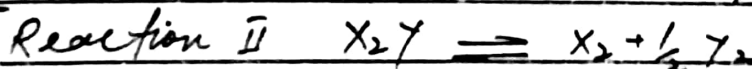
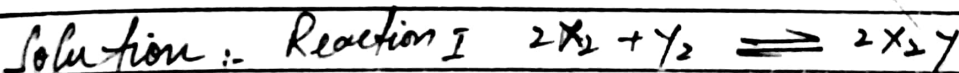
$$5.6 \times 10^{-3} \text{ atm}$$

Two equilibria are shown below.



(A) $\frac{1}{\sqrt{2}}$ (B) $\frac{1}{2}$ (C) $\frac{1}{4}$ (D) -2

The numerical value of K_c for reaction I is 2.
Under the same conditions, what is the numerical value of K_c for reaction II?



taking square root of equation I

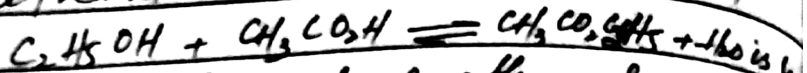
$$\sqrt{\frac{[X_2Y]^2}{[X_2]^2[Y_2]}} = \sqrt{2}$$

$$\frac{[X_2Y]}{[X_2][Y_2]^{\frac{1}{2}}} = \sqrt{2}$$

$$[X_2][Y_2]^{\frac{1}{2}}$$

(16)

The equilibrium constant K_c for the reaction to form ethyl ethanoate from ethanol and ethanoic acid

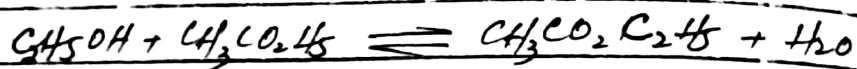


When 2.00 mol each of ethanol and ethanoic acid are allowed to reach equilibrium at $60^\circ C$, what is the number of moles of ethyl ethanoate formed?

- (A) $\frac{1}{3}$ (B) $\frac{2}{3}$ (C) $\frac{1}{4}$ (D) $\frac{3}{4}$

Solution:-

$$K_c = \frac{[CH_3CO_2C_2H_5][H_2O]}{[CH_3CO_2H][C_2H_5OH]}$$



Initial	1 mol	1 mol	0	0
Equilibrium	1-x	1-x	x	x

$$4 = \frac{[x][x]}{[1-x][1-x]}$$

$$4 = \frac{x^2}{(1-x)^2}$$

Taking square root both sides

$$\sqrt{4} = \sqrt{\frac{x^2}{(1-x)^2}}$$

$$2 = \frac{x}{1-x}$$

(17)

At a certain temperature and 2 atm pressure N_2O_4 is 60% dissociated.

- (a) Calculate K_p
 (b) Hence, calculate the degree of dissociation when the pressure is increased to 5 atm at a same temperature.

Solution



Amount reacted	x	0
At equilibrium	$0.4x$	$1.2x$
Value of x	$0.4x + 1.2x = 2$	
	$x = 1.25$	

$$N_2O_4 = 0.4 \times 1.25 = 0.5$$

$$NO_2 = 1.2 \times 1.25 = 1.5$$

Alternative method

$$K_p = \frac{(NO_2)^2}{(N_2O_4)}$$

$$\frac{(1.5)^2}{0.5}$$

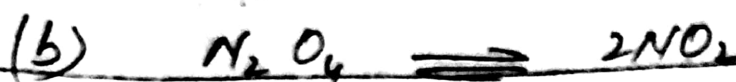
$$K_p = 4.5 \text{ atm}$$

$$\text{partial pressure of } N_2O_4 = \frac{\text{moles of } N_2O_4}{\text{Total moles}} \times P_T$$

$$\frac{0.4}{1.6} \times 2 = 0.5 \text{ atm}$$

$$\text{partial pressure of } NO_2 = \frac{1.2}{1.6} \times 2 = 1.5 \text{ atm}$$

$$K_p = \frac{(1.5)^2}{0.5} = 4.5 \text{ atm}$$



mole ratio $\begin{matrix} 1 & 0 \end{matrix}$
 $t=0$

amount reacted $\begin{matrix} x & 2x \end{matrix}$
 and formed

at equilibrium $\begin{matrix} 1-x & 2x \end{matrix}$

Total moles $\begin{matrix} 1-x+2x \\ 1+x \end{matrix}$

total pressure = 5 atm

$$\text{partial pressure of } NO_2 = \frac{2x}{1+x} \times 5$$

$$\text{partial pressure of } N_2O_4 = \frac{1-x}{1+x} \times 5$$

$$K_p = \frac{(p_{NO_2})^2}{(p_{N_2O_4})}$$

$$4.5 = \frac{\left(\frac{2x}{1+x} \times 5\right)^2}{\left(\frac{1-x}{1+x} \times 5\right)}$$

$$x = 0.43$$

Therefore, the degree of dissociation is 43%.

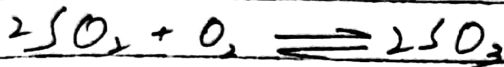
As x is the amount reacted from one mole

When SO_2 and O_2 in a mole ratio of 2:1 at a total initial pressure of 3 atm, react to produce SO_3 which has a partial pressure of 1.9 atm at equilibrium.

(a)

SO₂ and O₂ at equilibrium, also calculate the value of K_p.

Solution



Initial mole 2 1 0

initial pressure 2 atm 1 atm 0 atm

at equilibrium 0.1 atm 0.05 atm 1.9 atm

moles are taken equal to pressure because
 $p \propto n$

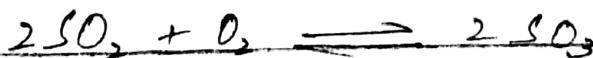
$$\text{So } K_p = \frac{(1.9)^2}{(0.1)^2(0.05)}$$

$$722 \text{ atm}^{-1}$$

Alternate method

$$\text{partial pressure of SO}_2 = \frac{2}{3} \times 3 = 2 \text{ atm}$$

$$\text{partial pressure of O}_2 = \frac{1}{3} \times 3 = 1 \text{ atm}$$



Initial pressure 2 atm 1 atm 0

equilibrium 0.1 atm 0.05 atm 1.9 atm

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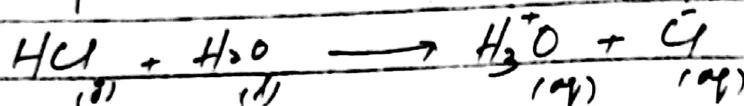
(20)

Acid-Base equilibria

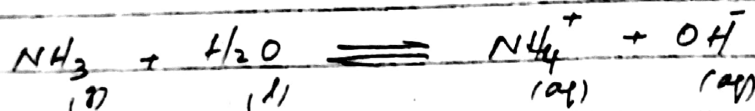
The Lowry-Bronsted theory of acids

According to Lowry Bronsted theory acids are those which donate proton while bases are those which accept proton.

H^+ is a proton as it contains only proton



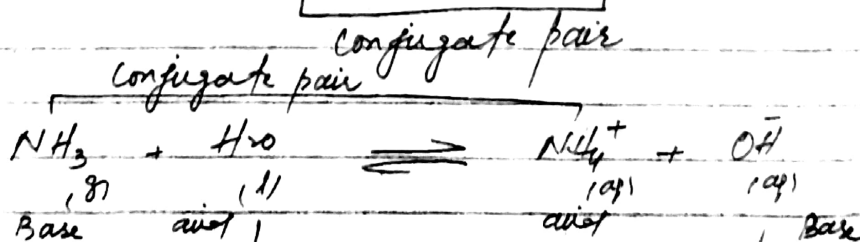
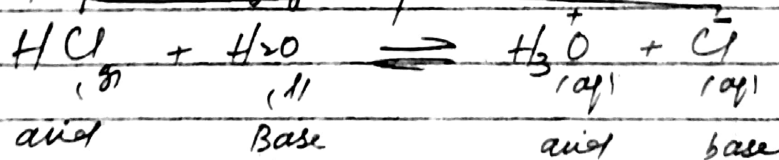
Acid Base



Base acid

Conjugate acids and conjugate bases

A substance formed after accepting a proton is called as conjugate acid and a substance formed after removal of proton is called conjugate base.



(21)
Strong acids have weak conjugate
base while weak acids have strong
conjugate bases.

Similarly strong bases have weak
conjugate acids and weak bases
have strong conjugate acids.

Rate of reaction OR Reaction Kinetics

The study of speed of reaction is called reaction kinetics.

The increase in the concentration of products or decrease in the concentration of reactants per unit time is called the rate of reaction.

Rate of reaction = $\frac{\text{change in concentration}}{\text{Time}}$

unit of rate reaction is $\text{mol dm}^{-3} \text{sec}^{-1}$

Factors affecting rate of reaction in the light of collision theory

Collision theory:- According to

Collision theory, in order to react with each other particles must collide.

If colliding particles do not have enough energy to react, an unsuccessful collision will take place.

If reacting particles have enough energy to react, they may change into products when they collide. This is called successful or effective collision.

Activation energy:- The minimum energy that colliding particles must possess in order to be converted

into products is called activation energy

According to collision theory
Rate of reaction increases if
→ the frequency of collisions increase
→ the proportion of particles with energy greater than activation energy increases.

Effect of concentration on the rate of reaction

Increase in concentration increases the rate of reaction because with the increase in concentration particles get closer together, this results in more frequent collisions between reacting particles.

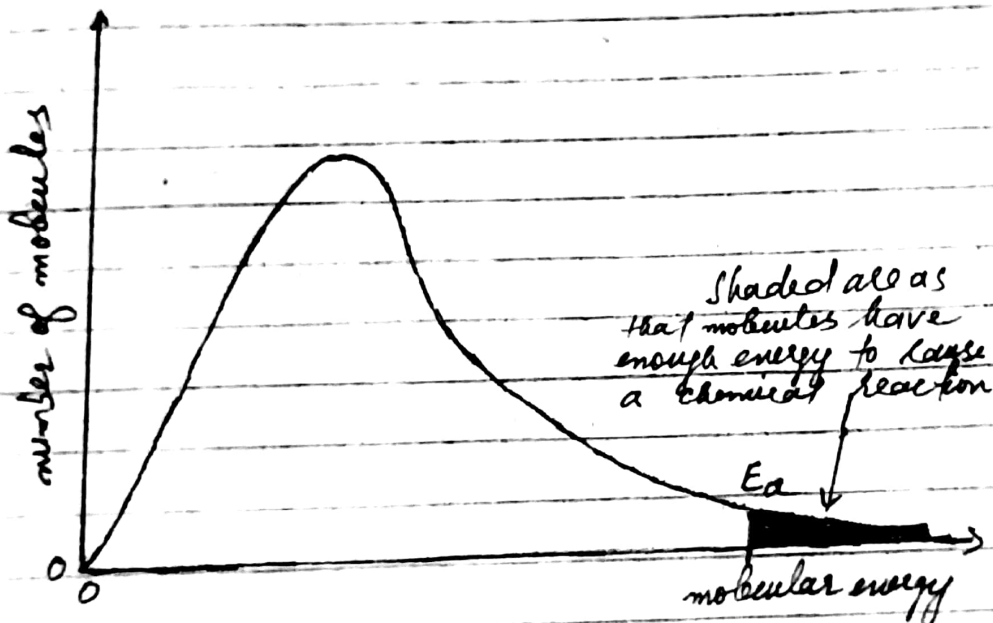
Effect of pressure (only applicable on gaseous reactions)

Increase in pressure, decreases the volume and brings particles closer together, this results in more frequent collisions between reacting particles and increases the rate of reaction.

Effect of temperature :- In order to understand the effect of temperature on the rate of reaction we need to keep in view this fact that in any substance at any given temperature,

the same amount of energy. A few particles have relatively small amount of energy. A few particles have relatively large amount of energy. Most particles will have an amount of energy somewhere in between.

The distribution of energy at a given temperature can be shown with the help of a graph. This is called Boltzmann distribution curve.

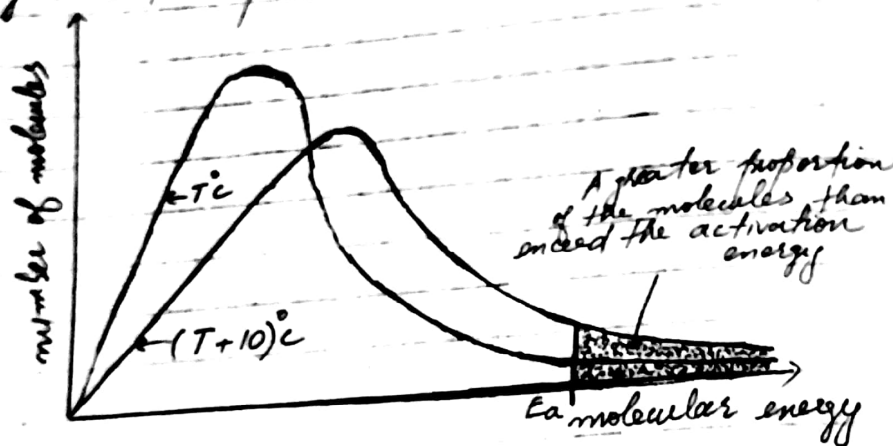


When we increase the temperature, the average kinetic energy of the particles increases, particles move faster and collide more frequently.

However experiments show us that the effect of temperature on rate of reaction cannot be totally explained by more frequent collisions. The key factor is that the proportion of successful collisions (collisions which result in a reaction)

particles possessing energy greater than activation energy increases. This is the more important factor. For a 10°C rise in temperature, the rate of a reaction doubles.

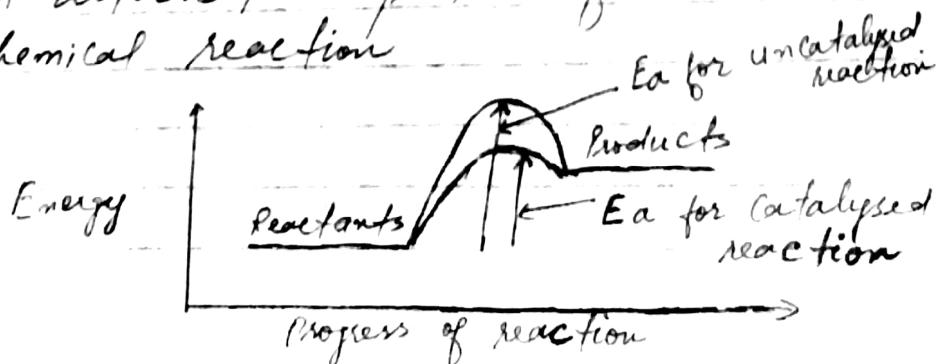
Boltzmann distribution curve of molecular energies at temp $T^{\circ}\text{C}$ and $(T+10)^{\circ}\text{C}$



Effect of Catalyst on the rate of reaction

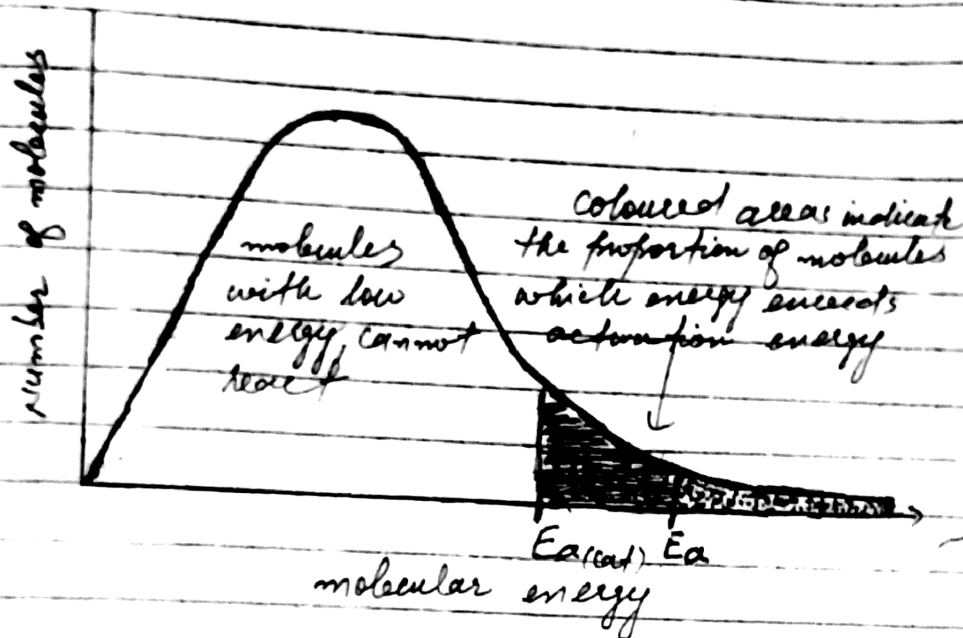
Catalyst is a substance which speeds up a chemical reaction without being used up during reaction.

Catalyst speeds up a reaction by lowering activation energy and by providing an alternate path for the chemical reaction.



(05)

We can also show the effect of catalyst on a Boltzmann distribution curve



Catalyst does affect the shape of the Boltzmann distribution. However, by providing a lower activation energy, a greater proportion of molecules have sufficient energy to react. The shaded areas under the curve represents the number of molecules which energy is greater than activation energy.

Enzymes as Biological catalyst

Enzymes are the biological catalysts. They are large protein molecules which speed up biochemical reactions which take place in living organisms.