17. If the speed of light is 3.0×10 ms^{-1}, calculate the distance covered by light in 2.00 ns. [**Ans.:** 0.600 m]

18. State the law of definite proportions. Explain it with the help of an example.

19. Burning a sample of a hydrocarbon gas gives 3.38 g CO_2 and 0.690 g H_2O. A volume of 10L (measured at STP) of this hydrocarbon weighs 11.6 g. Calculate the molecular formula of this hydrocarbon. [**Ans.:** C_2 H_2]

20. In three moles of ethane (C_2H_6), Calculate the following :

(i) Number of moles of carbon atoms

(ii) Number of moles of Hydrogen atoms

(iii) Number of Molecules of ethane

3 - MARK QUESTIONS

1. (a) State and explain Avogadro's law. Illustrate it with an example.

(b) 10.0 L of a welding gas weighs 11.6 g at STP. Calculate the molar mass of this gas. [**Ans.:** 26.0 g/mol]

2. (a) Calculate the mass of $CaCO_3$ required to react completely with 25mL of 0.75 M HCl. [**Ans.:** 0.938 g]

(b) Calculate volume of CO_2 released at STP in this reaction. [**Ans.:** 0.21 L]

3. Dinitrogen and dihydrogen react with each other to produce ammonia according to following chemical equation :

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

(a) Calculate the mass of ammonia gas formed if 2.0 kg of nitrogen gas reacts with 1.0 kg of hydrogen gas.

(b) Which of the two reactants is the limiting reagent and why ?

(c) Which of the two reactants will remain unreacted and what will be the amount left unreacted ? [Ans.: m (NH_3) = 2.571 kg, H_2 will remain unreacted its mass is 571.5 g]

4. (a) Calculate the molarity of solution prepared by dissolving 175.5 g NaCl in enough water to form 1.0 L of brine solution.

(b) Calculate molality of solution if its density is 1.25 g ml^{-1}.

(c) Calculate the mole fraction of NaCl.

5. Calculate the number of atoms in :

(a) 5.0 L oxygen gas at STP (b) 4.4 g of CO_2

(c) 52 u of He

UNIT-2

STRUCTURE OF ATOM

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

	ELECTRON	PROTON	NEUTRON
Discovery	Sir. J. J. Thomson (1869)	Goldstein (1886)	Chadwick (1932)
Nature of charge	Negative	Positive	Neutral
Amount of charge	1.6×10^{-19} Coloumb	1.6×10^{-19} Coloumb	–
Mass	9.11×10^{-31} kg	1.672614×10^{-27} kg	1.67492×10^{-27} kg

- Nucleus was discovered by Rutherford in 1911.
- Atomic number (Z) : the number of protons present in the nucleus (Moseley 1913).
- **Mass Number (A) :** Sum of the number of protons and neutrons present in the nucleus.
- Wavelength, frequency and wave velocity are related to each other by

  $c = \nu\lambda$ where c = velocity in light = 3.0×10^{-8} m/s
  ν = frequency of s^{-1} or Hz
  λ = wavelength in metres

- Wavenumber $(\bar{\nu})$ is the reciprocal of wavelength $\left(\bar{\nu} = \frac{1}{\lambda}\right)$.
- According to Planck's quantum theory, the energy is emitted or absorbed not continuously but discontinuously in the form of energy packets called quanta. A quantum of light is called photon. The energy of a quantum is E = $h\nu$, where h = Planck's constant, ν = frequency of radiation.
- The line spectrum of hydrogen consists of Lyman Series (in UV region), Balmer series (visible region), Paschen, Brackett and Pfund series (IR region).

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

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

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

  For, Lyman series : $n_1 = 1$, $n_2 = 2, 3, 4, ...$
  Balmer series : $n_1 = 2$, $n_2 = 3, 4, 5, ...$
  Paschen series : $n_1 = 3$ and $n_2 = 4, 5, 6 .....$

(3) Magnetic orbital quantum number (m_l)
For a given value of 'l', m_l has a total of $(2l + 1)$ values ranging from $-l$ to $+l$ including '0'. It determines the orientation of orbital.

(4) Magnetic spin quantum number (m_s)
It can take the values of $+½$ or $-½$ and determines the orientation of spin.

- **Pauli's Exclusion Principle :** "No two electrons in an atom can have the same set of four quantum numbers." Two electrons can have same values for n, l and m_l provided their spins are opposite (m_s is different). Therefore an orbital can have at the most two electrons if they have opposite spins.
- **Hund's Rule of maximum Multiplicity :** "The electrons start pairing only when all the degenerate orbitals of a subshell are singly occupied with parallel spins." *e.g.,* N : $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$.
- **Aufbau Principle :** "Orbitals are filled up in increasing order of their energy with the help of pauli principle and Hund's rule."
  1. Orbitals are filled up in the increasing order of their $(n + 1)$ values.
  2. If two orbitals have same $(n + 1)$ values, then the one which has lower n value, will be filled up first.

  Increasing order of energy :
  $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s$

  Exception of Aufbau principle : Extra stability is associated with the exactly half-filled and fully-filled orbitals. Thus the $p^3, p^6, d^5, d^{10}, f^7, f^{14}$ etc. have extra stability, *i.e.,* lower energy and therefore, more stable.

1 - MARK QUESTIONS

1. Indicate the number of electrons, protons and neutrons in the element $^{238}_{92}U$.
[**Ans.** $e = 92$, $p = 92$, $n = 146$]

2. Name the experiment used in determination of the charge of an electron.

3. Arrange the electron (e), protons (p) and alpha particle (α) in the increasing order for the values of e/m (charge/mass). [**Ans.** $\alpha < p < e$]

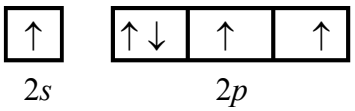
4. Calculate the mass of one mole of electron. [Given : $m_e = 9.11 \times 10^{-31}$ kg]
[**Ans.** 0.55 mg]

5. Write the dimensions of Planck's constant. Mention some other physical quantity, which has the same dimension.

6. Name the element which was discovered in the sun by spectroscopic method.
[**Ans.** Helium (He)]

7. Which of the following will not show deflection from the path on passing through an electric field,

27. Which principle is not obeyed in writing of electronic configuration :



2- MARK QUESTIONS

1. Give examples of each of the following :

(a) Isotope of $^{35}_{17}Cl$ (b) Isobar of $^{40}_{18}Ar$

(c) Isotone of $^{15}_{7}N$ (d) Isoelectronic species of S^{2-}

[**Ans.** (a) $^{37}_{17}Cl$ (b) $^{40}_{20}Ca$ (c) $^{16}_{8}O$ (d) K^+, Ca^{2+}, Ar, Cl^-, S^{2-}]

2. Describe the cathode ray experiment. How will you detect the spot where the rays strike ?

3. Outline Rutherford's contribution to understand the nucleus of an atom.

4. Calculate the percentage of higher isotope of neon which has average atomic mass 20.2 and the isotopes have the mass numbers 20 and 22.

[**Ans.** 10 % $^{22}_{10}Ne$]

5. Account for the following :

(a) Cathode rays are produced only when the pressure of the gas inside the discharge tube is very very low.

(b) Can a thin foil of aluminium be used in place of gold (Au) in Rutherford experiment ? Give suitable explanation.

[**Hint :** Lighter nuclei cannot exhibit proper deflection of α-particles.]

6. Distinguish between an atomic emission spectrum and an atomic absorption spectrum.

7. The energies of electrons are said to be quantized. Explain.

8. A laser used to read compact disc (CD) emits red light of wavelength 700 nm. How many photons does it emit each second if its power is 1 W ?

[**Ans.** 3.5×10^{18} s^{-1}]

9. Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-1}.

10. Show that the circumference of Bohr orbit for the hydrogen atom is an integral multiple of the de Broglie wavelength associated with the electron revolving around the nucleus.

Anomalous Properties of Second Period Elements

Each element of second period, *i.e.,* first element of each of group 1 and 2 and groups 13-17 shows many properties which are not shown by its cogeners. Their anomalous behaviour is attributed to their small size, large charge/radius ratio, high electronegativity, non-availability of *d*-orbitals in their valence shell. Thus the first member of each group has only four valence orbitals (one 2*s* and three 2*p* orbitals) for bonding, whereas the second member of the group has nine valence orbitals (one 3*s*, three 3*p* and five 3*d* orbitals). As a consequence of this, maximum covalency of first member of each group is limited to '4', whereas the other members of the group can expand their valence shell to accommodate more than four pairs of electrons. For example, B from $[BF_4]^-$ and Al, $[AlF_6]^{3-}$. In addition to this, the first member of each group of *p*-block elements displays greater ability to form $p\pi$-$p\pi$ multiple bonds to itself (e.g. C = C, C ≡ C, N = N, N ≡ N, O = O) and to other second period elements (*e.g.,* C = O, C = N, C ≡ N, N = O) compared to subsequent members of the group.

1 - MARK QUESTIONS

1. Name the scientist who gave birth to the periodic table.

2. Name the property used by Mendeleev to classify the elements in his periodic table ?

3. State the Modern Periodic Law.

4 How many groups and periods are there in the long form of the periodic table ?

5. Write the IUPAC name and symbol for the element with atomic number 119.

6. How does ionization enthalpy vary in a group and in a period?

7. Arrange B, C, N, O elements in increasing order of electron gain enthalpy.

8. Write the electronic configuration of the element having atomic number 21.

9. Explain the term electron gain enthalpy.

10. Out of K and K^+, which one would have larger size ?

11. Arrange the following elements in the increasing order of metallic character:

B, Al, Mg, K

12. Predict the position of the elements in the periodic table having the electronic configuration :

$(n-1)d^1\ ns^2$ for $n = 4$

2 - MARK QUESTIONS

1. (a) State Newland's law of octaves.
(b) Write two anomalies of Mendeleev's periodic table.

2. Name the groups of elements classified as *s*-, *p*-, *d*- and *f*-blocks in the modern periodic table.

3. How are Li and Mg related to each other in the periodic table ? Write the name of another pair having such a relationship.

4. (a) Name the first and last member of the 3*d* series.

(b) To which block (*s*-, *p*-, *d*- or *f*-) does the element with atomic number 50 belong ?

5. The ionization enthalpy per mole of atomic hydrogen is 1.313×10^6 J. Calculate the energy of the electron in the ground state of the hydrogen atom.

[**Hint :** I.E./atom $= \dfrac{1.313\times10^{6}\ \text{J mol}^{-1}}{6.023\times10^{23}\ \text{mol}^{-1}} = 2.18\times10^{-18}$ J

I. E. $= E_{\infty} - E_1$] [**Ans.** $E_1 = -2.18 \times 10^{-18}$ J]

6. An element belong to third period of *p*-block elements. It has four electrons in the outermost shell. Predict its group. How many unpaired electrons are present in an atom of that element ?

7. Write the atomic number and electronic configuration of the elements of fourth period which has maximum number of unpaired electrons ?

8. Why do the periodic properties such as ionization enthalpy, electron gain enthalpy and electronegativity shows a decreasing trend down the group but an increasing trend along a period ? Explain your answer.

9. Identify the elements having the following description and write their electronic configuration also :

(a) Group 14, period 3

(b) Group 18, period 2

(c) Group 1, period 6 [**Ans.** (a) Si, (b) Ne, (c) Cs]

10. On the basis of quantum numbers, justify that fifth period of the periodic table should have eighteen elements.

11. Lanthanoids and actinoids are placed in separate rows at the bottom of the periodic table. Explain the reason for this arrangement.

Hybridisation may be defined as the phenomenon of intermixing of atomic orbitals of nearly the same energy belonging to different subshells so as to redistribute their energies and to give rise to new orbitals of equivalent energies and shapes. The new orbitals that are formed are called hybridised or hybrid orbitals.

No. of hybrid orbitals = No. of combining atomic orbitals of similar energy.

Table 1

Arrangement of the electron pairs about a cental atom A

Type of molecule	Total no. of electron pairs		Shape of molecule/Ions	Hybridisation type	Example
	Bond pairs	Lone pairs			
AB_2	2	–	Linear	sp	BeF_2
AB_3	3	–	Trigonal planar	sp^2	BF_3, $AlCl_3$
AB_2E	2	1	Bent	sp^3	SO_2, O_3
AB_4	4	–	Tetrahedral	sp^3	CH_4, NH_4^+
AB_3E	3	1	Pyramidal	sp^3	NH_3, PX_3 (X = F, Cl, Br, I)
AB_2E_2	2	2	Bent (angular)	sp^3	H_2O, OF_2, NH_2^-
AB_5	5	–	Trigonal bipyramidal	sp^3d	IF_5, PCl_5
AB_4E	4	1	See Saw/Irregular Tetrahedral	sp^3d	SF_4
AB_3E_2	3	2	Bent T-shaped	sp^3d	ClF_3
AB_2E_3	5		Linear	sp^3d	XeF_2, ICl_2^-, I_3^-
AB_6	5	–	Octahedral	sp^3d^2	SF_6, PF_6
AB_5E	5	1	Square pyramidal	sp^3d^2	BrF_5, $XeOF_4$, ClF_5
AB_4E_2	4	2	Square planar	sp^3d^2	XeF_4, ICl_4^-
AB_7	7	–	Pentagonal bipyramidal	sp^3d^3	IF_7

Hybridization scheme in complex ions (co-ordination entities) can be discussed with the help of valence bond theory.

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

2. Define an electrovalent bond. Write the factors that favour the formation of an electrovalent bond. Give two characteristics of an electrovalent compound.

3. Three elements have the following Lewis symbols :

A. ·B· :C·

(a) Place the elements in the appropriate groups of the periodic table.

(b) Show the charges on the ions formed by the elements.

(c) Write the formulae and the Lewis structures of the covalent compounds formed between :

(i) A and B (ii) A and C

4. Draw the Lewis structure of the species as mentioned below :

(a) in which the central atom has an incomplete octet.

(b) in which the central atom has an expanded octet.

(c) an odd electron molecule is formed.

5. How is the molecular orbital different from an atomic orbital ? Write the number of electrons which occupy the bonding molecular orbitals of H_2^- and H_2.

6. Which hybrid orbitals are used by carbon atoms in the following molecules :

(a) $CH_2=CH-C\equiv CH$ (b) CH_3COOH

7. The internuclear separation in a KCl molecule in the vapour is 2.60×10^{-8} cm. Assuming the complete transfer of electron (charge = 1.602×10^{-19} Coulombs) from K to Cl atom.

(a) Calculate the dipole moment of KCl molecule.

(b) Show the direction of the dipole moment.

(c) Calculate the percentage ionic character of KCl.

(Given : dipole moment of KCl is 3.36×10^{-29} coulomb-metre)

Ans. (i) -4.1652×10^{-29} c.m.

(ii) 80.1

[**Hint :** % ionic character $= \left(\frac{\mu_{obs}}{\mu_{ionic}} \times 100\right) = \frac{3.36 \times 10^{-29}\,cm}{4.1652 \times 10^{-29}\,cm} \times 100 = 80.1\%$]

[**Ans.** (i) 4.1652×10^{-29} c.m. (ii) 80.1%]

9. Which of the following species is diamagnetic or paramagnetic?

He_2^+, H_2, H_2^+.

[**Hint.** Liquid HCl is a covalent compound. HCL when dissolved in H_2O furnishes ions due to its palarnalure and high hychation energy]

(iii) NCl_5 does not exist while PCl_5 does.

(iv) H_2O is more polar than H_2S.

(v) BF_3 is non polar while NF_3 is polar.

[**Hint :** BF_3 has symmetrical triangular planar structure in which net dipole moment is zero, where NF_3 has pyramidal strcuture, where dipole moment is considerable.]

$\Delta_r G = 0$ At equilibrium

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

Important formulas used in thermodynamics calculations

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

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

$$\Delta_r S^{\varnothing} = \sum v_p \Delta S^{\varnothing} \text{ (products)} - \sum v_r \Delta S^{\varnothing} \text{ (reactants)}$$

$$\Delta_r H^{\varnothing} = \sum v_p \Delta_r H^{\varnothing} \text{ (products)} - \sum v_r \Delta_r H^{\varnothing} \text{ (reactants)}$$

$$\Delta_r G^{\varnothing} = \sum v_p \Delta_r G^{\varnothing} \text{ (products)} - \sum v_r \Delta_r G^{\varnothing} \text{ (reactants)}$$

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

$$-\Delta G = W_{useful}$$

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

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

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

(For definition of $\Delta_c H^{\theta}$, $\Delta_a H^{\theta}$, mean bond dissociation enthalpy (ΔH^{θ}_{A-B}), lattice enthalpy ($\Delta_L H^{\theta}$), $\Delta_{fus} H^{\theta}$, $\Delta_{vap} H^{\theta}$, $\Delta_{sub} H^{\theta}$, please refer NCERT text book Class XI, Part I, page 171 to 173.

Gibbs energy and equilibrium : A reversible reaction occur in either direction simultaneously so that a dynamic equilibrium is set up. This means that forward and reverse reaction should proceed with the decrease in Gibbs energy which is possible if the free energy of the system in minimum at equilibrium, *i.e.,* $\Delta_r G = 0$.

6. Standard enthalpy of formation of hydrazine [N_2H_4 (l)], hydrogen peroxide [H_2O_2 (l)] and water [H_2O (l)] are –50.4, –193.2 and –242.7 kJ/mol respectively. Calculate the standard enthalpy of formation for the following reaction :

$$N_2H_4\,(l) + 2H_2O\,(l) \rightarrow N_2\,(g) + 4H_2O\,(l)$$

7. In a process 701.0 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process ?

[**Ans.** q = + 701 J, W = – 394 J, ΔU = 307 J]

8. Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g Al from 35° C to 55° C. Molar heat capacity of Al is 24 J mol^{-1} K^{-1}.

[**Ans.** 1.09 kJ]

9. Under what conditions the following reactions occur spontaneously :

(a) Both ΔH and ΔS are negative for the reaction.

(b) Both ΔH and ΔS are positive for the reaction.

10. Calculate $\Delta_r H^\theta$ for the reaction :

$$H_2\,(g) + Br_2\,(g) \rightarrow 2HBr\,(g)$$

Bond enthalpy of various bonds are H–H = 436.0 kJ mol^{-1}, Br–Br = 192.0 kJ mol^{-1} and H–Br = 368.0 kJ mol^{-1}.

11. Hess's law is a corollary of the first law of thermodynamics. Explain.

12. Explain the following observations :

(a) When an ideal gas expands in vacuum there is neither absorption or evolution of heat but when a real gas expands cooling is observed.

(b) Although dissolution of NaCl in water is endothermic, but it readily dissolves.

13. (a) Decrease in enthalpy cannot be the sole criteria for spontaneity of a reaction. Justify with the help of an example.

(b) How can a chemical reaction with positive enthalpy and entropy changes be made entropy driven spontaneous reaction ?

14. All spontaneous reactions follow the criteria $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} > 0$. Starting from this relation, how can we derive a relationship between ΔG and spontaniety ?

15. The equilibrium constant for a reaction is 10. What will be the value of ΔG^θ ?

$$R = 8.314\ JK^{-1}\ mol^{-1},\ T = 300\ K$$

16. Calculate the entropy change in surroundings when 1.0 mol of H_2O (l) is formed under standard conditions. Given : $\Delta_f H^\theta$ [H_2O (l)] = –286.0 KJ mol^{-1}, T = 298 K.

decrease. Given the value of K= 61 for the reaction :

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 3NH_3\,(g) \text{ at 500 K.}$$

5. Consider the reaction :

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 3SO_3\,(g) \qquad \Delta_r H^\circ = -190 \text{ KJ/mol}$$

Indicate the direction in which the equilibrium will shift when :

(a) temperature is increased.

(b) pressure is decreased.

(c) an inert gas is added at constant volume and

(d) inert gas is added at constant pressure?

6. (a) Classify the following as homogeneous or heterogeneous equilibria :

(i) $2NO\,(g) + O_2\,(g) \rightleftharpoons 2NO_2\,(g)$

(ii) $Mg\,(s) + O_2\,(g) \rightleftharpoons 2MgO\,(s)$

(b) Consider the following transformations :

$A \rightleftharpoons B \qquad K_1 = 1$

$B \rightleftharpoons C \qquad K_2 = 2$

$C \rightleftharpoons D \qquad K_3 = 3$

Calculate the value of K for $A \rightleftharpoons D$

7. (a) Give one example each of a Lewis acid and a Lewis base.

(b) All Lewis bases are also Bronsted bases. Explain.

(c) K_b for NH_4OH and CH_3NH_2 are 1.8×10^{-5}, 4.4×10^{-4}. respectively. Which of them is stronger base and why?

8. Ammonia is prepared by Haber's process in which the following reaction occurs :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 93.6 \text{ KJ}$$

Mention the effect of following on the equilibrium conc. of ammonia :

(a) Increasing pressure

(b) Increasing temperature

(c) Use of a catalyst at an optimum temperature

9. Calculate the pH of following solution :

(i) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution.

(ii) 1.0 mL of 13.6M HCl is diluted with water to give 1.0L solution.

As its orbital is incomplete with $1s^1$ electronic configuration. It shows reactions by :

(a) loss of the only electron to give H^+.

(b) Gain of electron to form H^-.

(c) Sharing electrons to form a single covalent bond.

Hydrogen Peroxide (H_2O_2)

Oxidising action of H_2O_2 :

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (acidic medium)

$H_2O_2 + 2e^- \rightarrow 2OH^-$ (basic medium)

Reduction action of H_2O_2 :

$H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$ (acidic medium)

$H_2O_2 + 2OH^- \rightarrow 2H_2O + O_2 + 2e^-$ (basic medium)

H_2O_2 oxidises :

(a) Fe^{2+} to Fe^{3+} (acidic as well as basic medium)

(b) S^{2-} to SO_4^{2-} (acidic medium)

H_2O_2 reduces :

(a) MnO_4^- to Mn^{2+} (acidic medium)

(b) MnO_4^- to MnO_2 (basic medium)

(c) I_2 to I^- (basic medium)

Bleaching action

It acts as a bleaching agent and its bleaching action is due to the oxidation of colouring matter.

The strength of H_2O_2 solution is expressed as volume strength as given below :

Molarity × 11.2 = Volume strength of H_2O_2

Normality × 5.6 = Volume strength of H_2O_2

1 - MARK QUESTION

1. Justify the position of hydrogen in the periodic table.
2. Define 'autoprotolysis' of water.
3. Name the radioactive isotope of hydrogen.

8. Write ionic equations for each of the following reactions :

   (a) H_2O_2 reduces acidified potassium permanganate solution to colourless manganese sulphate.

   (b) H_2O_2 oxidises ferrous sulphate to ferric sulphate in acidic medium.

9. Explain why hydrogen peroxide acts as a bleaching agent ? Name the type of reaction involved in its bleaching action.

10. Write any four uses of dihydrogen.

3 - MARK QUESTIONS

1. Define the following with one example of each :

   (a) electron-deficient hydride

   (b) electron-precise hydride

   (c) electron-rich hydride

2. Account for the following :

   (a) PCl_5 exists but PH_5 does not

   (b) Water is responsible for moderation of the climate and the body temperature of living beings

   (c) Hard water is not suitable for boilers as well as for laundary.

   [Hint :

   (a) High $\Delta_{eg}H$ value of dihydrogen and less negative value of $\Delta_{eg}H$ of hydrogen do not favour to exhibit highest oxidation state of P and consequently the formation of PH_5, although P exhibit +3, +5 oxidation state.

   (b) High heat of vapourisation and high heat capacity.

   (c) Hard water form precipitate with soap and deposition of salts in the form of scales.]

3. Complete the following reactions :

   (a) $Ca_3H_2 + H_2O \rightarrow$

   (b) $AlCl_3\ (g) + H_2O \rightarrow$

   (c) $CaO\ (s) + H_2O \rightarrow$

4. Write chemical emulation involved in the preparation of hydrogen peroxide from

   (a) Barium peroxide

   (b) Peroxide sulphate

   (c) 2-Ethyl anthraquinol

5. Explain the following terms :
   (a) Hydrogenation
   (b) Syn gas
   (c) Water-shift reaction
6. What is permutit method for the removal of permanent hardness of water ? Give the name and chemical formula of the inorganic salt and the reaction involved in this method.
7. Assign the reason for the following observations :
   (a) The temporary hardness of water is removed by boiling.
   (b) In the Clark's method, only calculated amount of lime is added to hard water for removal of hardness.
   (c) Regeneration of sodium zeolite is essential by brine.
8. Complete the following reactions :
   (a) $CO\,(g) + H_2\,(g) \xrightarrow[\text{catalyst}]{\Delta}$
   (b) $Zn + NaOH \xrightarrow{\text{heat}}$
   (c) $P_4O_{10}\,(s) + 6H_2O \rightarrow$
9. Comment on the reaction of dihydrogen with :
   (a) Chlorine
   (b) Sodium
   (c) Copper(II) oxide

   [Hint :
   (a) H_2 reduces chlorine into chloride [Cl^-] ion and itself get oxidised to H^+ ion by chlorine to form HCl.
   (b) Dihydrogen is reduced by Na to form NaH, *i.e.*, Na^+H^-.
   (c) H_2 reduces Cu(II) oxide to copper Cu(0) and itself get oxidised to H_2O.]
10. Explain the following
    (a) The density of ice is less than that of liquid water?
    (b) The boiling point of water is less than that of H_2S.
    (c) NaH has higher reducing character than H_2O.
11. Classify the following reactions as hydrolysis, redix and hydration reaction.

10. Write balanced chemical equation of hydrolysis of sodium oxide, sodium peroxide, sodium superoxide.

11. Comment on the following :

(a) Lituim is the only alkali metal to form nitride directly.

(b) Thee mobilities of the alkali metal ions in aqueous solution are

$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

(c) E° for the reaction

$M^{2+}(aq) + 2e^- \rightarrow M(s)$ (where M = Ca, Sr or Ba) is nearly constant.

12. Choose the correct answer :

(a) when of the alkali metal is having the least melting point.

(i) Na (ii) K (iii) Rb (iv) Cs.

(b) Which one of the alkali metal give hydrated salts.

(i) Li (ii) Na (iii) K (iv) Cs.

(c) Which one of the alkali earth metal carbonates is thermally the most stable ?

(i) $MgCO_3$ (ii) $CaCO_3$ (iii) $SrCO_3$ (iv) $BaCO_3$

5 MARK QUESTIONS

Explain why :

(a) The following reaction :

$$-\overset{|}{\underset{|}{C}}-Cl + MF \rightarrow -\overset{|}{\underset{|}{C}}-F + MCl$$, proceed better with KF than with NaF.

(b) Sodium wire is used to remove moisture from benzene but cannot be used for drying alcohol.

(c) Li metal is kept wrapped in paraffin wax and not stored in kerosene.

(d) The crystalline salts of alkaline earth metals contain more water of crystallization than corresponding alkali metals.

(e) LiCl is more covalent than NaCl.

[**Hint :** (a) KF is more ionic than NaF because Na^+ ion is smaller in size than K^+. Thus KF will undergo above nucleophilic substitution.

(b) Sodium removes moisture from benzene by reacting with H_2O, however, C_2H_5OH reacts with sodium.

(ii) $PbCl_4$ is less stable than $SnCl_4$ but $PbCl_2$ is more stable than $SnCl_2$.

(iii) Gallium has higher ionization enthalpy than aluminium.

(b) Identify the compounds X and Y in the following reactions :

(i) $Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + X$

(ii) $X \xrightarrow[370\ K]{\Delta} HBO_2 \xrightarrow[> 370\ K]{\Delta} Y$

3. Compare the general trends in the following properties of the elements in groups 13 and 14 :

(a) Atomic size

(b) Ionization enthalpy

(c) Metallic character

(d) Oxidation states

(e) Nature of halides

4. When metal 'X' is treated with sodium hydroxide, a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound (A) is soluble in dilute HCl to form compound (C). The compound (A) when heated strongly gives (D), which is used to extract metal. Identify (X), (A), (B), (C) and (D). Write chemical equations to support their identities.

5. Assign reasons :

(a) Aluminium alloyes are used to make body.

(b) Conc. HNO_3 can be transported in aluminium countainens.

(c) Aluminium utensils should not be kept overnight.

(d) Aluminium wire is used to make transmission cables.

(e) A mixture of diture NaOH and aluminium pieces is ased to open drain.

6. Name the following —

(a) The crystalline form of silica used in modern-radio and T.V. broadcasting and mobile-radio communication!

(b) The oxide of carbon which forms a complex with haemoglobin 300 times more faster than O_2.

(c) The allotrope of Carbon which has $\Delta_f H° = 0$.

(d) Group 13 element which is used to measure high temperature !

(e) A type of polymer which is semiorganic in nature !

Purification and Characterization of Organic Compounds

(1) Lassaigne's test for nitrogen : Lassiagne's extract is heated with $FeSO_4$ solution in presence of alkali, the solution is cooled and acidified with dil. H_2SO_4. If a green or blue colouration is obtained, it confirms the presence of N in the organic compound. The chemisty of the test is :

$$\underset{\text{From organic compound}}{Na + C + N} \xrightarrow{\Delta} NaCN$$

$$2NaCN + FeSO_4 \rightarrow Fe[CN]_2 + Na_2SO_4; \qquad Fe[CN]_2 + 4NaCN \rightarrow \underset{\text{Sod. ferrocyanide}}{Na_4[Fe(CN)_6]}$$

$$3Na_4[Fe(CN)_6] + 4Fe^{3+} \rightarrow \underset{\text{Ferric ferrocyanide (Prussian Blue)}}{Fe_4[Fe(CN)_6]_3} + 12Na^+$$

This test is very delicate and is given by all compounds containing C and N. As such NH_2NH_2, NH_4Cl, $NaNO_3$ etc. do not respond to this test since they do not contain carbon.

Formation of blood red colour indicates the presence of both N and S.

$$\underset{\text{From organic compound}}{Na + C + N + S} \xrightarrow{\Delta} \underset{\text{Sod. thiocyanate or Sod. sulphocyanide}}{NaSCN}$$

$$Fe^{3+} + \overset{+}{N}a\overset{-}{S}C\overset{-}{N} \rightarrow \underset{\text{Ferric thiocyanate (blood red colour)}}{[Fe(SCN)_6]^{3+}} + Na^+$$

(2) Detection of sulphur : If S is present, during fusion with Na metal, Na_2S is formed which may be tested as follows :

(i) With sodium nitroprusside, violet colouration is produced.

$$\underset{\text{Sodium nitroprusside}}{Na_2S + Na_2[Fe(CN)_5NO]} \rightarrow \underset{\text{(Violet colour)}}{Na_4[Fe(CN)_5NOS]}$$

(ii) With lead acetate, black ppt. of PbS is formed.

$$Na_2S + (CH_3COO)_2Pb \rightarrow \underset{\text{(Black ppt.)}}{PbS} + 2CH_3COONa$$

(3) Detection of halogens :

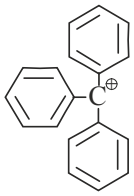
(a) Lassaigne's test : When the organic compounds is fused with Na metal, the halogens combine with Na to form sodium halides.

The presence of these halides is tested with $AgNO_3$ solution.

(i) A white ppt. soluble in NH_4OH and insoluble in dil. HNO_3 indicates chlorine.

$$Na + X \xrightarrow{\Delta} NaX$$

8. Which of the following carbocation is most stable :

(a) 

(b) $(CH_3)_3\overset{\oplus}{C}CH_2$

(c) $(CH_3)_3\overset{\oplus}{C}$

(d) $CH_3CH_2\overset{\oplus}{C}H_2$

(e) $H_3C-\overset{\oplus}{C}H-CH_2CH_3$

Arrange the above carbocations in the decreasing order of their stability.

9. Explain the following technique of separation of organic compounds with suitable examples :

(a) Crystallization

(b) Distillation

(c) Sublimation

(d) Chromatography

(e) Differential extraction

10. Discuss the chemistry of Lassaigne's test. Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur and halogens.

11. Name a suitable technique of separation of the components from a mixture of :

(a) calcium sulphate and camphor

(b) water and aniline

(c) a mixture of dyes

(d) copper sulphate and sodium chloride

(e) a mixture of amino acids

(f) glycerol and spentlye in soap industry.

12. Explain the terms inductive effect and electromeric effect. Arrange the following compounds in the increasing order of their acidic and basic strength :

products. A volume of 10.0 L (measured at STP) of this welding gas found to weigh 11.6 g. Calculate :

(a) Empirical formula

(b) Molar mass of the gas

(c) Molecular formula

19. An organic compound on analysis gave following data

(i) 0.25g of compound on complete combustion gave 0.37g CO_2 and 0.2g of water.

(ii) 0.25g of compound on analysis by Duma's method gave 32 ml of nitrogen at N.T.P.

Calculate the parcentage of C, H and N in compound.

UNIT-14

ENVIRONMENTAL CHEMISTRY

(1) Main regions of the atmosphere are (i) troposphere, (ii) stratosphere, (iii) mesosphere and (iv) thermosphere.

(2) The addition of any undesirable material in air, water and soil by natural source or due to human activity to such a level of concentration which adversely affects the environment is called environmental pollution.

(3) Pollutants can be (i) gaseous air pollutants (*e.g.,* SO_2, NO_2, CO_2, H_2S, hydrocarbons, ozone etc.) and (ii) particulate pollutants (*e.g.,* dust, mist, fumes, smoke, smog etc.)

(4) **Green House Effect :** Warming of the earth by absorption and re-emission of solar radiations is called green house effect. Gases responsible for the green house effect are CO_2, CH_4, N_2O, CFCs, O_3 and water vapours.

(5) The word **smog** is a combination of smoke and fog. Classical smog occurs in cool humid climate and photochemical smog occurs in warm, dry and sunny climate. Classical smog is a mixture of smoke, fog and sulphur dioxide. It is reducing in nature while photochemical smog is oxidising in nature. The common components of photochemical smog are O_3, NO, acrolein, formaldehyde and peroxyacetyl nitrate (PAN). Both O_3 and PAN act as powerful eye irritants. O_3 and NO irritate the nose and throat and their high concentration causes headache, chest pain, dryness of the throat, cough and difficulty in breathing. It also causes corrosion of metals, stones, building materials, rubber and painted surfaces.

(6) In 1980, Ozone hole was detected over south pole. The ozone layer is depleting because of the presence of certain chemicals like CFC's in the stratosphere. The most serious effect of the depletion of ozone layer is that the ultraviolet radiation coming from the sun can pass through the stratosphere and reach the surface of the earth and can lead to ageing of skin, cataract, sunburn, skin cancer, killing of many phytoplanktons, damage to fish productivity etc.

(7) Water pollution is defined as the contamination of water by substance which make it harmful for health of animals, plants or aquatic life and make it unfit for domestic, industrial and agricultural use.

$$\lambda = \frac{c}{v} = \frac{3 \times 10^8 \text{ m/s}}{4.37 \times 10^{14} \text{ s}^{-1}}$$

$\therefore \lambda = 0.686 \times 10^{-6}$ m

$\therefore \lambda = 686$ nm **(½ Mark)**

(*ii*) Here $n_1 = 6$ & $n_2 = 1$

The energy gap between two orbits for a hydrogen atom is given as

$$\Delta E = 2.18 \times 10^{-18} \left(\frac{1}{n_1^2} \frac{-1}{n_2^2} \right)$$ **(½ Mark)**

$$= 2.18 \times 10^{-18} \text{J} \left(\frac{1}{6^2} - \frac{1}{1^2} \right)$$

$$= 2.18 \times 10^{-18} \text{J} \left(\frac{1 - 36}{36} \right)$$

$$\Delta E = -2.11 \times 10^{-18} \text{J}$$ **(½ Marks)**

Since ΔE is negative energy is emitted, frequency of photon is given by

$$\nu = \frac{\Delta E}{h}$$ **(½ Mark)**

$$= \frac{2.18 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ Js}}$$

$= 3.18 \times 10^{15} \text{ s}^{-1}$

$= 3.18 \times 10^{15}$ Hz **(½ Mark)**

Ans 21. (*i*) For n = 1,

Value of l = n – 1

= 1 – 1

= 0

For each value of l,

Value of $m_l = -1, \ldots\ldots, 0, \ldots\ldots, +1$ **(1 Mark)**

Therefore,

For n = 1, l = 0,

$m_l = 0$

Thus the value of $m_l = 1$ is not possible. **(1 Mark)**

(*ii*) Electronic configuration of Cu^{2+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

(1 Mark)

Ans 22. (*i*) Resonating structure of O_3 molecule **(1 Mark)**

(*ii*) In NF_3, N atom involves Sp^3 hybridization and one position is occupied by a lone pair. Therefore the molecule is trigonal pyramidal. But in BF_3, B in involves SP^2 hybridization having trigonal planar geometry. Thus NF_3 is trigonal pyramidal while BF_3 is trigonal planar, even though both are tetra atomic molecules. **(1 Mark)**

(*iii*) $C_3 \rightarrow Sp^3$

$C_4 \rightarrow SP$ **(½ × 2 Marks)**

Ans 23. (*i*) If the concentration of SO_2 is increased the equilibrium will shift in the forward direction to consume the reactant SO_2.

(1 Mark)

(*ii*) If the concentration of SO_3 increased the equilibrium will shift in the backward direction to consume the product SO_3. **(1 Mark)**

(*iii*) If the temperature is increased, the equilibrium will shift in the backward direction as the increase in temperature will be compensated by absorbing heat. **(1 Mark)**

Ans 24. (*i*) **Common ion effect :** The suppression in degree of dissociation of weak electrolyte by adding in it a strength electrolyte having the common ion is called common ion effect. **(1 Mark)**

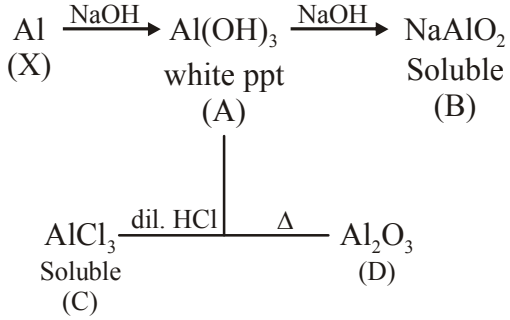
(*ii*) **Buffer Solution :** Buffer solution is that which resist the change in pH on addition of small amount of acid or base in it.

(1 Mark)

its octet Si is linked to four O atoms around it by sigma bond & these constitutes network structure, which is responsible for its solid state. **(1 Mark)**

OR

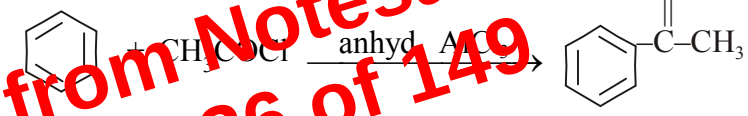
Ans 29.



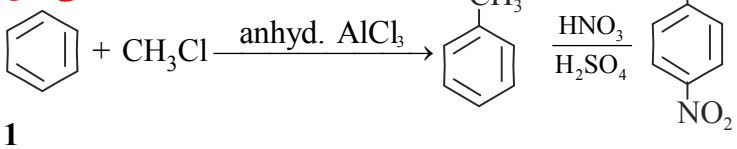
2 Marks for writing reactions

1 Marks for identifying X

½ mark each for correctly identifying A, B, C and D.

Ans 30. (*a*) (*i*) 

1

(*ii*) 

1

(*iii*) $CH_3\ COOH + NaOH \rightarrow CH3COONa \xrightarrow[NaOH]{CaO} CH_4$ **1**

(*b*) $CH_3CH_2CH_2CH_2CH = CH_2 + HBr \rightarrow CH_3CH_2CH_2CH_2CH_2CH_2Br$

(*c*) The H attached to *sp* hybrid carbon becomes acidic due to high electronegativity of (*sp* hybridised). C

OR