

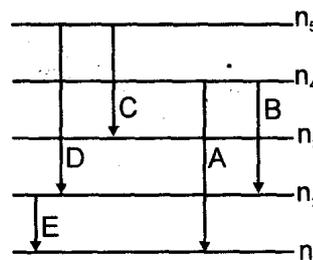
**PHYSICAL
CHEMISTRY
PART-1**

ATOMIC STRUCTURE

ONLY ONE OPTION CORRECT

1. Probability of finding the electron's wave of 'S' orbital doesn't depend upon –
 (A) Distance from nucleus (r) (B) Energy of 's' orbital
 (C) Principal quantum number (D) Azimuthal quantum number

2. For a hypothetical H like atom which follows Bohr's model, some spectral lines were observed as shown. If it is known that line 'E' belongs to the visible region, then the lines possibly belonging to ultra violet region will be (n₁ is not necessarily ground state)
 [Assume for this atom, no spectral series shows overlaps with other series in the emission spectrum]



- (A) B and D (B) D only
 (C) C only (D) A only
3. The number of photons emitted in 10 hours by a 60W sodium lamp (λ , of photon = 6000 Å)
 (A) 6.50×10^{24} (B) 6.40×10^{23} (C) 8.40×10^{23} (D) 3.40×10^{23}

[Take $h\nu = 12400 \text{ eV}\text{\AA}$, $h = \text{Planck's constant}$, $c = \text{speed of light}$]

4. Radius of 3rd orbit of Li²⁺ ion is 'x' cm then de-broglie wavelength of electrons in the 1st orbit of H is
 (A) $\frac{2\pi x}{3}$ cm (B) $6\pi x$ cm (C) $3\pi x$ cm (D) $\frac{2\pi x}{6}$ cm

5. Ratio of frequency of revolution of electron in the 2nd excited state of He and 2nd state of hydrogen is:
 (A) $\frac{32}{27}$ (B) $\frac{27}{32}$ (C) 1/54 (D) 27/2

6. In any subshell, the maximum number of electrons having same value of spin quantum number is:
 (A) $\sqrt{l(l+1)}$ (B) $l + 2$ (C) $2l + 1$ (D) $4l + 2$

7. A proton accelerated from rest through a potential difference of 'V' volts has a wavelength λ associated with it. An alpha particle in order to have the same wavelength must be accelerated from rest through a potential difference of
 (A) V volt (B) 4V volt (C) 2V volt (D) $\frac{V}{8}$ volt

8. Consider the ground state of Cr atom (Z = 24). The numbers of electrons with the azimuthal quantum numbers, $l = 1$ and 2 are, respectively:
 (A) 16 and 5 (B) 12 and 5 (C) 16 and 4 (D) 12 and 4

9. Number of electrons having $l + m$ value equal to zero in ${}_{26}\text{Fe}$ may be
 (A) 13 (B) 14 (C) 7 (D) 12

10. 4000 Å photon is used to break the iodine molecule, then the % of energy converted to the K.E. of iodine atoms if bond dissociation energy of I₂ molecule is 246.5 kJ/mol.
 (A) 8% (B) 12% (C) 17% (D) 25%

ONE OR MORE THAN ONE OPTION CORRECT

11. If the wave number of 1st line of Balmer series of H-atom is 'x' then:

(A) wave number of 1st line of Lyman series of the He⁺ ion will be $\frac{108x}{5}$

(B) wave number of 1st line of Lyman series of the He ion will be $\frac{36x}{5}$

(C) the wave length of 2nd line of Lyman series of H-atom is $\frac{5}{32x}$

(D) the wave length of Lyman series of H-atom is $\frac{32x}{5}$

12. The wave functions of 3s and 3p_z orbitals are given by

$$\psi_{3s} = \frac{1}{9\sqrt{3}} \left(\frac{1}{4\pi} \right)^{1/2} \left(\frac{z}{a_0} \right)^{3/2} \left(6 - \frac{4zr}{a_0} + \frac{4z^2r^2}{9a_0^2} \right) e^{-zr/3a_0}$$

$$\frac{1}{9\sqrt{6}} \left(\frac{3}{4\pi} \right)^{1/2} \left(\frac{z}{a_0} \right)^{3/2} \left(4 - \frac{2zr}{3a_0} \right) \left(\frac{2zr}{3a_0} \right) e^{-zr/3a_0} \cos \theta$$

from these we can conclude

- (A) number of nodal surface for 3p_z & 3s orbitals are equal
 (B) the angular nodal surface of 3p_z orbital has the equation $\theta = \pi/2$
 (C) The radial nodal surfaces of 3s orbital and 3p_z orbitals are at equal distance from the nucleus
 (D) 3s electron has greater penetrating power into the nucleus in comparison to 3p, electrons
13. In a hydrogen like sample electron is in 2nd excited state, the Binding energy of 4th state of this sample is 13.6 eV, then
 (A) A 25 eV photon can set free the electron from the second excited state of this sample.
 (B) 3 different types of photon will be observed if electrons make transition up to ground state from the second excited state
 (C) If 23 eV photon is used then K. E. of the-ejected electron is 1 eV.
 (D) 2nd line of Balmer series of this sample has same energy value as 1st excitation energy of H-atoms.
14. 1st excitation potential for the H-like (hypothetical) sample is 24 V. Then:
 (A) Ionisation energy of the sample is 36 eV (B) Ionisation energy of the sample is 32 eV
 (C) Binding energy of 3rd excited state is 2 eV (D) 2nd excitation potential of the sample is

$$\frac{32 \times 8}{9} \text{ V}$$

15. A hydrogen like atom in ground state absorbs 'n' photons having the same energy and it emits exactly 'n' photons when electronic transition takes place. Then the energy of the absorbed photon may be
 (A) 91.8 eV (B) 40.8 eV (C) 48.4 eV (D) 54.4 eV

16. In a hydrogen like sample two different types of photons A and B are produced by electronic transition. Photon B has its wavelength in infrared region if photon A has more energy than B, then the photon A may belong to the region.
 (A) ultraviolet (B) visible (C) infrared (D) None
17. Hydrogen atoms in a particular excited state 'n', when all returned to ground state, 6 different photons are emitted. This of the following is/are incorrect.
 (A) Out of 6 different photons only 2 photons have speed equal to that of visible light.
 (B) If highest energy photon emitted from the above sample is incident on the metal plate having work function 8 eV, AKE of liberated photo-electron may be equal to or less than 4.75 eV.
 (C) Total number of radial nodes in all the orbitals of nth shell is 24.
 (D) Total number of angular nodes in all the orbitals in (n-1)th shell is 23.
18. In a H-like sample electrons make transition from 4th excited state to 2nd state then
 (A) 10 different spectral lines are observed
 (b) 6 different spectral lines are observed
 (C) number of lines belonging to the balmier series is 3
 (D) Number of lines belonging to paschen series is 2.

PARAGRAPH BASED QUESTIONS

Comprehension # 2

If hydrogen atoms (in the ground state) are passed through an homogeneous magnetic field, the beam is split into two parts. This interaction with the magnetic field shows that the atoms must have magnetic moment. However, the moment cannot be due to the orbital angular momentum since $\ell = 0$. Hence one must assume existence of intrinsic angular momentum, which as the experiment shows, has only two permitted orientations.

Spin of the electron produces angular momentum equal to $S = \sqrt{s(s+1)} \frac{h}{2\pi}$ where $S = \frac{1}{2}$.

Total spin of an atom = $+\frac{n}{2}$ or $-\frac{n}{2}$

Where n is the number of unpaired electron.

The substances which contain unpaired electrons in their orbitals behave as paramagnetic substances. The paramagnetism is expressed in terms of magnetic moment.

The magnetic moment of an atom

$$\mu_s = \sqrt{s(s+1)} \frac{eh}{2\pi mc} = \sqrt{\frac{n}{2} \left(\frac{n}{2} + 1 \right)} \frac{eh}{2\pi mc} \quad s = \frac{n}{2}$$

$$\Rightarrow \mu_s = \sqrt{n(n+2)} \text{ B.M}$$

n - number of unpaired electrons

$$1. \text{ B.M. (Bohr magneton)} = \frac{eh}{4\pi mc}$$

If magnetic moment is zero the substance is di-magnetic.

19. Which of the following ion has highest magnetic moment.
 (A) Fe^{e+} (B) Mn²⁺ (C) Cr³⁺ (D) V³⁺
20. If an ion of ²⁵Mn has a magnetic moment of 3.873 B. M. Then Mn is in which state.
 (A) + 2 (B) + 3 (C) + 4 (D) + 5

21. Which of the following is a paramagnetic substance.
 (A) Mg^{2+} (B) Cu^+ (C) Mn^{+7} (D) Ti^{+2}
22. The number of unpaired electrons in Mn^{4+} ($Z = 25$) is –
 (A) Four (B) Two (C) Five (D) Three

Comprehension # 2

The French physicist Louis de Broglie in 1924 postulated that matter, like radiation, should exhibit a dual behaviour. He proposed the following relationship between the wavelength λ of a material particle, its linear momentum p and planck constant h .

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

The de Broglie relation implies that the wavelength of a particle should decrease as its velocity increases. It also implies that for a given velocity heavier particles should have shorter wavelength than lighter particles. The waves associated with particles in motion are called matter waves or de Broglie waves. These waves differ from the electromagnetic waves as they

- (i) have lower velocities
- (ii) tame RE electrical and magnetic fields and
- (iii) are not emitted by the particle under consideration.

The experimental confirmation of the de Broglies relation was obtained when Davisson and Gerber, in 1927, observed that a beam of electrons is diffracted by a nickel crystal. As diffraction is a characteristic property of waves, hence the beam of electron behaves as a wave, as proposed by de broglie.

23. If proton, electron and α -particle are moving with same kinetic energy then the order of their de-Broglie's wavelength.
 (A) $\lambda_p > \lambda_e > \lambda_a$ (B) $\lambda_a > \lambda_p > \lambda_e$ (C) $\lambda_a < \lambda_p < \lambda_e$ (D) $\lambda_e = \lambda_p < \lambda_a$
24. Using Bohr's theory, the transition, so that the electrons de-Broglie wavelength becomes 3 times of its original value in He^+ ion will be
 (A) $2 \longrightarrow 6$ (B) $2 \longrightarrow 4$ (C) $1 \longrightarrow 4$ (D) $1 \longrightarrow 6$
25. De-Broglie wavelength of an electron travelling with speed equal to 1% of the speed of light
 (A) 400 pm (B) 120 pm (C) 242 pm (D) 375 pm

Comprehension #3

If an electron is in any higher state $n = n_2$ and makes a transition to ground state, then total no. of different photons emitted is equal to $\frac{n \times (n-1)}{2}$.

If an electrons is in any higher state $n = n_2$ and makes a transition to another excited state $n = n_1$, then total no. of different photons emitted is equal to $\frac{\Delta n (\Delta n + 1)}{2}$, where $\Delta n = n_2 - n_1$.

Note: In case of single isolated atom if electron make transition from n^{th} state to the ground state then max. number of spectral lines observed = $(n - 1)$.

26. Two samples are taken, in 1st sample mole ratio of H to H⁺ is 1: 2. In 2nd sample mole ratio of H to He⁺ is 2: 1. If n_1 is number of spectral lines produced by 1st sample and number of spectral lines produced by 2nd sample is n_2 then $n_1 : n_2$ will be –
(There is sufficient number of both types of atom and both are in same excited state in both sample)
(A) 2 : 1 (B) 1 : 2 (C) 1 : 1 (D) None of these
27. Which of the following statements is/are true?
(I) If H atoms are in 3rd state then number of maximum spectral line produced by 2 atoms will be equal to number of maximum spectral lines produced by 3 H-atoms
(II) For third excited state, maximum number of spectral line produced by He⁺ and maximum number of spectral line produced by 4 H – atom are not equal.
(III) Energy evolved from 3 to 2 transitions in He cannot be used for any transition in Li²⁺.
(A) I & III (B) II & III (C) All (D) I & II.
28. In a sample one H atom is in 1st excited state, two He⁺ ions is in 2nd excited state and three Li²⁺ ions is in 3rd excited state are present then maximum, number of spectral line which can be obtained when all possible transition terminated at $n = 1$.
(A) 11 (B) 12 (C) 13 (D) 17

MATRIX MATCH

29. **Match the following:**
 P_n = potential energy, E_n = total energy
 f = frequency, Z = atomic number
 v_n = velocity in n^{th} orbit
 T_n = time period in n^{th} orbit

Column I	Column II
(A) $E_n \propto r^y$, $y = ?$	(p) 1/2
(B) E_n/P_n	(q) 1
(C) $\frac{1}{f_n^{x-1}} \propto Z$, $x = ?$	(r) 2
(D) $(v_n \times T_n)^t \propto r_n$, $t = ?$	(s) - 1

30. Match the following:

B.E. – Binding energy

I.E. – Ionization energy:

Column I

Column II

(A) of He atom in an excited state (p) Infrared region

(B) $7 \rightarrow 3$ transition in H-atom (q) 3.4 eV

(C) $5 \rightarrow 1$ transition in H-atom (r) 13.6 eV

(D) Series limit of Balmer series in H-atom (s) 10 Spectral lines observed

31. Match the following:

Column I

Column II

(A) $n = 6 \rightarrow n = 3$ (In H-atom)

(p) 10 lines in the spectrum

(B) $n = 7 \rightarrow n = 3$ (In H-atom)

(q) Spectral lines in visible region

(C) $n = 5 \rightarrow n = 2$ (In H-atom)

(r) 6 lines in the spectrum

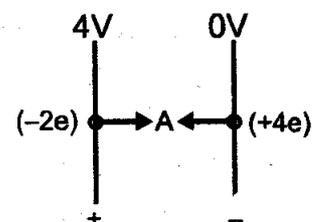
(D) $n = 6 \rightarrow n = 2$ (In H-atom)

(s) Spectral lines in infrared region

INTEGER TYPE

32. Find out the number of waves made by a Bohr electron in one complete revolution in its 3rd orbit.

33. In the assembly as shown below, the potential difference across the plates is 4 volts. A positive particle of charge $+4e$ is projected from the negative plate with an initial kinetic energy of 4eV and the negative particle of charge $-2e$ is projected from the positive plate. Both the particles reach point 'A' with zero kinetic energy.



Find the initial kinetic energy of the negative particle in eV.

34. Electrons in a sample of H – atoms make transitions from state $n = x$. to some lower excited state. The emission spectrum from the sample is found to contain only the lines belonging to a particular series. If one

Of the photons had an energy of 0.6375 eV. Then find the value of x . [Take $0.6375 \text{ eV} = \frac{3}{4} \times 0.85\text{eV}$]

35. Find the number of electrons in chromium (${}_{24}\text{Cr}$) which have orbital angular momentum equal to

$$\frac{h}{\sqrt{2}\pi}$$

36. A hydrogen like atom (atomic; number Z) is in a higher excited state of quantum number n . This excited atom can make a transition to the first excited state by successively emitting two photons of energies 10.20 eV and 17.00 eV respectively. Alternatively, the atom from the same excited state can make a transition to the second excited state by successively emitting two photons of energy 4.25 eV and 5.95 eV respectively. Determine the values of n and Z (ionisation energy of hydrogen atom = 13.6 eV).

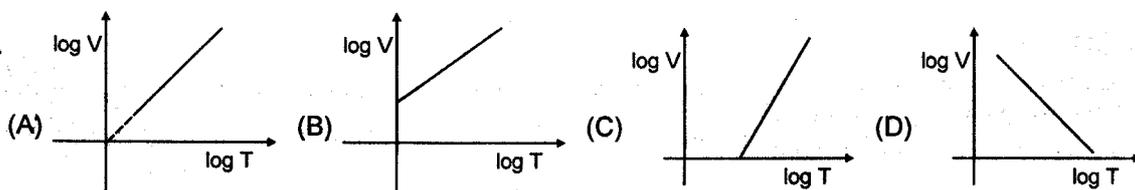
GASEOUS STATE

ONLY ONE OPTION CORRECT

1. If density of vapours of a substance of molar mass 18 gm / mole at 1 atm pressure and 500 K is 0.36 kg m^{-3} , then value of Z for the vapours is : (Take $R = 0.082 \text{ L atm mole}^{-1} \text{ K}^{-1}$)
- (A) $\frac{41}{50}$ (B) $\frac{50}{41}$ (C) 1.1 (D) 0.9

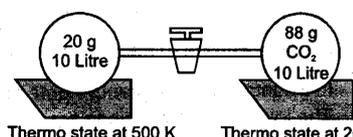
2. Equal amount (mass) of methane and ethane have their total translational kinetic energy in the ratio 3: 1 then their temperatures are in the ratio.
- (A) 5 : 8 (B) 45 : 8 (C) 15 : 8 (D) 8 : 5

3. Which of the following sketches is an isobar $\left(\frac{nR}{p} > 1\right)$



4. A sample of water gas has a composition by volume of 50% H_2 , 45% CO and 5% CO_2 . Calculate the volume in litre at S.T.P. of water gas which on treatment with excess of steam will produce 5 litre H_2 . The equation for the reaction is : $\text{CO} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2$
- (A) 4.263 Litre (B) 5.263 Litre (C) 6.263 Litre (D) 7.263 Litre

5. Flask A of volume 10 liter containing 20 gram of H_2 and flask B of volume 10 litre containing 88 gram CO_2 are connected by a connector having negligible volume. When valve of the connector is opened what is the composition of H_2 gas in flask B after opening the valve.



- (A) 10% (B) 13% (C) 15% (D) 20%

6. Consider the reaction, $2\text{X}(\text{g}) + 3\text{Y}(\text{g}) \longrightarrow \text{Z}(\text{g})$
Where gases X and Y are insoluble and inert to water and Z form a basic solution. In an experiment 3 mole each of X and Y are allowed to react in 15 lit flask at 500 K. When the reaction is complete, 5L of water is added to the flask and temperature is reduced to 300 K. The pressure in the flask is (neglect aqueous tension)
- (A) 1.64 atm (B) 2.46 atm (C) 4.92 atm (D) 3.28 atm

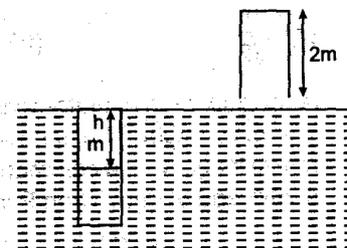
7. Three gases A, B and C are at same temperature if their r.m.s speed are in the ratio $1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$ then their molar masses will be in the ratio
- (A) 1 : 2 : 3 (B) 3 : 2 : 1 (C) $1 : \sqrt{2} : \sqrt{3}$ (D) $\sqrt{3} : \sqrt{2} : 1$

8. There are n containers having volumes V, 2V,, nV. A fixed mass of a gas is filled in all containers connected with stopcock. All containers are at the same temperature if pressure of first container is P then final pressure when all stopcocks are opened is:

- (A) $\frac{np}{n(n+1)}$ (B) $\frac{2np}{n(n+1)}$ (C) $\frac{3np}{n(n+1)}$ (D) $\frac{np}{2n(n+1)}$

9. SO_2 and CH_4 are introduced in a vessel in the molar ratio 1 : 2. The ratio of molecules of two gases present in the container when their rate becomes equal is
 (A) 1 : 2 (B) 2 : 1 (C) 4 : 1 (D) 1 : 4

10. A 2 m long tube closed at one end is lowered vertically into water until the closed end is flush with the water surface. See figure below. Calculate the water level height in the tube of hydrostatic water head, Temperature = 25°C, Density of water (pressure).



- (A) 1.01 m (B) 0.29 m
 (C) 1.71 m (D) 0.92 m
11. At a certain temperature for which $RT = 25 \text{ lit. atm. mol}^{-1}$, the density is $0.020 P^2$, where P is the pressure in atmosphere. The molecular weight is
 (A) 25 (B) 50 (C) 75

12. A mixture of carbon monoxide and carbon dioxide is found to have a density of 1.7 g/lit at S.T.P. The mole fraction of carbon monoxide is
 (A) 0.37 (B) 0.40 (C) 0.30 (D) 0.50

13. If equal weights of oxygen and nitrogen are placed in separate containers of equal volume at the same temperature, which one of the following statements is true?
 (mol wt: $\text{N}_2 = 28$, $\text{O}_2 = 32$)
 (A) Both flasks contain the same number of molecules.
 (B) The pressure in the nitrogen flask is greater than the one in the oxygen flask.
 (C) More molecules are present in the oxygen flask.
 (D) Molecules in the oxygen flask are moving faster on the average than the ones in the nitrogen flask.

14. The molecular radius for a certain gas = 1.25 Å. What is a reasonable estimate of the magnitude of the van der Waals constant, b, for the gas?
 (A) 0.98×10^{-2} litre/mole (B) 1.43×10^{-2} litre/mole (C) 1.97×10^{-2} litre/mole (D) 3.33×10^{-2} litre/mole

15. Given the value of their van der Waals' constant 'a' arrange the following gases in the order of their expected liquification pressure at a temperature T. T is below the critical point of all the gases.

Gas	CH_4	Kr	N_2	Cl_2			
'a' (atmL ² . Mol ⁻¹)		2.283	2.439	1.408 6.579			
(A)	$\text{CH}_4 < \text{Kr} < \text{N}_2 < \text{Cl}_2$	(B)	$\text{N}_2 < \text{CH}_4 < \text{Kr} < \text{Cl}_2$	(C)	$\text{Cl}_2 < \text{Kr} < \text{CH}_4 < \text{N}_2$	(D)	$\text{Cl}_2 < \text{N}_2 < \text{Kr} < \text{CH}_4$

16. The critical volume of a gas is $0.072 \text{ lit. mol}^{-1}$. The radius of the molecule will be, in cm

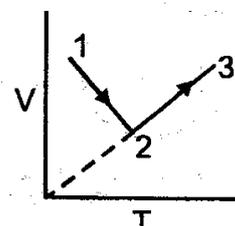
- (A) $\left(\frac{3}{4\pi} \times 10^{-23}\right)^{\frac{1}{3}}$ (B) $\left(\frac{4\pi}{3} \times 10^{-23}\right)^{\frac{1}{3}}$ (C) $\left(\frac{3\pi}{4} \times 10^{-23}\right)^{\frac{1}{3}}$ (D) $\left(\frac{3}{4\pi} \times 10^{-8}\right)^{\frac{1}{3}}$

17. The van der Waals' constant 'b' for N_2 and H_2 has the values $0.039 \text{ lit mol}^{-1}$ and $0.0266 \text{ lit mol}^{-1}$. The density of solid N_2 is 1 g cm^{-3} . Assuming the molecules in the solids to be close packed with the same percentage void, the density of solid H_2 would be (in g cm^{-3})
 (A) 0.114 (B) 0.682 (C) 1.466 (D) 0.071

18. Which of the following statements is not true?
 (A) The ratio of the mean speed to the rms speed is independent of the temperature.
 (B) The square of the mean speed of the molecules is equal to the mean squared speed at a certain temperature.
 (C) Mean kinetic energy of the gas molecules at any given temperature is independent of the mean speed.
 (D) The difference between rms speed and mean speed at any temperature for different gases diminishes as larger if larger molar masses are considered.
19. If 10^{23} gas molecules each having a mass of $1a^{25}$ kg, placed in a 1 L container, moving with rms speed of 10^5 cm/sec. then the total KE of gaseous molecules and pressure exerted by molecules, respectively are :
 (A) 10 kJ, 3.33×10^6 Pa (B) 5 kJ, 3.33×10^8 Pa
 (C) 10 kJ, 3.37×10^7 Pa (D) 5 kJ, 3.33×10^7 Pa

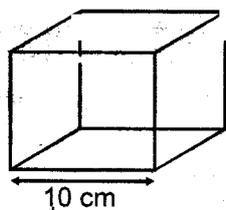
ONE OR MORE THAN ONE OPTION CORRECT

20. Following graph is constructed for the fixed amount of the gas.

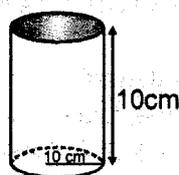


- (A) From 1 - 2 pressure will increase
 (B) From 2 - 3 pressure remains constant
 (C) Gas pressure at (3) is greater at state (1)
 (D) From 1 - 2 pressure will decrease
21. Which of following statements are correct
 (A) Average velocity of molecules of a gas in a container is zero.
 (B) All molecules in a gas are moving with the same speed.
 (C) If an open container is heated from 300 K to 400 K the fraction of air which goes out with respect to originally present is $\frac{1}{4}$.
 (D) If compressibility factor of a gas at STP is less than unity then its molar volume is less than 22.4 L at STP.
22. If the pressure of the gas contained in a closed vessel is increased by 20% when heated by 273°C then its initial temperature must have been.
 (A) 1092°C (B) 1029°C (C) 1365°C (D) 1365°K
23. Two flask A and B have equal volumes. Flask A contains hydrogen at 600 K while flask B has same mass of CH_4 at 300 K. Then choose the correct options.
 (A) In flask A the molecules move faster than B (B) In flask B the molecules move faster than A
 (C) Flask A contains greater number of molecules than B (D) Flask B contains more molecules than A

24. There are three closed containers in which equal amount of the gas are filled.



(I)



(II)

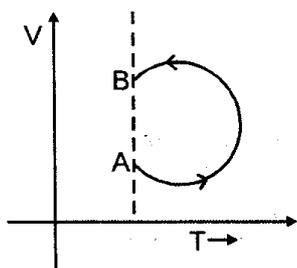


(III)

If the containers are placed at the same temperatures then find the correct options:

- (A) Pressure of the gas is minimum in (III) container (B) Pressure of the gas is equal in (I) & (II) container
 (C) Pressure of the gas is maximum in (I) (D) The ratio of pressure in II and III container is 3: 4

25. If the rms velocity of nitrogen and oxygen molecule are same at two different temperature and same pressure then.
- (A) Average speed of molecules is also same
 (B) density (gm/lit.) of nitrogen and oxygen is also equal.
 (C) Number of moles of each gas is also equal.
 (D) most probable velocity of molecules is also equal.
26. The pressure of 11 gm of a gas which is placed in a 4 litres container at 127°C is 2 atm, then the gas would be? (Take $R = 0.08 \text{ ltr. atm/mol K}$.)
 (A) N_2O (B) O_3 (C) NO_2 (D) CO_2
- 27.



With reference to the above graph, choose the correct alternatives

- (A) $P_B > P_A$ (B) $P_A > P_B$
 (C) Pressure first increases then decreases (D) Pressure first decreases then increases

PARAGRAPH BASED QUESTIONS

Comprehension #1

The system shown in the figure is in equilibrium, where A and B are isomeric liquids and form an ideal solution at T_K . standard vapour pressure of A and B are P_A° and P_B° respectively at T_K . We collect the vapour of A and B in two container of volume V , first container is maintained at $2T_K$ and

second container is maintained at $\frac{3T}{2} K$. At the temperature greater than T_K , both A and B exist

in only gaseous form. Total vapour pressure of the system at T_K is given as

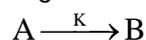
$$P_T = P_A^\circ X_A + P_B^\circ X_B$$

Where X_A and X_B are the mole fraction of A and B in liquid a mixture.

In container (1)

We assume that collected gases behave ideally at $2T_K$ and there can take place isomerisation reaction in which A converted into B by first order kinetics

Reaction is given as



In Container (II)

At the given temperature $\frac{3T}{2}$, A and B are ideal in nature and n

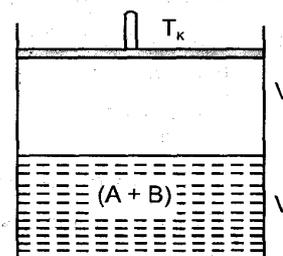
mixing in nature. A small pin hole is made into container. We can determine the initial rate of effusion of both gases in vacuum by the expression

$$r = \frac{kp}{\sqrt{m}}$$

Where P = pressure difference between system and surrounding

K = positive constant

M = Molecular weight of the gas.



28. If partial vapour pressure of A is twice that of partial vapour pressure of B and total V.P. is equal to 2T at T = 50 K and V = 8.21 lit, then number of mole of A and B in vapour phase is :
- (A) $\frac{8}{3}, \frac{4}{3}$ (B) 3, 1 (C) 2, 2 (D) 1, 3
29. Vapour is collected and passed into a container of volume 8.21 lit, maintained at 50 K and after 5 min number of mole of B = $\frac{8}{3}$. Then calculate pressure developed into the container after two half lives.
- (A) 2 atm (B) 4 atm (C) 1 atm (D) 0.5 atm
30. If vapour is collected in container of volume 8.21 lit maintained at 75 K then ratio of initial rate of effusion of Gas A and B is given as:
- (A) 2 : 1 (B) 1 : 2 (C) 4 : 1 (D) 1 : 4

Comprehension # 2

Gas 'A' (Molar Mass of A = 128 g mol⁻¹) is taken in a closed container at the initial total pressure of 1000 mm of Hg. Pressure of the gas decreases to 900 torr in 5 seconds due to the diffusion through square cross section. Another similar size container is taken in which gaseous mixture of A and B are taken. (Molar mass of the mix is $\frac{472}{5}$) at the total pressure of 5000 torr (molar mass of B = 72 g mol⁻¹). A rectangular cross-section is made in this container and gases are allowed to diffuse. Width of this rectangular cross-section is same as the side of the square cross section and length of the rectangular cross-section is 50% more than the width. Assume that the gases A and B are non reacting and rate of diffusion of the gases are only dependent upon the initial total pressure and it is independent of the change in the pressure due to diffusion. Assume all other conditions to be identical.

31. Gas diffused out initially from 2nd container has composition:
- (A) $\frac{1}{A} = \frac{3}{7}$ (B) $X_B = \frac{3}{5}$ (C) $X_A = \frac{1}{3}$ (D) $X_B = \frac{1}{4}$
32. Ratio of the number of moles of A and B left in the container after 10 seconds from the diffusion starts is:
- (A) $\frac{7}{9}$ (B) $\frac{2}{3}$ (C) $\frac{8}{11}$ (D) $\frac{9}{13}$
33. What is the time after which container will have same number of moles of A and B:
- (A) 15 sec. (B) 50 sec. (C) 25 sec. (D) $\frac{50}{3}$ sec.

Comprehension # 4

In the Figure, isotherms of CO₂ at several temperatures near the critical point are shown. At the critical point (critical state), the distinction between the liquid and gaseous states disappear and the density of the gaseous substance is equal to that in the liquid state. For every gas this occurs at specific values of temperature and pressure, called critical temperature and critical pressure respectively. At temperatures and pressures above the critical point value, a gas is said to be in a supercritical state. Critical constants are evaluated by solving the Vander Waals equation which is a cubic in volume. The values are $T_c = \frac{8a}{27Rb}$,

$P_c = \frac{8a}{27b^2}$, $V_c = 3b$. (where a and b are Van Der Waals constants).

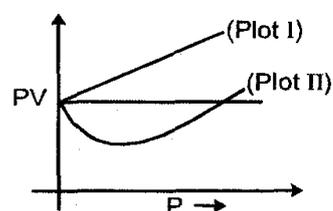
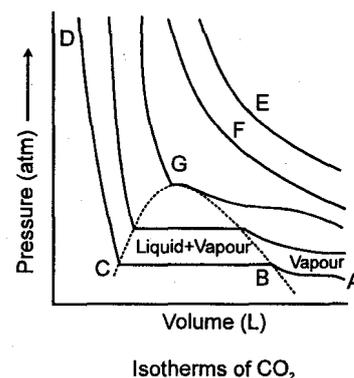
At critical point $Z = \frac{P_c V_c}{RT_c} = \frac{3}{8}$

In the supercritical region the behaviour is studied by plotting Z vs P plots. The variation in this region is studied with respect to boyles temperature a ($T_B = \frac{a}{Rb}$). At temperature higher than C_B the variation is linear

(Plot I) and at temperature lower than C_B the variation is non linear

(Plot II)

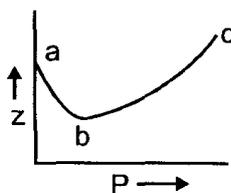
With reference to the passage answers the following questions:



34. For a real gas at a given temperature, which of the following facts is not correct?

- (A) PV may increase with the increase in pressure.
- (B) PV may decrease with the increase in pressure
- (C) PV will not change with the change in pressure
- (D) PV will increase with the increase in pressure

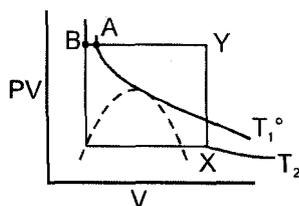
35. In the figure representing variation of the compressibility factor z of a real gas with pressure:



- (A) ab shows that the gas is more compressible than ideal gas
- (B) bc shows that the gas is less compressible than ideal gas.

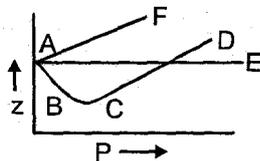
- (C) bc may be explained by $P\bar{V} = RT - \frac{a}{V}$
- (D) be may be explained by $p\bar{V} = RT + Pb$

36. A gas at C_2° is condensed to liquid following the path XYAB. The liquid appears at the point:



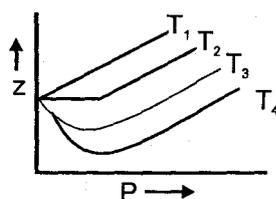
- (A) Y at C_2°
- (B) A at C_2°
- (C) B at C_1°
- (D) A at C_1°

37. Which statement(s) about the behaviour of a real gas is/are wrong?
 (A) A gas exerts more pressure compared to an ideal gas.
 (B) A gas can be compressed more compared to an ideal gas.
 (C) A gas with high value of Vander waals constant, a is highly liquefiable.
 (D) H_2 and He are less compressible compared to an ideal gas at ordinary
38. The figure shows the effect of pressure on the compressibility factor, Z of a gas :



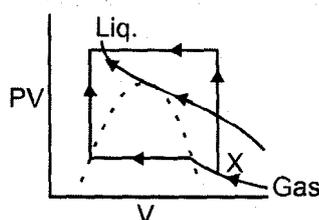
The wrong conclusion(s) is/are:

- (A) The curve AE can be explained by $PV = RT$
 (B) The curve AF and CD can be explained by $PV = KT + Pb$
 (C) The curve AB can be explained by $PV = RT - \frac{a}{V}$
 (D) All the three curves AF, AE and AD shows the real behaviour
39. Two vander waals gases have same value of ' a ' but different value of b which of the following statement is correct.
 (A) The smaller the value of b larger will be compressibility
 (B) The larger the value of b , larger will be compressibility
 (C) Both have same compressibility
 (D) All the with smaller value of b will occupy larger volume
40. Two Vander waals gases have same value ' b ' but different ' a ' value then which of the following statement is correct under similar condition.
 (A) Both gases will occupy same volume
 (B) Gas having a larger value of ' a ' will occupy lesser volume
 (C) Gas having a larger value of ' a ' will occupy larger volume
 (D) Can not be predicted
41. From the given plot between z and P for a real gas the correct is:



- (A) $T_1 = \frac{2a}{Rb}$ (B) $T_2 = \frac{a}{Rb}$ (C) $T_3 = \frac{a}{Rb}$ (D) $T_4 = \frac{2a}{Rb}$

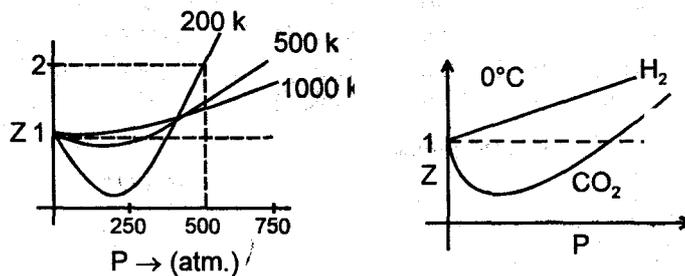
42. A gas can be condensed to liquid through the paths I, II, and III, as shown in figure. The path(s) through which the gas changes to liquid abruptly is (are)



- (A) I and II (B) II and III (C) I and III (D) II

Comprehension # 5

Sketch shows the plot of Z v/s P for of a hypothetical gas for one mole at three distinct temperature.



Boyle's temperature is the temperature at which a gas shows ideal behaviour over a pressure range in the low pressure region. Boyle's temperature $(T_b) = \frac{a}{Rb}$. If a plot is obtained at temperatures well below Boyle's temperature then the

curve will show negative deviation, in low pressure region and positive deviation in the high pressure region. Near critical temperature the curve is more likely as CO_2 and the temperature well above critical temperature curve is more like H_2 at 0°C as shown above. At high pressure suppose all the constant temperature curve varies linearly with

pressure according to the following equation:

$$Z = 1 + \frac{pb}{RT} \quad (R = 2 \text{ cal mol}^{-1} \text{ K}^{-1}).$$

43. Which of the following is correct:

(A) $\frac{a}{b} < 0.4 \text{ kcal mol}^{-1}$

(B) $0.4 \text{ kcal mol}^{-1} < \frac{a}{b} < 2 \text{ kcal mol}^{-1}$

(C) $\frac{a}{b} < 0.4 \text{ kcal mol}^{-1}$

(D) $\frac{a}{b} = 1 \text{ K Cal mol}^{-1}$

44. For 500 K plot value of Z changes from 2 to 2.2 if pressure is varied from 1000 atm to 1200 atm (high pressure) then the value of $\frac{b}{RT}$ will be

(A) 10^{-3} atm^{-1}

(B) $2 \times 10^{-3} \text{ atm}^{-1}$

(C) $5 \times 10^{-4} \text{ atm}^{-1}$

(D) 10^{-4} atm^{-1}

45. As shown in the figure at 200 K and 500 atm value of compressibility factor is 2 (approx). Then volume of the gas at this point will be

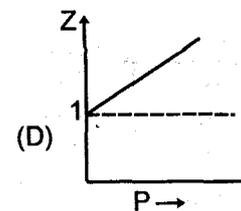
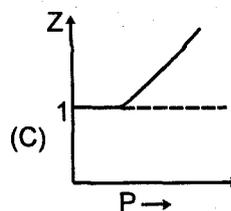
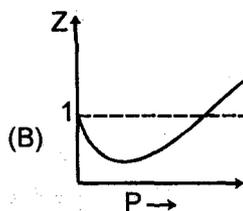
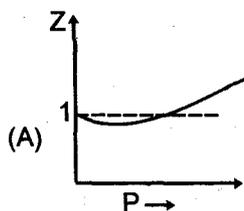
(A) 0.01 L

(B) 0.09 L

(C) 0.065 L

(D) 0.657 L

46. Plot at Boyle's temperature for the gas will be



47. In very high pressure region if Z v/s P is plotted at 1200 K for the above gas then it will have greatest slope.

(A) True

(B) False

(C) Can't say

(D) not related to the paragraph

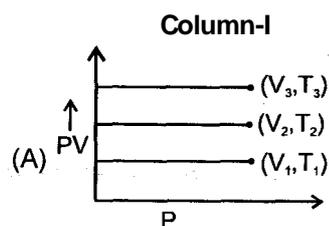
MATRIX MATCH

48. Match the following:

- Column-I**
- (A) H_2 ($a = 0.244 \text{ litre}^2 - \text{atm mole}^{-2}$;
 $b = 0.02 \text{ litre mole}^{-1}$)
- (B) He ($a = 0.03412 \text{ litre}^2 - \text{atm mole}^{-2}$;
 $b = 0.02370 \text{ litre mole}^{-1}$)
- (C) CO_2 ($a = 3.592 \text{ litre}^2 - \text{atm mol}^{-2}$;
 $b = 0.0426 \text{ litre mole}^{-1}$)
- (D) H_2O ($a = 5.464 \text{ litre}^2 - \text{atm mol}^{-2}$;
 $b = 0.03049 \text{ litre mole}^{-1}$)

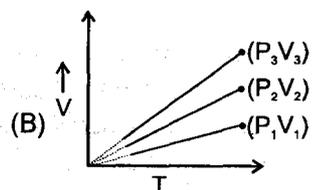
- Column-II**
- (p) Maximum boiling point
- (q) Minimum boiling point
- (r) Critical temperature < Boyle temp.
- (s) Minimum critical temperature

49. For a fixed amount of the gas match the two column:

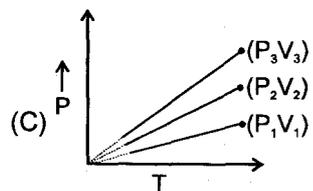


Column II

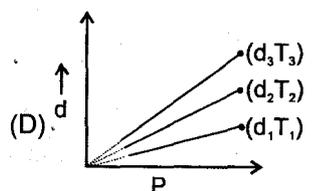
(P) $T_1 > T_2 > T_3$



(q) $p_1 > p_2 > p_3$

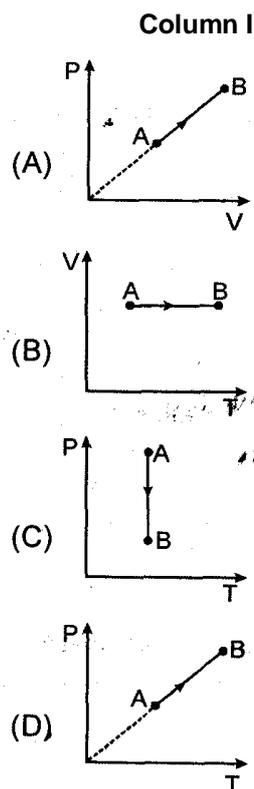


(r) $V_1 > V_2 > V_3$



(s) $d_1 > d_2 > d_3$

50. Match the following



Column II

- (p) Temperature is increasing
- (q) Temperature is constant
- (r) Volume is constant
- (s) Pressure is increasing

51.

Column I

- (A) An unknown gas at STP having
- (B) He gas at NTP having density less
- (C) H₂ gas at NTP
- (D) O₂ gas at NTP having density $\frac{10}{7}$ g/L.

Column II

- (p) Behaves as an ideal gas Boyle's temperature 0°C
- (q) Attractive tendencies are dominant between molecules than $\frac{1}{5.6}$ g/L.
- (r) Gas is less compressible with respect to an ideal gas
- (s) For gas, Critical temperature < Boyle's temperature
- (t) Molar volume of gas is greater than 22.4 L

52. Match the column:

Assume the gas to be ideal and match the following :

Column-I

- (A) K.E. of 4gram of Helium molecule
- (B) Increase in the energy of 32 gram of oxygen Molecule on raising temperature
- (C) Increase in energy of 1 mole of NO₂ on raising Temperature by 1°C at constant volume
- (D) Increases in energy of 1 mole of NO₂ on raising Temperature

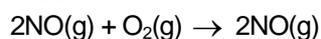
Column-II

- (p) $\frac{5}{2}$ R
- (r) 4 R
- (s) 1.5 RT

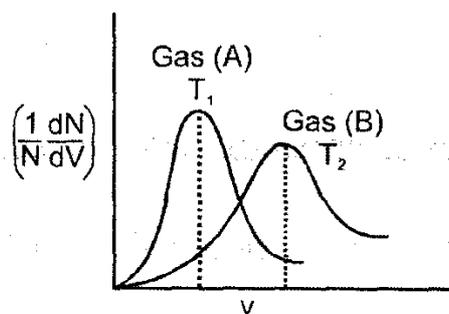
INTEGER TYPE

53. Calculate the change in pressure (in atm) when 2 mole of NO and 16 g O₂ in a 6.25 litre originally at 27°C react to produce the maximum quantity of NO₂ possible according to the equation.

(Take $R = \frac{1}{12}$ ltr. Atm/mol K)



54. 2 moles of Ne gas and 5 moles of He gas, both samples having average velocity 7×10^2 m/s, are mixed. Find the average translational kinetic energy per mole of the given gas mixture (in joules). Report your answer as 'X' where $X = (\text{Average translational KE in joules}) \times 0.002$. The reported answer should be upto nearest integer.
55. A 1L gas mixture of CO, CO₂ and N₂ was mixed with 1L O₂ and allowed to burn completely. The product gas mixture, when passed subsequently through KOH solution and alkaline pyragalol solution, suffered a total contraction of 1.6 L. On the other hand, if the product gas mixture was mixed with excess of CO gas and again allowed to burn, the new product mixture suffered a contraction of 2.3 L on passing through KOH solution. Find the volume % of CO in the initial mixture. Report your answer as 'Y' where $Y = (\text{Volume \% of CO})/10$.
56. A flask of 8.96 L capacity contains a mixture of N₂ and H₂ at 273 K and 1 atm pressure. If the mixture is made to react to form NH₃ gas at the same temperature, the pressure in the flask reduces to 0.85 atm. Find the partial pressure of NH₃ gas in the final mixture in atm. Report your answer as 'y' where $y = (\text{Partial pressure of NH}_3) \times 20$.
57. According to Maxwell's distribution of molecular speeds, the following graph has been drawn for two different samples of gases A and B at temperature T₁ and T₂ respectively. Then, give the correct set of INCORRECT statements: Report your answer as sum of the numbers of incorrect statements. For example, if statements (1) & (2) are incorrect, then report answer as $(1 + 2) = 3$.

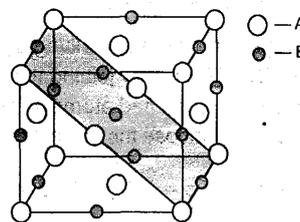


- (1) If $T_1 = T_2$, then gas B can be SO₂ and gas A can be CO₂.
 (2) If gases A and B are CO₂ & N₂O, then $T_1 > T_2$.
 (3) If $T_1 < T_2$, then gases A and B cannot be CO₂ and SO₂ respectively
 (4) None of these
58. A vessel contains two gases A and B in the mass ratio 2: 1 respectively. If the above gas mixture is allowed to diffuse through a hole, the molar composition of the mixture coming initially out of the hole is 1 : 4. Find the simplest whole number ratio of the mole fractions of gases A and B present in the vessel in the beginning respectively. If the simplest whole number ratio is a : b, then report your answer as 'X' where $X = \left(\frac{a}{b}\right) \times 6$

SOLID STATE

ONLY ONE OPTION CORRECT

1. A crystal is made of particles A and B. A forms FCC packing and B occupies all the octahedral voids. If all the particles along the plane as shown in fig removed, then, the formula of the crystal would be:

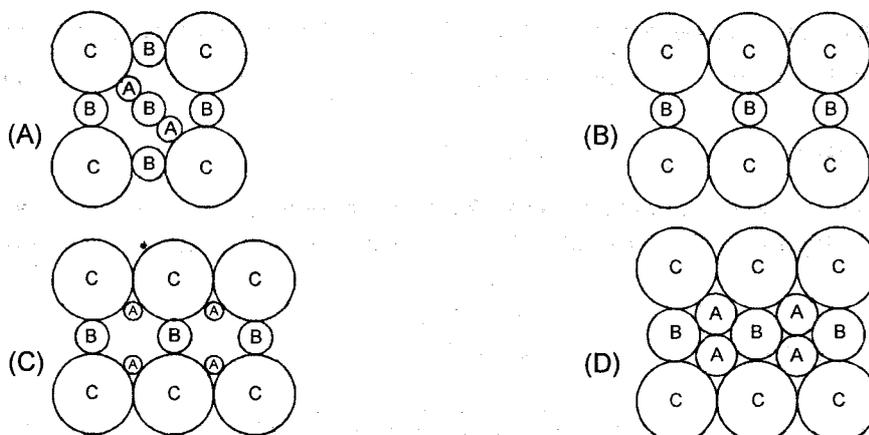
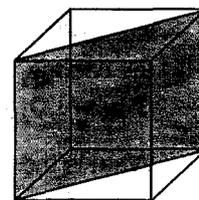


- (A) AB
(B) A_5B_7
(C) A_7B_5
(D) None of these.

2. A crystal is made of particle X, Y & Z. X forms FCC packing, Y occupies all octahedral voids of X and Z occupies all tetrahedral voids of X, if all the particles along one body diagonal are removed then the formula of the crystal would be –

- (A) XYZ_2 (B) X_2YZ_2 (C) $X_5Y_4Z_5$ (D) $X_5Y_4Z_8$

3. In a hypothetical solid C atoms are found to form cubical close pack atoms occupy all tetrahedral voids & B atoms occupy all octahedral voids are of appropriate size, so that there is no distortion in CCP lattice. Now if a plane as shown in the following figure is cut. Then the cross section of this plane will look like.

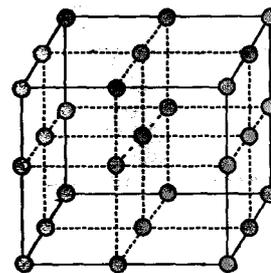


4. In hexagonal close packing of sphere in three dimensions.
- (A) In one unit cell there are 12 octahedral voids and all are completely inside the unit cell.
(B) In one unit cell there are six octahedral voids and all are completely inside the unit cell.
(C) In one unit cell there are six octahedral void and of which three are completely inside the unit cell and other three are partially inside the unit cell.
(D) In one unit cell there are 12 tetrahedral voids, all are completely inside the unit cell.

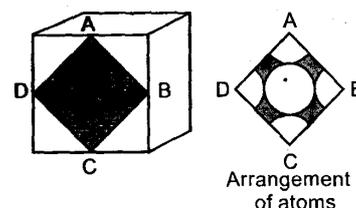
5. Diamond has face-centred cubic lattice. There are two atoms at $(0,0,0)$ and $\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$ coordinates. The ratio of the carbon-carbon bond distance to the edge of the unit cell is

- (A) $\sqrt{\frac{3}{16}}$ (B) 4 (C) $\frac{1}{4}$ (D) $\frac{1}{\sqrt{2}}$

6. The following diagram shows arrangement of lattice point with $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$. Choose the correct options.
- (A) The arrangement is SC with each lattice point surrounded by 6 nearest neighbours.
 (B) The arrangement is SC with each lattice point surrounded by 8 nearest neighbours.
 (C) The arrangement is FCC with each lattice point surrounded by 12 nearest neighbours.
 (D) The arrangement is BCC with each lattice point surrounded by 8 nearest neighbours.



7. Consider a cube containing n unit cells of a cubic system. A plane obtained by joining the mid points of the edges on one of its identical faces had atoms arranged as shown. Let p be the packing fraction. Choose the correct option:



- (A) $n=1, p = \frac{22}{21\sqrt{2}}$ (B) $n = 8, p = \frac{11}{21}$
 (C) $n=8, p = \frac{11}{14}$ (D) $n = 1, p = \frac{11\sqrt{3}}{28}$
8. Spinel is an important class of oxides consisting of two types of metal ions with the oxide ions arranged in CCP pattern. The normal spinel has $1/8$ of the tetrahedral holes occupied by one type of metal ion and $1/2$ of the octahedral holes occupied by another type of metal ion. Such a spinel is formed by Zn^{2+} , Al^{3+} and O^{2-} with Zn^{2+} in the tetrahedral holes. If CCP arrangement of oxide ions remains undistorted in the presence of all the cations, formula of spinel and fraction of the packing fraction of crystal are respectively :
- (A) $ZnAl_2O_4, 77\%$ (B) $ZnAl_2O_4, 74\%$ (C) $Zn_2Al_4O_4, 74\%$ (D) $Zn_3Al_2O_6, 74\%$
9. What is the maximum number of layers of atoms in close packed planes that will lie within two imaginary parallel planes having a distance between them of $13\sqrt{\frac{2}{3}} R$ (where R is the radius of atom) in the copper crystal (FCC) ? Consider the atoms to be within the parallel planes if their centres are on or within the two parallel planes.
- (A) 5 (B) 6 (C) 7 (D) 8
10. A transition Metal M can exist in two oxidation states $+2$ and $+3$. It forms an oxide whose empirical formula is given by M_xO where $x < 1$. Then the ratio of metal ions in $+3$ state to those in $+2$ state in oxide is given by :
- (A) $\frac{1-x}{1+x}$ (B) $1+2x$ (C) $1+\frac{x}{2}$ (D) $\frac{2(x-1)}{3x-2}$
11. Analysis show that nickel oxide consist of nickel ion with 96% ions having d^8 configuration and 4% having d^7 configuration. Which amongst the following best represents the formula of the oxide.
- (A) $Ni_{1.02}O_{1.00}$ (B) $Ni_{0.96}O_{1.00}$ (C) $Ni_{0.96}O_{0.98}$ (D) $Ni_{0.98}O_{1.00}$
12. PCl_5 molecule has
- (A) three fold axis of symmetry (B) two fold axis of symmetry
 (C) both (D) none of these

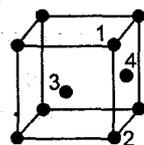
13. Which of the following statements is correct about the conduction of electricity in pure crystal of silicon at room temperature?
- (A) The conduction is due to electrons present in fully occupied lowest energy states.
 (B) The conduction is due to only some electrons capable of leaving the bonds at room temperature.
 (C) The conduction is only due to the holes formed from the release of electrons.
 (D) The conduction is due to the movement of both the electrons released and holes formed.

ONE OR MORE THAN ONE OPTION CORRECT

14. In the fluorite structure if the radius ratio is $\left(\sqrt{\frac{3}{2}} - 1\right)$, how many ions does each cation touch ?
- (A) 4 anions (B) 12 cations (c) 8 anions (D) No cations

15. The co-ordination number of FCC structure for metals is 12, since
- (A) each atom touches 4 others in same layer, 3 in layer above and 3 in layer below.
 (B) each atom touches 4 others in same layer, 4 in layer above and 4 in layer below.
 (C) each atom touches 6 others in same layer, 3 in layer above and 3 in layer below.
 (D) each atom touches 3 others in same layer, 6 in layer above and 6 in layer below.

16. In an FCC unit cell, atoms are numbered as shown below. The atoms not touching each other are : (Atom numbered 3 is face centre of front face).



- (A) 3 & 4 (B) 1 & 3 (C) 1 & 2 (D) 2 & 4
17. In a AB unit cell (Rock salt type) assuming A⁺ forming FCC :
- (A) The nearest neighbour of A⁺ is 6B⁻ ion. (B) The nearest neighbour of B⁻ is 6A⁺ ion.
 (C) The second neighbour of A⁺ is 12A⁺. (D) The packing fraction of AB crystal is 0.79.
18. The HCP and CCP structure for a given element would be expected to have :
- (A) the same co-ordination number. (B) the same density.
 (C) the same packing fraction. (D) all the above.

PARAGRAPH BASED QUESTIONS

Comprehension # 1

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (HCP), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible.

These spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these three spheres touches three spheres of the bottom layer. Finally, the second layer is covered with third layer that is identical to the bottom layer in relative position.

Total number of atoms per unit = $\frac{1}{6}$ (corners atoms) + $\frac{1}{2}$ (face-atoms) + 3 (body centered atoms).

$$= \frac{1}{6} \times 12 + \frac{1}{2} \times 2 + 3 = 2 + 1 + 3 = 6.$$

19. If in place of above HCP, close packing of sphere is changed such that 4 body centered atoms are arranged in middle layer, 4 atoms above the middle layer and 4 below the middle layer, what will be the co-ordination number of new closed packed arrangement ?
 (A) 12 (B) 13 (C) 14 (D) cannot be predicted.
20. If the angles $\angle Q'QP$ be changed to 150° , then what will be the contribution of atom at this position per unit cell ?
 (A) $\frac{1}{24}$ (B) $\frac{1}{12}$ (C) $\frac{1}{6}$ (D) $\frac{5}{24}$
21. If only the angles of position P, P', K and K' is changed from 120° to 60° , and the angle of positions Q, Q', R, R', M, M', L and L' is changed from 120° to 150° shown in figure, then what will be effect in density of the crystal ?
 (A) will decrease (B) will increase (C) no effect (D) cannot be predicted.

Comprehension # 2

Only those atoms which form four covalent bonds produce a repetitive three dimensional structure using only covalent bonds, e.g., diamond structure. The latter is based on a FCC lattice where lattice points are occupied by carbon atoms. Every atom in this structure is surrounded tetrahedrally by four others. Germanium, silicon and grey tin also crystallize in the same way as diamond. (Given : $N_A = 6 \times 10^{23}$, $\sin 54^\circ 44' = 0.8164$).

22. If edge length of the cube is 3.60A, then radius of carbon atom is
 (A) 0.78 A (B) 0.92 A (C) 0.64 A (D) 0.35 A.
23. If the edge length is 3.60A, density of diamond crystal is
 (A) 3.92 gm/cc (B) 2.40 gm/cc (C) 3.37 gm/cc (D) 2.58 gm/cc.
24. Total number of diamond unit cells in 1.2 gm of diamond sample is
 (A) 6.0×10^{21} (B) 6.0×10^{22} (C) 7.5×10^{21} (D) 5.0×10^{22} .

Comprehension #3

CuSO_4 crystallise in rock salt structure. Its cell parameter can be determined by various experimental methods like electrical conductivity measurement, colligative properties measurement, pH measurement etc. A cubic crystal of CuSO_4 of edge length 17.1 mm is dissolved in water to make 500 ml solution of pH 5. ($3^{1.5} = 1.14$) Given : $\text{Cu}(\text{H}_2\text{O})_6^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{Cu}(\text{H}_2\text{O})_5(\text{OH})]^+ + \text{H}_3\text{O}^+$; $K = 10^{-5}$

25. Moles of CuSO_4 dissolved in water to make above solution is
 (A) 10^{-5} (B) 2×10^{-5} (C) 2×10^{-4} (D) 10^{-4}
26. Edge length of FCC unit cell of copper sulphate is
 (A) 120A (B) 170A (C) 150A (D) 200 A
27. If the given solution is made 1 M with respect to $[\text{Cu}^{2+}]$ becomes 10^{-15} M therefore K_f for the formation of $\text{Cu}(\text{NH}_3)_4^{2+}$ is
 (A) 10^{10} (B) 10^8 (C) 2×10^8 (D) 2×10^{10}

MATRIX MATCH

28. Match the column :

Column-I

- (A) Cubic
- (B) Orthorhombic
- (C) Tetragonal
- (D) Rhombohedral

Column-II

- (p) Have 2-fold axis of symmetry.
- (q) Have all axial angles identical.
- (r) Have all edge lengths identical.
- (s) More than one types of Bravais lattices are found.

29.

Column-I

(Arrangement in unit cell, (Coordination number of cation : radius ratio in higher limit) Anion)

- (A) Cations in CCP and anions in alternate tetrahedral voids
- (B) Cations in simple cubic and anions in the body centre.
- (C) Anions in CCP and cations in all tetrahedral voids.
- (C) Cations in CCP and anions in all octahedral voids

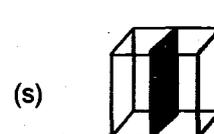
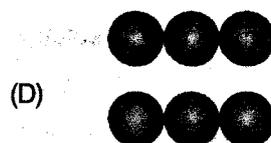
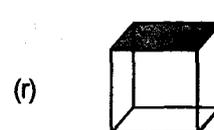
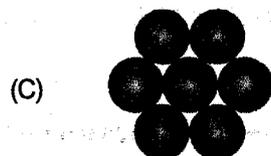
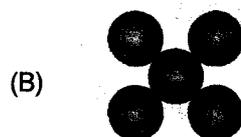
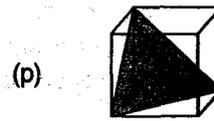
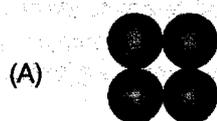
Column-II

- (p) ratio of number of cation to anion in one unit cell is 1 : 1
- (q) ratio of coordination number of cation to anion is 1 : 1.
- (r) ratio of number of cation to anion just touching each other is not 1.
- (s) number of next neighbours of ion is greater than 10.

30.

Match the followings

Column I (Arrangement of the atoms/ions) Column II (Planes in fcc lattice)



31.

Match the column

Column-I

- (A) AB (Zinc blended)
- (B) AB (Rock salt)
- (C) AB₂ (Fluorite)
- (D) AB₂ (Anti-Fluorite)

Column-II

(p) $d(\text{gm/cm}^3) =$

$\frac{4 \times \text{molar mass}}{\text{Avogadro's number} \times \text{Volume of unit cell}}$

Avogadro's number \times Volume of unit cell

- (q) All the voids along one of the body diagonal are not occupied
- (r) Voids along one face plane are not occupied.
- (s) Anion & cation have similar surroundings.

32 Match the column :

Column-I

- (A) Arrangement of wurtzite structure
(B) Packing fractions in diamond
(C) ZnO become yellow on heating
(D) Schottky defects

Column-II

- (p) non stoichiometric defect
(q) HCP
(r) $Ne^{-\frac{E_a}{2KT}}$
(s) 0.34

INTEGER TYPE

33. Edge length of M^+X^- (fcc structure) is 7.2 \AA and radius of cation is 1.6 \AA . Assuming M^+X^- contact along cell edge. The radius of X^- ion is $x \text{ \AA}$. What is the value of x ?
34. The pycnometric density of sodium chloride crystal is $2.165 \times 10^3 \text{ kgm}^{-3}$. While its X-rays density is $2.165 \times 10^3 \text{ kgm}^{-3}$. The fraction of unoccupied sites in NaCl crystal is $x \times 10^3$. What is the value of x ?
35. How many atoms are there in a cube base unit cell having one atom on each corner and two atoms on each body diagonal of cube?
36. The crystal AB (rock salt structure) has molecular weight $6.023 y \text{ u}$, where, y is an arbitrary number in u . If the minimum distance between cation and anion is $y^{1/3} \text{ Nm}$ and the observed density is 20 kg m^{-3} . Find the density in kgm^{-3} .

SOLUTION & COLLIGATIVE PROPERTIES

ONLY ONE OPTION CORRECT

1. Three solutions are prepared by adding 'w' gm of 'A' into 1kg of water, w gm of B into another 1 kg of water and 'w' gm of 'C' in another 1 kg of water (A, B, C are non electrolytic). Dry air is passed from these solutions in sequence (A \longrightarrow B \longrightarrow C). The loss in weight of solution A was found to be 2 gm while solution B gained 0.5 gm and solution C lost 1 gm. Then the relation between molar masses of A, B and C is :
- (A) $M_A : M_B : M_C = 4 : 3 : 5$ (B) $M_A : M_B : M_C = \frac{1}{4} : \frac{1}{3} : \frac{1}{5}$
(C) $M_C > M_A > M_B$ (D) $M_B > M_A > M_C$
2. How many milli moles of sucrose should be dissolved in 500 gms of water so as to get a solution which has a difference of 103.57°C between boiling point and freezing point.
($K_f = 1.86 \text{ K Kg mol}^{-1}$, $K_b = 0.52 \text{ K Kg mol}^{-1}$)
(A) 500 mmoles (B) 900 mmoles (C) 750 mmoles (D) 650 mmoles
3. Barium ions, CN^- and Co^{2+} form an ionic complex, If this complex is 75% ionised in aqueous solution with Vent Hoff factor (i) equal to four and paramagnetic moment is found to be 1.73 BM (due to spin only) then the hybridisation state of Co (II) in the complex will be :
(A) sp^3d (B) d^2sp (C) sp^3d^2 (D) dsp^3
4. Select the correct statement:
(A) The semipermeable membrane is the cause of osmotic pressure.
(B) Osmosis results from decrease in entropy
(C) Osmotic pressure depends on temperature and concentration but is independent of the nature of the membrane.
(D) The passage of solvent molecules occur only in one direction through a semipermeable membrane.
5. The incorrect statement is
(A) Vapour pressure of a liquid always increases by increasing temperature.
(B) Vapour pressure only depends on temperature and not on the nature of substance.
(C) Vapour pressure does not depend on the quantity of the liquid taken and the surface area of the liquid.
(D) Vapour pressure is not a colligative property & is independent of the concentration of the liquid.
6. The molar heat of vaporization of toluene is ΔH_v . If its vapour pressure at 315 K is 60 torr & that at 356K is 300 torr then $\Delta H_v = ?$ ($\log 2 = 0.3$)
(A) 37.5 kJ/mole (B) 3.75 kJ/mole (C) 37.5 J/mol (D) 3.75 J/mole
7. Relative decrease in vapour pressure of an aqueous solution containing 2 moles $[\text{Cu}(\text{NH}_3)_3\text{Cl}] \text{Cl}$ in 3 moles H_2O is 0.50. On reaction with AgNO_3 , this solution will form (assuming no change in degree of ionisation of substance on adding AgNO_3)
(A) 1 mol AgCl (B) 0.25 mol AgCl (C) 0.5 mol AgCl (D) 0.40 mol AgCl
8. Which of the following has been arranged in order of decreasing freezing point?
(A) $0.05 \text{ M KNO}_3 > 0.04 \text{ M CaCl}_2 > 0.140 \text{ M sugar} > 0.075 \text{ M CuSO}_4$
(B) $0.04 \text{ M BaCl}_2 > 0.140 \text{ M sucrose} > 0.075 \text{ M CuSO}_4 > 0.05 \text{ M KNO}_3$
(C) $0.075 \text{ M CuSO}_4 > 0.140 \text{ M sucrose} > 0.04 \text{ M BaCl}_2 > 0.05 \text{ M KNO}_3$
(D) $0.075 \text{ M CuSO}_4 > 0.05 \text{ M NaNO}_3 > 0.140 \text{ M sucrose} > 0.04 \text{ M BaCl}_2$
9. A solution of x moles of sucrose in 100 grams of water freezes at -0.2°C . As ice separated the freezing point goes down to 0.25°C . How many grams of ice would have separated?
(A) 18 grams (B) 20 grams (C) 25 grams (D) 23 grams

10. An ideal mixture of liquids A and B with 2 moles of A and 2 moles of B has a total vapour pressure of 1 atm at a certain temperature. Another mixture with 1 mole of A and 3 moles of B has a vapour pressure greater than 1 atm. But if 4 moles of C are added to the second mixture, the vapour pressure comes down to 1 atm. Vapour pressure of C, $P_C^\circ = 0.8$ atm. Calculate the vapour pressures of pure A and pure B.
 (A) $P_A^\circ = 1.4$ atm, $P_B^\circ = 0.7$ atm (B) $P_A = 1.2$ atm, $P_B^\circ = 0.6$ atm
 (C) $P_A = 1.4$ atm, $P_B^\circ = 0.6$ atm (D) $P_A^\circ = 0.6$ atm, $P_B^\circ = 1.4$ atm
11. A sample of air is saturated with benzene (vapor pressure = 100 mm Hg at 298 K) at 298K, 750mm Hg pressure. If it is isothermally compressed to one third of its initial volume, the final pressure of the system is
 (A) 2250 torr (B) 2150 torr (C) 2050 torr (D) 1950 torr
12. Available solutions are 1L of 0.1 M NaCl and 2L of 0.2 M CaCl₂. Using only these two solutions what maximum volume of a solution can be prepared having $[Cl^-] = 0.34$ M exactly. Both electrolytes are strong
 (A) 2.5 L (B) 2.4 L (C) 2.3 L (D) None of these
13. Calculate the osmotic pressure of the solution prepared in the above question $T = 300$ K, ($R = 0.082$ L atm mol⁻¹K⁻¹)
 (A) 10.8 atm (B) 12.8 atm (C) 5.6 atm (D) None of these
14. Consider equivocal aqueous solutions of NaHSO₄ and NaCl with ΔT_b and ΔT_b as their respective boiling point elevations. The value of $\lim_{x \rightarrow 0} \frac{\Delta T_b}{\Delta T_b}$ will be :
 (A) 1 (B) 1.5 (C) 3.5 (D) 3
15. A solute 'S' undergoes a reversible trimerization when dissolved in a certain solvent. The boiling point elevation of its 0.1 molal solution was found to be identical to the boiling point elevation in case of a 0.08 molal solution of a solute which neither undergoes association nor dissociation. To what percent had the solute 'S' undergone trimerization?
 (A) 30% (B) 40% (C) 50% (D) 60%
16. The vapor pressures of benzene, toluene and a xylene are 75 Torr, 22 Torr and 10 Torr at 20°C. Which of the following is not a possible value of the vapor pressure of an equimolar binary/ternary solution of these at 20°C ? Assume all form ideal solution with each other.
 (A) $48\frac{1}{2}$ (B) 16 (C) $35\frac{2}{3}$ (D) $53\frac{1}{2}$
17. 3.24 g of Hg(NO₃)₂ (molar mass = 324) dissolved in 1000 g of water constitutes a solution having a freezing point of - 0.0558°C while 21.68 g of HgCl₂ (molar mass = 271) in 2000 g of water constitutes a solution with a freezing point of - 0.0744°C. The K_f for water is $1.86 K - Kg mol^{-1}$. About the state of ionization of these two solids in water it can be inferred that:
 (A) Hg(NO₃)₂ and HgCl₂ both are completely ionized
 (B) Hg(NO₃)₂ is fully ionized but HgCl₂ is fully unionized
 (C) Hg(NO₃)₂ and HgCl₂ both are completely unionized
 (D) Hg(NO₃)₂ is fully unionized but HgCl₂ is fully ionized
18. For a solution of 0.849 g of mercurous chloride in 50 g of HgCl₂(f) the freezing point depression is 1.24°C. K_f for HgCl₂ is 34.3. What is the state of mercurous chloride in HgCl₂ ? (Hg - 200, Cl - 35.5)
 (A) as Hg₂Cl₂ molecules (B) as HgCl molecules
 (C) as Hg⁺ and Cl⁻ ions (D) as Hg₂²⁺ and Cl⁻ ions

ONE OR MORE THAN ONE OPTION CORRECT

19. Vapour pressure of solution containing 6g of a non-volatile solute in 180 g water is 20.0 Torr. If 1 mole water is further added vapour pressure increases by 0.02 Torr. Which of the following is true ?
 (A) The molecular weight of solute is 54g mol^{-1}
 (B) The vapour pressure of pure water is 20.22 Torr
 (C) Addition of more water in the solution will further raise the vapour pressure of solution
 (D) The vapour pressure of pure water is 22.22 Torr
20. Two liquids A and B form an ideal solution. The solution has a vapor pressure of 700 Torr at 80°C . It is distilled till $2/3^{\text{rd}}$ of the solution is collected as condensate. The composition of the condensate is $x'_A = 0.75$ and that of the residue is $x''_A = 0.30$. If the vapor pressure of the residue at 80°C is 600 Torr, which of the following is/are true?
 (A) The composition of the original liquid was $x_A = 0.6$.
 (B) The composition of the original liquid was $x_A = 0.4$.
 (C) $P_A^\circ = \frac{2500}{3}$ Torr. (D) $P_B^\circ = 500$ Torr.
21. For chloroform and acetone or for a solution of chloroform and acetone if p , (observed (actual)) is compared with p_s (Theoretical (Raoult)) then which of the following is /are true ?
 (A) $p_s(\text{actual}) < p_s(\text{Raoult})$
 (B) $\lim_{x_{\text{chloroform}} \rightarrow 0} (P_{\text{acetone}}^0 - P_s(\text{actual})) = 0$
 (C) $\lim_{x_{\text{acetone}} \rightarrow 0} (P_{\text{chloroform}}^0 - P_s(\text{actual})) = 0$
 (D) $P_{\text{acetone}}^0 > P_{\text{chloroform}}^0$ near room temperature

PARAGRAPH BASED QUESTIONS

Comprehension # 1

IDEAL SOLUTION FIXED TEMPERATURE

Consider two liquids 'B' and 'C' that form an ideal solution. We hold the temperature fixed at some value T that is above the freezing points of 'B' and 'C'. We shall plot the system's pressure P and against x_B the overall mole fraction of B in the system .:

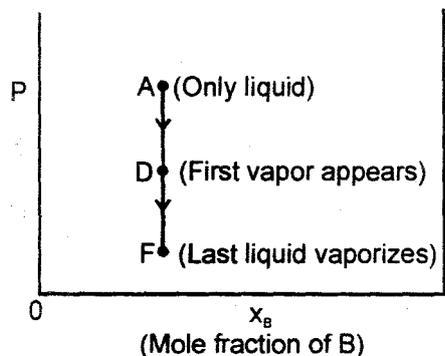
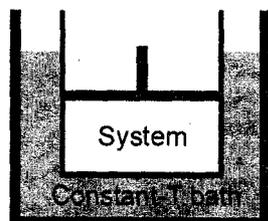
$$x_B = \frac{n_{B,\text{total}}}{n_{\text{total}}} = \frac{n_B^l + n_B^v}{n_B^v + n_B^l + n_C^l + n_C^v}$$

Where n_B^l and n_B^v are the number of moles of B in the liquid and vapor phases, respectively. For a close system x_B , is fixed, although n_B^l and n_B^v may vary.

Let the system be enclosed in a cylinder fitted with a piston and immersed in a constant-temperature bath. To see what the P -versus- x_B phase diagram looks like, let us initially set the external pressure on the piston high enough for the system to be entirely liquid (point A in figure) As the pressure is lowered below that at A, the system eventually reaches a pressure where the liquid just begins to vaporize (point D). At point D, the liquid has composition x_B^l where x_B^l at D is equal to the overall mole fraction x_B since only an infinitesimal amount of liquid has vaporized. What is the composition of the first vapour that comes off ? Raoult's law, $P_B \equiv x_B^v P_B^0$ relates the vapour-phase mole fractions to the liquid composition as follows:

$$x_B^v = \frac{x_B^l p_B^0}{P} \text{ and } x_C^v = \frac{x_C^l p_C^0}{P} \dots\dots\dots(i)$$

Where P_B^0 and P_C^0 are the vapour pressures of pure 'B' and pure 'C' at T, where the system's pressure P equals the sum $P_B + P_C$ of the partial pressures, where $x_B^{\ell} = \frac{n_B^{\ell}}{(n_B^{\ell} + n_C^{\ell})}$, and the vapor is assumed ideal.

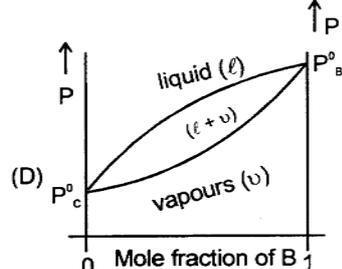
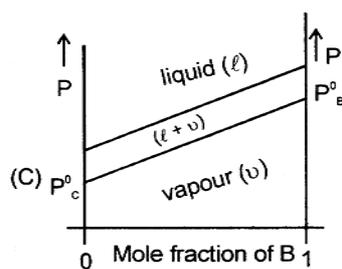
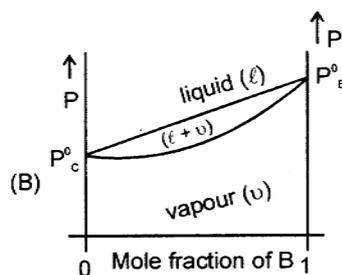
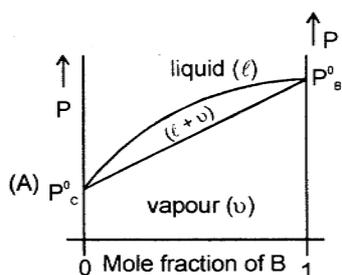


$$\frac{x_B^v}{x_C^v} = \frac{x_B^{\ell} P_B^*}{x_C^{\ell} P_C^*} \quad \text{ideal solution} \quad \dots\dots\dots(2)$$

Let B be the more volatile component, meaning that $P_B^0 > P_C^0$. Above equation then shows that $x_B^v / x_C^v > x_B^{\ell} / x_C^{\ell}$. The vapor above an ideal solution is richer than the liquid in the more volatile component. Equations (1) and (2) apply at any pressure where liquid-vapor equilibrium exists, not just at point D.

Now let us isothermally lower the pressure below point D, causing more liquid to vaporize. Eventually, we reach point F in figure, where the last drop of liquid vaporizes. Below F, we have only vapor. For any point on the line between D and F liquid and vapor phases coexist in equilibrium.

22. If the above process is repeated for all other compositions of mixture of C and B. If all the points where vapours start converting into liquid are connected and all the points where vapours get completely converted into liquid are connected then obtained graph will look like.



23. The equation of the curve obtained by connecting all those points where the vapors of above mixture (all mixtures of different composition are taken) just start forming will be
- (A) $P = P_C^0 + (P_C^0 - P_B^0) X_B^\ell$ (B) $P = P_B^0 + (P_B^0 - P_C^0) X_B^\ell$
- (C) $P = \frac{P_B^0 P_C^0}{X_B^0 (P_C^0 - P_B^0) + P_B^0}$ (D) $P = \frac{P_B^0 P_C^0}{X_B^\ell (P_C^0 - P_B^0) + P_B^0}$
24. Two liquids A and B have the same molecular weight and form an ideal solution. The solution has a vapor pressure of 700 Torr at 80°C. It is distilled till 2/3rd of the solution (2/3rd moles out of total moles) is collected as condensate. The composition of the condensate is $x'_A = 0.75$ and that of the residue is $X''_A = 0.30$. If the vapor pressure of the residue at 80°C is 600 Torr, find the original composition of the liquid.
- (A) $X_A = 0.5$ (B) $X_B = 0.6$ (C) $X_A = 0.6$ (D) $X_B = 0.3$

Comperhension#2

The pressure of two pure liquid A and B which form an ideal solution are 400 mm Hg and 800 mm Hg respectively at temp T. A liquid containing 3 : 1 molar composition of A and B present in a cylinder closed by a piston on which pressure can be varied. The solution is slowly vaporised at temp T by decreasing the applied pressure starting with a pressure of 760 mm Hg. A pressure gauge (in mm) Hg is connected which given the reading of pressure applied.

25. The reading of pressure Gauge at which only liquid phase exists.
- (A) 499 (B) 399 (C) 299 (D) None
26. The reading of pressure Gauge at bubble point is
- (A) 500 (B) 600 (C) 700 (D) None
27. The reading of pressure Gauge at which only vapour phase exists is
- (A) 501 (B) 457.14 (C) 425 (D) 525

Comprehension # 3

Colligative property measurement is one of the techniques used in the measurement of chemical quantities with reasonable accuracy. If a 40.65 gm sample of K_2SO_4 and $BaSO_4$ is dissolved in 900 gm of pure water to form a solution 'A' at 57°C, its vapour pressure is found to be 39.6 torr while vapour pressure of pure water at 57°C is 40 torr. Density of solution A is 1.24 gm/ml.

In a different experiment when small amount of pure $BaSO_4$ is mixed with water at 57°C it gives the osmotic rise of 4.05×10^{-5} atm. ($R = 0.082$ Lt.-atm/mol-K ; $K = 39$, $Ba = 137$, $S = 32$, $O = 16$)

28. Percentage of K_2SO_4 in the sample is :
- (A) 65.75% (B) 71.34% (C) 60.35% (D) 78.74%
29. Solubility product of $BaSO_4$ in water at 57°C is :
- (A) 5×10^{-15} (B) 3.125×10^{-13} (C) 5.625×10^{43} (D) 2.25×10^{-12}
30. Concentration of Ba^{2+} ions in solution 'A' is :
- (A) 3.5×10^{-11} M (B) 4.7×10^{-15} M (C) 2.3×10^{43} M (D) 3.9×10^{-12} M
31. Boiling point of solution A is (K_b water = 0.54 K-kg/mol) :
- (A) 0.3K (B) 0.1K (C) 0.04K (D) 0.05 K

Comprehension # 4

A system of greater disorder of molecules is more probable. The disorder of molecules is reflected by the entropy of the system. A liquid vaporizes to form a more disordered gas. When a solute is present, there is additional contribution to the entropy of the liquid due to increase randomness. As the entropy of solution is higher than that of pure liquid, there is weaker tendency to form the gas. Thus, a solute (non volatile) lowers the vapour pressure of a liquid, and hence a higher boiling point of the solution. Similarly, the greater randomness of the solution opposes the tendency to freeze. In consequence, a lower temperature must be reached for achieving the equilibrium between the solid (frozen solvent) and the solution. Elevation of B.Pt. (ΔT_b) and depression of F.Pt. (ΔT_f) of a solution are the colligative properties which depend only on the concentration of particles of the solute, not their identity. For dilute solutions, ΔT_b and ΔT_f are proportional to the molality of the solute in the solution.

$$\Delta T_b = K_b m \quad K_b = \text{Ebullioscopic constant} = \frac{RT_b^{02} M}{1000 \Delta H_{\text{vap}}}$$

$$\text{And } \Delta T_f = K_f m \quad K_f = \text{Cryoscopic constant} = \frac{RT_f^{02}}{1000 \Delta H_{\text{fus}}}$$

(M = molecular mass of the solvent)

The values of K_b and K_f do depend on the properties of the solvent. For liquids, $\frac{\Delta H_{\text{vap}}}{T_b^0}$ is almost constant.

[**Troutan's Rule**, this constant for most of the **Unassociated liquids** (not having any strong bonding like Hydrogen bonding in the liquid state) is equal to 90J/mol.]

For solutes undergoing change of molecular state in solution (ionization or association), the observed ΔT values differ from the calculate ones using the above relations. In such situations, the relationships are modified as $\Delta T_b = iK_b m$; $\Delta T_f = iK_f m$

Where i = Van't Hoff factor, greater than unity for ionization and smaller than unity for association of the solute molecules.

32. Depression of freezing point of which of the following solutions does represent the cryoscopic constant of water?
- (A) 6% by mass of urea in aqueous solution
(B) 100 g of aqueous solution containing 18 g of glucose
(C) 59 g of aqueous solution containing 9 g of glucose
(D) 1 M KCl solution in water.
33. Dissolution of a non-volatile solute into a liquid leads to the –
- (A) decrease of entropy
(B) increase in tendency of the liquid to freeze
(C) increases in tendency to pass into the vapour phase.
(D) decrease in tendency of the liquid to freeze
34. To aqueous solution of NaI, increasing amounts of solid HgI_2 is added. The vapor pressure of the solution
- (A) decreases to a constant value
(B) increases to a constant value
(C) increases first and then decreases
(D) remains constant because HgI_2 is sparingly soluble in water.

35. A liquid possessing which of the following characteristics will be most suitable for determining the molecular mass of a compound by cryoscopic measurements?
 (A) That having low freezing point and small enthalpy of freezing
 (B) That having high freezing point and small enthalpy of freezing
 (C) That having high freezing point and small enthalpy of vaporization
 (D) That having large surface tension
36. A mixture of two immiscible liquids at a constant pressure of 1 atm boils at a temperature
 (A) equal to the normal boiling point of more volatile liquid.
 (B) equal to the mean of the normal boiling points of the two liquids.
 (C) greater than the normal boiling point of either of the liquid.
 (D) smaller than the normal boiling point of either of the liquid.

. MATRIX MATCH

37.

Column I	Column II
(A) Acetone + CHCl_3	(p) $\Delta S_{\text{nu.}} > 0$
(B) Ethanol + Water	(q) > 0
(C) $\text{C}_2\text{H}_5\text{Br} + \text{C}_2\text{H}_5\text{I}$	(r) $\Delta H_m < 0$,
(D) Acetone + Benzene	(s) Maximum boiling azeotropes
	(t) Minimum boiling azeotropes

38.

Column — I	Column — II
Assuming all the solutes are non volatile and all solutions are ideal.	
(A) 10 ml 0.1 M NaOH aqueous solution is added to 10 ml 0.1 M HCl aqueous solution	(p) Osmotic pressure of solution increases
(B) 10 ml 0.1 M NaOH aqueous solution is added to 10 ml 0.1M CH_3COOH aqueous solution	(q) Vapour pressure of solution increases
(C) 10 ml 0.1 M HCl aqueous solution is added to 10 ml 0.1 M NH_3 aqueous solution	(r) Boiling point of solution increases
(D) 10 ml 0.1 M HCl aqueous solution to 10 ml 0.1 M KOH aqueous solution	(s) Freezing point of solution increases

39. For a binary liquid solution of A and B. p_A^0 = pure vapour pressure of A. p_B^0 = pure vapour pressure of B. X_A = mole fraction of A in liquid phase. Y_A = mole fraction of A in vapour phase.

- | Column — I | Column — II |
|---|-----------------|
| (A) $p_2 > p_1$ [Ideal liquid solution] | (p) $X_A < Y_A$ |
| (B) Azeotropic mixture | (q) $X_A < Y_A$ |
| (C) Equimolar ideal mixture of A & B with $P_A^0 < P_B^0$ | (r) $X_B < Y_B$ |
| (D) Equimolar ideal mixture of A & B with $P_A^0 = P_B^0$ | (S) $Y_B > Y_A$ |

INTEGER TYPE

40. A solution of A and B with 30 mole percent of A is in equilibrium with its vapour which contains 60 mole percent of A. Assuming ideality of the solution and its vapour calculate the ratio of vapour pressure of pure A to that of pure B. (Report your answer as ratio x 2)

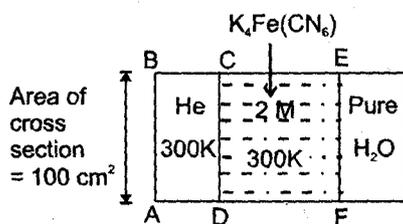
41. 0.0125 mol of sucrose is dissolved in 100 gm of water and it undergoes inversion according to following equation



If elevation in boiling point of solution is 0.104°C calculate $\frac{1}{10}$ mol percentage of sugar inverted ($K_{b,H_2O}=0.52$).

42. 25 ml of FeC_2O_4 dissolved in 186 gm of water calculate depression in freezing point if 10 ml of same FeC_2O_4 titrated with 30 ml of 0.4 M KMnO_4 in acidic medium (k_f for $\text{H}_2\text{O} = 1.86$, Assume 100% ionisation of FeC_2O_4).

- 43.



CD : Fixed wall, EF : SPM, Fixed wall : allows the pressure transfer but no mass transfer.

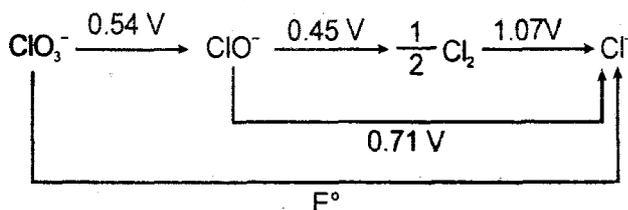
If 16 gm Helium present in ABCD chamber calculate the length of this chamber in cm if no osmosis takes place through SPM EF. Assume 75% ionisation of $\text{K}_4\text{Fe}(\text{CN})_6$.

44. In 10^3 Litre sample of hard water CaSO_4 and MgSO_4 present If elevation in Boiling point is 0.000052°C . Calculate the degree of Hardness of hard water in ppm. (K_b for $\text{H}_2\text{O} = 0.52$)

ELECTROCHEMISTRY

ONLY ONE OPTION CORRECT

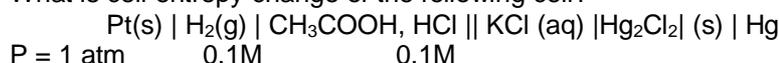
1.



The E° in the given diagram is,

- (A) 0.5 (B) 0.6 (C) 0.7 (D) 0.8

2. What is cell entropy change of the following cell?



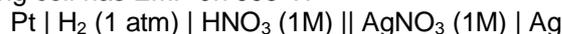
$P = 1 \text{ atm}$ 0.1M 0.1M

Emf of the cell is found to be 0.045 V at 298 K and temperature coefficient is $3.4 \times 10^{-4} \text{ V K}^{-1}$

Given $K_a(\text{CH}_3\text{COOH}) = 10^{-5} \text{ M}$

- (A) 60 (B) 65.2 (C) 69.2 (D) 63.5

3. Following cell has EMF 0.7995 V.



If we add enough KCl to the Ag cell so that the final Cl^- is 1M. Now the measured emf of the cell is 0.222 V. The K_{sp} of AgCl would be :

- (A) $1 \times 10^{-9.8}$ (B) $1 \times 10^{-19.6}$ (C) 2×10^{-10} (D) 2.64×10^{-14}

4. The solubility of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2] \text{ClO}_4$ _____ if the $\lambda_{\text{Co}(\text{NH}_3)_4\text{Cl}_2^+} = 50$, $\lambda_{\text{ClO}_4^-} = 70$, and the measured resistance was 33.5Ω in a cell with cell constant of 0.20 is _____.

- (A) 59.7 mmol/L (B) 49.7 mmol/L (C) 39.7 mmol/L (D) 29.7 mmol/L

5. We have taken a saturated solution of AgBr. K_{sp} of AgBr is 12×10^{-14} . If 10^{-7} mole of AgNO_3 are added to 1 litre of this solution then the conductivity of this solution in terms of 10^{-7} Sm^{-1} units will be

[Given $\lambda_{\text{Ag}^+}^\circ = 4 \times 10^{-3} \text{ Sm}^2 \text{ mol}^{-1}$ $\lambda_{\text{Br}^-}^\circ = 6 \times 10^{-3} \text{ Sm}^2 \text{ mol}^{-1}$, $5 \times 10^{-3} \text{ Sm}^2 \text{ mol}^{-1}$]

- (A) 39 (B) 55 (C) 15 (D) 41

6. At 298K the standard free energy of formation of $\text{H}_2\text{O}(\ell)$ is -237.20 kJ/mole while that of its ionisation into H^+ ion and hydroxyl ions OH^- each 80 kJ/mole, then the emf of the following cell at 298 K will be $\text{H}_2(\text{g}, 1 \text{ bar}) \mid \text{H}^+ (1\text{M}) \parallel \text{OH}^- (1\text{M}) \mid \text{O}_2 (\text{g}, 1\text{bar})$

- (A) 0.40 V (B) 0.81 V (C) 1.23 V (D) -0.40 V

7. Which of the following cell can produce Highest electric work.

- (A) $\text{pt}, \text{H}_2 \mid \text{NH}_4\text{Cl} \parallel 0.1\text{MCH}_3\text{COOH} \mid \text{H}_2, \text{pt}$ (B) $\text{pt}, \text{H}_2 \mid 0.1\text{MHCl} \parallel 0.1\text{MNaOH} \mid \text{H}_2, \text{pt}$
 (C) $\text{pt}, \text{H}_2 \mid 0.1\text{MHCl} \parallel 0.1\text{MCH}_3\text{COOK} \mid \text{H}_2, \text{pt}$ (D) $\text{pt}, \text{H}_2 \mid 0.1\text{MCH}_3\text{COOK} \parallel 0.1\text{MHCl} \mid \text{H}_2, \text{pt}$

8. A hydrogen electrodes is immersed in a solution with $\text{pH} = 0$ (HCl). By how much will the potential (reduction) change if an equivalent amount of NaOH is added to the solution. (Take $P_{\text{H}_2} = 1 \text{ atm}$) $T = 298 \text{ K}$.

- (A) increase by 0.41V (B) increase by 50mV (C) decrease by 0.41V (D) decrease by 59mV

9. At what $\frac{[\text{Br}^-]}{\sqrt{[\text{CO}_3^{2-}]}}$ does the following cell have its reaction at equilibrium?
 $\text{Ag(s)} \mid \text{Ag}_2\text{CO}_3\text{(s)} \mid \text{Na}_2\text{CO}_3\text{(aq)} \parallel \text{KBr(aq)} \mid \text{AgBr(s)} \mid \text{Ag(s)}$
 $K_{\text{SP}} = 8 \times 10^{-12}$ for Ag_2CO_3 and $K_{\text{SP}} = 4 \times 10^{-13}$ for AgBr
- (A) $\sqrt{1} \times 10^{-7}$ (B) $\sqrt{2} \times 10^{-7}$ (C) $\sqrt{3} \times 10^{-7}$ (D) $\sqrt{4} \times 10^{-7}$
10. Calculate the EMF of the cell at 298 K $\text{Pt} \mid \text{H}_2(1\text{atm}) \mid \text{NaOH}(x\text{M}), \text{NaCl}(x\text{M}) \mid \text{AgCl(s)} \mid \text{Ag}$
 If $E^\circ_{\text{Cl}^-/\text{AgCl}/\text{Ag}} = + 0.222 \text{ V}$
- (A) 1.048 V (B) - 0.04 V (C) - 0.604
 (B) Emf depends on x and cannot be determined unless value of x is given
11. A current of 0.1A was passed for 2hr through a solution of cuprocyanide (CuCN) and 0.3745g of copper was deposited on the cathode. Calculate the current efficiency for the copper deposition.
- (A) 79% (B) 39.5% (C) 63.25% (D) 63.5%
12. With t taken in seconds and I taken in Amp, the variation of I follows the equation $t^2 + I^2 = 25$ what amount of Ag will be electrodeposited with this current flowing in the interval 0-5 second ? (Ag : 108)
- (A) 22mg (B) 66mg (C) 77mg (D) 88mg
13. A resistance of 50Ω is registered when two electrodes are suspended into a beaker containing a dilute solution of a strong electrolyte such that exactly half of the them are submerged into solution. If the solution is diluted by adding pure water (negligible conductivity) so as to just completely submerge the electrodes, the new resistance offered by the solution would be
- (A) 50Ω (B) 100Ω (C) 25Ω (D) 200Ω
14. The standard reduction potential of a silver chloride electrode is 0.2 V and that of a silver electrode is 0.79 V. The maximum amount of AgCl that can dissolve in 10^6 L of a 0.1 M AgNO_3 solution is
- (A) 0.5 mmol (B) 1.0 mmol (C) 2.0 mmol (D) 2.5 mmol
15. Calculate the cell EMF in mV for
 $\text{Pt} \mid \text{H}_2(1\text{atm}) \mid \text{HCl}(0.01\text{M}) \mid \text{AgCl(s)} \mid \text{Ag(s)}$ at 298 K If ΔG°_r values are at 25°C
 $- 109.56 \frac{\text{kJ}}{\text{mol}}$ for AgCl(s) and $- 130.79 \frac{\text{kJ}}{\text{mol}}$ for $(\text{H}^+ + \text{Cl}^-)$ (aq)
- (A) 456 mV (B) 654 mV (C) 546 mV (D) None of these.
16. Adiponitrile is manufactured electrolytically from acrylonitrile
 $\text{CH}_2 = \text{CHCN} \longrightarrow \text{CN} - (\text{CH}_2)_4 - \text{CN}$
 How many kg of adiponitrile (molecular mass = 108) is produced in 9.65 hr using a current of 3750 A with 80% efficiency/
- (A) 30 kg (B) 58 kg (C) 60 kg (D) 80 kg
17. It is observed that the voltage of a galvanic cell using the reaction $\text{M(s)} + x\text{H}^+ \longrightarrow \text{M}^{x+} + \frac{x}{2}\text{H}_2$ varies linearly with the log of the square root of the hydrogen pressure and the cube root of the M^{x+} concentration. The value of x is
- (A) 2 (B) 3 (C) 4 (D) 5
18. Acetic acid has $K_a = 1.8 \times 10^{-5}$ while formic acid had $K_a = 2.1 \times 10^{-4}$. What would be the magnitude of the emf of the cell
- $$\text{Pt}(\text{H}_2) \left| \begin{array}{l} 0.1\text{M acetic acid} + \\ 0.1\text{M sodium acetate} \end{array} \right| \left| \begin{array}{l} 0.1\text{M formic acid} + \\ 0.1\text{M sodium formate} \end{array} \right| \text{Pt}(\text{H}_2) \text{ at } 25^\circ\text{C}$$
- (A) 0.0315 volt (B) 0.0629 volt (C) 0.0455 volt (D) 0.0545 volt

19. Consider the cell $\text{Ag(s)}|\text{AgBr(s)}|\text{Br(aq)}||\text{AgCl(s)}|\text{Cl(aq)}|\text{Ag(s)}$ at 25°C . The solubility product constants of AgBr & AgCl are respectively 5×10^{-13} & 1×10^{-10} . For what ratio of the concentrations of Br^- & Cl^- ions would the emf of the cell be zero ?
 (A) 1 : 2000 (B) 1 : 100 (C) 1 : 500 (D) 200 : 1
20. Value of Λ_m^∞ for SrCl_2 in water at 25°C from the following data:

Conc. (mol/l)	0.25	1
$\Lambda_m (\Omega^{-1} \text{cm}^2 \text{mol}^{-1})$	260	250

 (A) 270 (B) 260 (C) 250 (D) 255
21. Calculate the useful work of the reaction $\text{Ag(s)} + 1/2\text{Cl}_2(\text{g}) \longrightarrow \text{AgCl(s)}$
 Given $E^\circ_{\text{Cl}_2/\text{Cl}^-} = +1.36 \text{ V}$, $E^\circ_{\text{AgCl}/\text{Ag,Cl}^-} = 0.22 \text{ V}$
 If $P_{\text{Cl}_2} = 1 \text{ atm}$ and $T = 298 \text{ K}$
 (A) 110 kJ/mol (B) 220 kJ/mol (C) 55 kJ/mol (D) 1000 kJ/mol
22. Which of these ions Cu^+ , Co^{3+} , Fe^{2+} is stable in aqueous medium.
 Given : $E^\circ_{\text{Cu}^{2+}/\text{Cu}^+} = 0.15 \text{ volt}$; $E^\circ_{\text{Cu}^+/\text{Cu}} = 0.53 \text{ V}$; $E^\circ_{\text{Co}^{3+}/\text{Co}^{2+}} = 1.82 \text{ V}$;
 $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}$; $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$; $E^\circ_{\text{O}_2, \text{H}^+/\text{H}_2\text{O}} = 1.23 \text{ V}$
 (A) Cu^+ , Co^{3+} (B) Co^{3+} (C) Cu^+ (D) Co^{3+} , Cu^+ , Fe^{2+}
23. Select the correct statement if -
 $E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.4 \text{ V}$, $E^\circ_{\text{Sn}^{4+}/\text{Sn}^{2+}} = 0.1 \text{ V}$, $E^\circ_{\text{MnO}_4^-, \text{H}^+/\text{Mn}^{2+}} = 1.5 \text{ V}$, $E^\circ_{\text{I}_2/\text{I}^-} = 0.5 \text{ V}$
 Here,
 (A) MnO_4^- is the strongest Oxidizing Agent and Mg is the strongest Reducing Agent.
 (B) $\text{Sn}^{4+} + 2\text{I}^- \longrightarrow \text{Sn}^{2+} + \text{I}_2$ is a spontaneous reaction.
 (C) $\text{Mg}^{2+} + \text{Sn}^{2+} \longrightarrow \text{Mg} + \text{Sn}^{4+}$ is a spontaneous reaction.
 (D) Here, Weakest oxidizing agent is Sn^{4+} and weakest reducing agent is Mn^{2+} .
24. What is the value of pK_b (CH_3COOH^-) if $\lambda_m^\infty = 390$ & $\lambda_m = 7.8$ for 0.04 of a CH_3COOH at 25°C
 (A) 9.3 (B) 9.2 (C) 4.7 (D) 4.8
25. The temperature coefficient of a standard Cd-cell is $-5.0 \times 10^{-5} \text{ V K}^{-1}$ whose emf at 25°C is 1.018 V. During the cell operation, the temperature will -
 (A) increase (B) decrease (C) either (D) remains constant

ONE OR MORE THAN ONE OPTION CORRECT

26. In which of the following cell (s) : $E_{\text{cell}} = E_{\text{cell}}^\circ$?
 (A) $\text{Cu(s)}|\text{Cu}^{2+}(0.01\text{M})||\text{Ag}^+(0.1\text{M})|\text{Ag(s)}$ (B) $\text{Pt}(\text{H}_2)|\text{pH} = 1 ||\text{Zn}^{2+}(0.01\text{M})|\text{Zn(s)}$
 (C) $\text{Pt}(\text{H}_2)|\text{pH} = 1 ||\text{Zn}^{2+}(1\text{M})|\text{Zn(s)}$ (D) $\text{Pt}(\text{H}_2)|\text{H}^+ = 0.1 ||\text{Zn}^{2+}(0.01\text{M})|\text{Zn(s)}$
27. Which one is/are correct among the following?
 Given, the half cell emf's $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.337$, $E^\circ_{\text{Cu}^+/\text{Cu}} = 0.521$
 (A) Cu^+ disproportionates
 (B) Cu and Cu^{2+} comproportionates (reverse of disproportionates into Cu^+).
 (C) $E^\circ_{\text{Cu}|\text{Cu}^{2+}} + E^\circ_{\text{Cu}^+|\text{Cu}}$ is positive
 (D) All of these
28. Indicate the **correct** statements:
 (A) Conductivity cells have cell constant values independent of the solution filled into the cell.
 (B) DC (direct current) is not used for measuring the resistance of a solutn.
 (C) Kohlrausch law is valid both for strong and weak electrolytes.
 (D) The k decreases but λ_M and λ_E increase on dilution.

29. The standard redox potential E° of the following systems are
- | System | E° (volts) |
|---|-------------------|
| (i) $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ | 1.51 |
| (ii) $\text{Sn}^{2+} \longrightarrow \text{Sn}^{4+} + 2\text{e}^-$ | - 0.15 |
| (iii) $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ | 1.33 |
| (iv) $\text{Ce}^{3+} \longrightarrow \text{Ce}^{4+} + \text{e}^-$ | - 1.61 |
- The oxidizing power of the various species are related as
 (A) $\text{Cr}_2\text{O}_7^{2-} > \text{MnO}_4^-$ (B) $\text{Ce}^{4+} > \text{Sn}^{4+}$ (C) $\text{Ce}^{4+} > \text{MnO}_4^-$ (D) $\text{MnO}_4^- > \text{Sn}^{4+}$

PARAGRAPH BASED QUESTIONS

Comprehension # 1

A fuel cell is a cell that is continuously supplied with an oxidant and a reductant so that it can deliver a current indefinitely.

Fuel cells offer the possibility of achieving high thermodynamic efficiency in the conversion of Gibbs energy into mechanical work. Internal combustion engines at best convert only the fraction $(T_2 - T_1)/T_2$ of the heat of combustion into mechanical work.

While the thermodynamic efficiency of the fuel cell is given by, $\eta = \frac{\Delta G}{\Delta H}$, where ΔG is the Gibbs

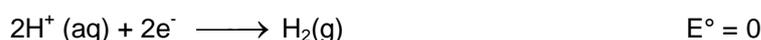
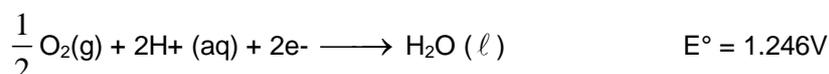
energy change for the cell reaction and ΔH is the enthalpy change of the cell reaction.

A hydrogen-oxygen fuel cell may have an acidic or alkaline electrolyte.

$$\text{Pt}|\text{H}_2(\text{g})|\text{H}^+(\text{aq.})||\text{H}_2\text{O}(\ell)|\text{O}_2(\text{g})|\text{Pt}; \frac{2.303RT}{F} = 0.06$$

The above fuel cell is used to produce constant current supply under constant temperature & 30 atm constant total pressure condition in a cylinder. If 10 moles H_2 and 5 moles of O_2 were taken initially. Rate of combustion of O_2 is 10 milli moles per minute.

The half cell reactions are



To maximize the power per unit mass of an electrochemical cell, the electronic and electrolytic resistances of the cell must be minimized. Since fused salts have lower electrolytic resistances than aqueous solutions, high-temperature electrochemical cells are of special interest for practical applications.

30. Calculate e.m.f. of the given cell at $t = 0$. ($\log 2 = 0.3$).
 (A) 1.255 V (B) 1.35 V (C) 1.3 V (D) 1.246 V
31. The above fuel cell is used completely as an electrolytic cell with Cu voltameter of resistance 26.94Ω using Pt electrodes. Initially Cu voltameter contains 1 litre solution of 0.05M CuSO_4 . [H^+] in solution after electrolysis (Assuming no change on volume of solution).
 (A) 0.015 M (B) 0.03 M (C) 0.025 M (D) 0.01 M
32. If $\lambda_m^\infty(\text{Cu}^{2+}) = 0.01 \text{ S m}^2 \text{ mole}^{-1}$, $\lambda_m^\infty(\text{H}^+) = 0.035 \text{ S m}^2 \text{ mole}^{-1}$ and $\lambda_m^\infty(\text{SO}_4^{2-}) = 0.016 \text{ S m}^2 \text{ mole}^{-1}$, specific conductivity of resulting solution left in sopper voltameter after above electrolysis is
 (A) 2.57 S m^{-1} (B) 1.75 S m^{-1} (C) 1.525 S m^{-1} (D) 2.25 S m^{-1}

Comprehension # 2

The molar conductance of NaCl varies with the concentration as shown in the following table.

$$\lambda_m^C = \lambda_m^\infty - b\sqrt{C}$$

Where λ_m^C = molar specific conductance

λ_m^∞ = molar specific conductance at infinite dilution

C = molar concentration

Molar Concentration of NaCl	Molar Conductance In $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$
4×10^{-4}	107
9×10^{-4}	97
16×10^{-4}	87

When a certain conductivity cell (C) was filled with $25 \times 10^{-4} \text{M}$ NaCl solution. The resistance of the cell was found to be 1000 ohm. At infinite dilution, conductance of Cl^- and SO_4^{2-} are $80 \text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ and $160 \text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ respectively.

Comprehension # 3

METALLURGY OF COPPER

Electrolytic purification of copper is required since the product of the Bessemer convert is impure. Sheets of pure copper are made the cathodes and blister copper is used as the cathodes. The bath contains CuSO_4 , H_2SO_4 and NaCl. Metallic copper goes into solution as Cu^{+2} ions at the anode and deposited at the cathode. Zinc and iron go into solution and do not deposit at the cathode along with copper. Silver goes into solution as Ag^+ ions, but forms sludge in the electrolysis cell. The noble metals such as gold and platinum do not dissolve; they fall to the bottom when released from the copper anode. They help to pay for the copper refining process.

33. In what form will silver be recovered from the plating bath?
(A) Ag^+ (B) AgCl (C) Ag (D) Ag – Cu alloy
34. The different chemical behaviour of various metal ions (for example only Cu is deposited on the cathode) involved are explainable best using
(A) their amount in impure copper (B) the electrochemical series
(C) their ionization potentials (D) their hydration energies
35. The voltage is kept low enough during the operation. This is to ensure that
(A) Fe^{+2} and Zn^{+2} ions are kept in solution only
(B) there is no risk of electric shocks to the plant operators
(C) gold and platinum do not dissolve in solution and are recovered as solids
(D) temperature control is maintained to effect reaction rate control
36. What approximate purity may be achieved in this process ?
(A) 90% (B) 95% (C) 99% (D) 99.9%
37. The most important role of various electrolytes added to the electrorefining bath in this case is
(A) to reduce the temperature of bath
(B) to result in good electrical connectivity so as to have high production rates
(C) so that the anode acts as an attackable electrodes
(D) to enhance the viscosity of electrolyte thus preventing leakage from bath.

Comprehension # 4

A solution that is relatively resistance to change in pH is called a buffer solution. We can also say that the solution is buffered the simplest way to achieve substantial conc. Of both acid and base in the same solution to use a conjugate acid-base pair. The most common form of buffer solution contains a weak acid and its conjugate base or a weak base and its conjugate acid.

By using buffer concept. A student prepare 2L buffer solution of 0.0330 M NaH_2PO_4 . The solution is divided in half between the two compartment (each containing 1L buffe) of an electrolysis is carried out for 212 min with a constant current of 1.25 A. [Assumes that $\text{pK}_a(\text{H}_2\text{PO}_4^-) = 7.2$]

38. The concentration of $[\text{H}^+]$ consumed by HPO_4^{2-} at anode is:
 (A) 0.165 M (B) 0.330 M (C) 1.00 M (D) 0.0825 M
39. pH in 1st compartment cell (at anode) is:
 (A) 7.2 (B) 6.72 (C) 7.67 (D) 7.0
40. pH in 2nd compartment cell (at cathode) is:
 (A) 7.2 (B) 6.72 (C) 7.67 (D) 7.0

MATRIX MATCH

41. **Match Matrix**
- | | |
|---|--|
| (A) $\text{Zn} \text{Zn}^{2+} (C) \text{Zn}^{2+} (2C) \text{Zn}$ | (p) Spontaneous cell reaction |
| (B) $\text{H}_2(\text{P}) \text{HCl}(1\text{N}) \text{H}_2(\text{P})$ | (q) Working cell representation |
| (C) $\text{Cu} \text{Cu}^{2+} (0.01\text{M}) \text{Ag}^+ (0.1\text{M}) \text{Ag}$ | (r) Concentration of cation in cathodic Compartment increases upto equilibrium |
| (D) $\text{AgCl} \text{Ag} (\text{KCl}, 0.1 \text{ M}) \text{Ag}^+ (0.01\text{M}) \text{Ag}$ | (s) Concentration cell |
42. **Match the following:**
- | Column I | Column II |
|-------------------------------|---|
| (A) Concentration cell | (p) $\text{H}_2 + \frac{1}{2} \text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{electrical energy}$ |
| (B) Spontaneous cell reaction | (q) $E_{\text{cell}}^0 = 0$ |
| (C) Daniel cell | (r) $E_{\text{cell}} > 0$ |
| (D) Hofmann voltameter | (s) Galvanic cell |
| (E) Fuel cell | (t) $\text{H}_2\text{O} + \text{electrical energy} \longrightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$ |
43. Assume inert electrolyte used in salt bridge in all the given cells is KCl. (K_a of $\text{HCOOH} = 2 \times 10^{-4}$)
- | Column I | Column - II |
|--|---|
| (A) $\text{Zn} \text{ZnSO}_4(1\text{M}) \text{ZnSO}_4(2\text{M}) \text{Zn}$ | (p) Spontaneous cell reaction. |
| (B) $\text{Cu} \text{CuCl}_2(1\text{M}) \text{CuSO}_4(2\text{M}) \text{Cu}$ | (q) Osmotic pressure of cathodic solution is greater than that of anodic solution . |
| (C) $\text{Ag} \text{AgCl}(\text{sat. sol.}) \text{AgNO}_3(1\text{M}) \text{Ag}$ | (r) At equilibrium condition of the cell, freezing point of anodic solution is higher than of cathodic solution |
| (D) $\text{Pt} \text{H}_2 \text{HCOOH} (1\text{M}) \text{HCl} (1\text{M}) \text{H}_2 \text{Pt}$ | (s) At equilibrium condition of the cell, boiling point of cathodic solution is higher than that of anodic solution |

44. Match the column:

Column – I

- (A) Molten PbCl_2 using inert electrode
 (B) Sodium chloride solution using inert electrode
 (C) Silver nitrate solution with silver electrode
 (D) Sodium nitrate solution using inert electrode

Column – II

- (p) Metal of salt will reduced
 (q) $\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-$
 (r) Solution becomes basic after electrolysis
 (s) Solution becomes acidic after electrolysis
 (t) Solution become acidic after electrolysis

45.

Column – I

(Quantities)

- (A) Molar conductance
 (B) emf of a cell in operation
 (C) Electrode potential
 (D) Standard reduction potential

Column – II

(Factors on which dependency exist)

- (p) Temperature
 (q) Concentration of species involved
 (r) Nature of substance involved
 (s) No. of electrons lost or gained in the reaction

INTEGER TYPE

46. In the acid base titration [$\text{H}_3\text{PO}_4(0.1 \text{ M}) + \text{NaOH} (0.1\text{M})$] e.m.f of the solution is measured by coupling this electrodes with suitable reference electrode. When alkali is added pH of solution is in accordance with equation, $E_{\text{cell}} = E_{\text{cell}}^0 + 0.059 \text{ pH}$.
 For H_3PO_4 $K_{a1} = 10^{-3}$; $K_{a2} = 10^{-8}$; $K_{a3} = 10^{-13}$
 What is the cell e.m.f. at the 1st end point of the titration if E_{cell}^0 at this stage is 1.3805 V.
47. 100 ml, 0.05 M CuSO_4 solution is electrolysed by using current of 0.965 A for 100 min. Find the pH of solution at the end of electrolysis.
48. The e.m.f. of a cell corresponding to the reaction

$$\text{An} + 2\text{H}^+(\text{aq}) \longrightarrow \text{Zn}^{2+}(0.1\text{M}) + \text{H}_2(\text{g})(1\text{atm})$$
 is 0.26 volt at 25° C. Calculate the pH of the solution at the hydrogen electrode
 $E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ volt}$ and $E_{\text{H}^+/\text{H}_2}^0 = 0$
49. A fuel cell uses $\text{CH}_4(\text{g})$ and forms CO_3^{2-} at the anode. It is used to power a car with 80 Amp. For 0.96 hr. How many litres of $\text{CH}_4(\text{g})$ (stp.) would be required? ($V_m = 22.4 \text{ L/mol}$) ($F = 96500$). Assume 100% efficiency.
50. Small spherical ball of silver metal used in jewellery having diameter 0.1 cm, which is obtained by the electrolytic deposition. If total number of balls in jewellery is 10,000, then calculate the applied amount of electricity in coulombs, which is used on the deposition on electrodes having entire surface 0.12 m^2 . [Density of Ag = 10.5]
 It is assumed that 3.5% electricity consumed as wastage during electrolysis and 60% of electrode body immersed in electrode. [Given your answer in multiple of 10^4]

STOICHIOMETRY

ONLY ONE OPTION CORRECT

- H_2O_2 acts as both oxidising as well as reducing agent its product is H_2O , when act as oxidising agent and its product is O_2 when act as of reducing agent. The strength of '10 volume means one liter of H_2O_2 solution on decomposition at S.T.P. condition liberate 10 liters of oxygen gas ($\text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$)

15 gm MnO_4^{2-} sample containing inert impurity is completely reacting with 100 ml of '11.2 V' H_2O_2 , then what will be the % purity of $\text{Ba}(\text{MnO}_4)_2$ in the sample ? (Atomic mass Ba = 137, Mn = 55)

(A) 5% (B) 10% (C) 50% (D) none
- 1.2 gm of carbon is burnt completely in oxygen (limited supply) to produce CO and CO_2 . This mixture of gases is treated with solid I_2O_5 (to know the amount of CO produced), the liberated iodine required 120 ml of 0.1 M hypo solution for complete titration. The % of carbon converted into CO is :

(A) 60% (B) 100% (C) 50% (D) 30%
- Nitrogen (N), phosphorus (P) and Potassium (K) are the main nutrients in plant fertilizers. According to an industry convention, the numbers on the label refer to the mass % of N, P_2O_5 and K_2O in that order calculate the N : P : K ratio of a 30 : 10 : 10, fertilizer in terms of moles of each element and express it as x : y : 1.

(A) 10 : 0.67 : 1 (B) 20 : 0.37 : 1 (C) 0.37 : 10 : 1 (D) 5 : 2 : 1
- In what ratio should a 15% solution of acetic acid be mixed with a 3% solution of the acid to prepare a 10% solution (all percentages are mass/mass percentages) :

(A) 7 : 3 , (B) 5 : 7 (C) 7 : 5 (D) 7 : 10
- 105 ml of pure water at 4°C saturated with NH_3 gas yielded a solution of density 0.9 g/ml and containing 30% NH_3 by mass. Find the volume of resulting NH_3 solution.

(A) 66.67 ml (B) 166.67 ml (C) 133.33 ml (D) 266.67 ml
- The equivalent mass of H_3BO_3 (M = Molar mass of H_3BO_3) in its reaction with NaOH to form $\text{Na}_2\text{B}_4\text{O}_7$ is equal to –

(A) M (B) $\frac{M}{2}$ (C) $\frac{M}{4}$ (D) $\frac{M}{6}$
- x gram of pure As_2S_3 is completely oxidised to respective highest oxidation states by 50 ml of 0.1 M hot acidified KMnO_4 then x mass of As_2S_3 taken is : (Molar mass of $\text{As}_2\text{S}_3 = 246$)

(A) 22.4 g (B) 43.92 g (C) 64.23 g (D) None
- The number of moles of ferrous oxalate oxidised by one mole of KMnO_4 is

(A) $\frac{5}{2}$ (B) $\frac{2}{5}$ (C) $\frac{3}{5}$ (D) $\frac{5}{3}$
- How many moles of KMnO_4 are needed in a mixture of 1 mole of each FeSO_4 & FeC_2O_4 in acidic medium

(A) $\frac{4}{5}$ (B) $\frac{5}{4}$ (C) $\frac{3}{4}$ (D) $\frac{5}{3}$

10. In the reaction

$$\text{Na}_2\text{S}_2\text{O}_3 + 4\text{Cl}_2 + 5\text{H}_2\text{O} \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + 8\text{HCl}$$
the equivalent weight of $\text{Na}_2\text{S}_2\text{O}_3$ will be
(A) $M/4$ (B) $M/8$ (C) $M/1$ (D) $M/2$
(M = molecular weight of $\text{Na}_2\text{S}_2\text{O}_3$)
11. Which of the following equations is a balanced one-
(A) $5\text{BiO}_3 + 22\text{H}^+ + 2\text{M}^{n2} \rightarrow 5\text{Bi}^{3+} + 7\text{H}_2\text{O} + 2\text{MnO}_4^-$
(B) $5\text{BiO}_3 + 14\text{H}^+ + \text{Mn}^{2+} \rightarrow 5\text{Bi}^{3+} + 7\text{H}_2\text{O} + 2\text{MnO}_4^-$
(C) $2\text{BiO}_3 + 4\text{H}^+ + 2\text{M}^{n2+} \rightarrow 6\text{Bi}^{3+} + 2\text{H}_2\text{O} + \text{MnO}_4^-$
(D) $6\text{BiO}_3 + 12\text{H}^+ + 2\text{Mn}^{2+} \rightarrow 6\text{Bi}^{3+} + 6\text{H}_2\text{O} + 2\text{MnO}_4^-$
12. The following equations are balanced atomwise and charge wise.
(i) $\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 2\text{H}_2\text{O}_2 \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 2\text{O}_2$
(ii) $\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 5\text{H}_2\text{O}_2 \longrightarrow 2\text{Cr}^{3+} + 9\text{H}_2\text{O} + 4\text{O}_2$
(iii) $\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 7\text{H}_2\text{O}_2 \longrightarrow 2\text{Cr}^{3+} + 11\text{H}_2\text{O} + 5\text{O}_2$
The precise equation/equations representing the oxidation of H_2O_2 is/are
(A) (i) only (B) (ii) only (C) (iii) only (D) all the three
13. An excess of NaOH was added to 100 mL of a ferric chloride solution. This caused the precipitation of 1,425 g of $\text{Fe}(\text{OH})_3$. Calculate the normality of the ferric chloride solution
(A) 0.20 N (B) 0.50 N (C) 0.25 N (D) 0.40 N
14. In the reaction $\text{CrO}_5 + \text{H}_2\text{SO}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O} + \text{O}_2$ one mole of CrO_5 will liberate how many moles of O_2
(A) 5/2 (B) 5/4 (C) 9/2 (D) none of these
15. 0.4g of a polybasic acid H_nA (all the hydrogens are acidic) requires 0.5g of NaOH for complete neutralization. The number of replaceable hydrogen atoms in the acid and the molecular weight of 'A' would be :
(Molecular weight of the acid is 96 gms.)
(A) 1, 95 (B) 2, 94 (C) 3, 93 (D) 4, 92
16. A solution of $\text{Na}_2\text{S}_2\text{O}_3$ is standardized iodometrically against 0.1262 g of I_2 . This process requires 45 mL of the $\text{Na}_2\text{S}_2\text{O}_3$ solution. What is the strength of the $\text{Na}_2\text{S}_2\text{O}_3$?
(A) 0.2M (B) 0.1 M (C) 0.05M (D) 0.1 N
17. 25.0 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in water containing dilute H_2SO_4 , and the volume was made up to 1.0 L. 25.0 mL of this solution required 20 mL of an N/10 KMnO_4 solution for complete oxidation. The percentage of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in the acid solution is
(A) 78% (B) 98% (C) 89% (D) 79%
18. 1.0 mol of Fe reacts completely with 0.65 mol of O_2 to give a mixture of only FeO and Fe_2O_3 . The molar ratio of ferrous oxide to ferric oxide is
(A) 2 : 2 (B) 4:2 (C) 1:2 (D) 2: 7
19. 25 mL of a solution containing HCl and H_2SO_4 required 10 mL of a 1 N NaOH solution for neutralization. 20 mL of the same acid mixture on being treated with an excess of AgNO_3 gives 0.1425 g of AgCl. The normality of the HCl and the normality of the H_2SO_4 are respectively
(A) 0.40 N and 0.05 N (B) 0.05 N and 0.25 N
(C) 0.50 N and 0.25 N (D) 0.40 N and 0.5 N

20. If 10 gm of V_2O_5 is dissolved in acid and is reduced to V^{2+} by zinc metal, how many mole of I_2 could be reduced by the resulting solution if it is further oxidised to VO^{2+} ions ?
 [Assume no change in state of Zn^{2+} ions] ($V = 51, O = 16, I = 127$) :
 (A) 0.11 mole of I_2 (B) 0.22 mole of I_2 (C) 0.055 mole of I_2 (D) 0.44 mole of I_2

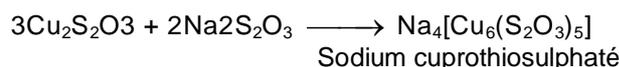
ONE OR MORE THAN ONE OPTION CORRECT

21. Which of the following samples of reducing agents is /are chemically equivalent to 25 ml of 0.2 N $KMnO_4$ to be reduced to Mn^{2+} and water.
 (A) 25 ml of 0.2 M $FeSO_4$ to be oxidized to Fe^{3+}
 (B) 50 ml of 0.1 M H_3AsO_3 to be oxidized to H_3AsO_4
 (C) 25 ml of 0.1 M H_2O_2 to be oxidized to H^+ and O_2
 (D) 25 ml of 0.1 M $SnCl_2$ to be oxidized to Sn^{4+}
22. There are two sample of Cl having polarity 1M and 0.25 M. Find volume of these sample taken in order to prepare 0.75 M HCl solution. (Assume no water is used)
 (A) 20 ml, 10 ml (B) 100 ml, 50 ml (C) 40 ml, 20 ml (D) 50 ml, 25 ml
23. Chloride of an element is given by the formula MCl_x , and it is 100% ionised in 0.01 M aqueous solution. Then
 (A) if $[Cl^-] = 0.03$ M then the value of x is 3.
 (B) if $[Cl^-] = 0.05$ M then the value of x is 5
 (C) $[M^{x+}] = 0.01$ M, irrespective of $[Cl^-]$
 (D) $[M^{x+}]$ depends on $[Al]$
24. If 100 ml of 1M H_2SO_4 solution is mixed with 100 ml of 98%(w/w) H_2SO_4 solution ($d = 1.84$ gm/ml) then :
 (A) concentration of solution remains same
 (B) volume of solution become 200 ml
 (C) mass of H_2SO_4 in the solution is 98 gm
 (D) mass of H_2SO_4 in the solution is 19.6 gm
25. 3 moles of the gas C_2H_6 is mixed with 60 gm of this gas and 2.4×10^{24} molecules of the gas is removed. The left over gas is combusted in the presence of excess oxygen then :
 ($N_A = 6 \times 10^{23}$) (Density of water = 1 gm/ml)
 (A) 2 Moles of C_2H_6 left for combustion
 (B) Volume of CO_2 at S.T.P. produced after combustion 44.8 litre.
 (C) Volume of water produced is 54 ml
 (D) None
26. Which of the following contains the same number of molecules?
 (A) 1g of O_2 , 2g of SO_2
 (B) 1g of CO_2 , 1g of N_2O
 (C) 112 ml of O_2 at STP, 224 ml of He at 0.5 atm and 273K
 (D) 1 g of oxygen, 1g of ozone
27. A 200 ml mixture of CO and CO_2 , is passed through a tube containing red hot charcoal. The volume becomes 260 ml. The volumes are measured under the same conditions of temperature and pressure. Amongst the following, select the correct statement(s).
 (A) Mole percent of CO_2 in the mixture is 60. (B) Mole fraction of CO in the mixture is 0.40
 (C) The mixture contains 40 ml of CO_2 (D) The mixture contains 40 ml of CO

PARAGRAPH BASED QUESTIONS

Comprehension # 1

632 g of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) reacts with copper sulphate to form cupric thiosulphate which is reduced by sodium thiosulphate to give cuprous compound which is dissolved in excess of sodium thiosulphate to form a complex compound sodium cuprothiosulphate ($\text{Na}_4[\text{Cu}_6(\text{S}_2\text{O}_3)_5]$).

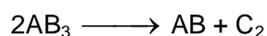


In this process, 0.2 mole of sodium cuprothiosulphate is formed. (O = 16, Na = 23, S = 32)

28. The average oxidation states of sulphur in $\text{Na}_2\text{S}_2\text{O}_3$ and $\text{Na}_2\text{S}_4\text{O}_6$ are respectively.
 (A) +5 & +2 (B) +2 & +2.5 (C) +5 & 2.5 (D) +2 & +4
29. Moles of sodium thiosulphate reacted and unreacted after the reaction are respectively.
 (A) 3 & 2 (B) 2 & 3 (C) 2.2 & 1.8 (D) 1.8 & 2.2
30. If instead of given amount of sodium thiosulphate, 2 moles of sodium thiosulphate along with 3 moles of CuSO_4 were taken initially. Then moles of sodium cuprothiosulphate formed is
 (A) 0 (B) 1 (C) 1.5 (D) 2

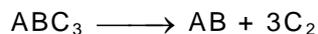
Comprehension it 2

We know that balancing of a chemical equation is entirely based on law of conservation of mass. However the concept of Principle of Atom Conservation (POAC) can also be related to law of conservation of mass in a chemical reaction. So, POAC can also act as a technique for balancing a chemical equation. For example, for a reaction



on applying POAC for, B & C and relating the 3 equations, we get : $\frac{n_{\text{ABC}_3}}{2} = \frac{n_{\text{AB}}}{2} = \frac{n_{\text{C}_2}}{3}$ (n_x : number of moles of X)

Thus, the coefficients of ABC_3 , AB & C_2 in the balanced chemical equation will be 2, 2 & 3 respectively and the balanced chemical equation can be represented as



Now answer the following questions :

31. Which of the following relation is correct regarding the numerical coefficients p, q, r in the balanced chemical equation :

$$p\text{A} + q\text{B}_2 \longrightarrow r\text{A}_2\text{B}_5$$
 (A) $2p = r$ (B) $q = 1.25p$ (C) $r = 2q$ (D) $q = 0.8p$
32. If the weight ratio of C and O_2 present is 1 : 2 and both of reactants completely consume and form CO and CO_2 and we will obtain a gaseous mixture of CO and CO_2 . What would be the weight ratio of CO and CO_2 in mixture.
 (A) 11 : 7 (B) 7 : 11 (C) 1 : 1 (D) 1 : 2

33. If the atomic masses of X and Y are 10 & 30 respectively, then the mass of XY_3 formed when 120g of Y_2 reacts completely with X is :
- Reaction $X + Y_2 \longrightarrow XY_3$
- (A) 133.3 g (B) 200 g (C) 266.6 g (D) 400 g

Comprehension # 3

Oleum is considered as a solution of SO_3 in H_2SO_4 , which is obtained by passing SO_3 in solution of H_2SO_4 . When 100 g sample of oleum is diluted with desired weight of H_2O then the total mass of H_2SO_4 obtained after dilution is known as % labelling in oleum.

For example, a oleum bottle labelled as '109% H_2SO_4 ' means the 109g total mass of pure H_2SO_4 will be formed when 100 g of oleum is diluted by 9 g of H_2O which combines with all the free SO_3 to form H_2SO_4 as



34. What is the % of free SO_3 in an oleum that is labelled as '104.5% H_2SO_4 '?
- (A) 10 (B) 20 (C) 40 (D) None of these
35. If excess water is added into a 100 g bottle sample labelled as "112% H_2SO_4 " and is reacted with 5.3 g Na_2CO_3 , then find the volume of CO_2 evolved at 1 atm pressure and 300 K temperature after the completion of the reaction : [R = 0.0821 L atm mol⁻¹ K⁻¹]
- $$H_2SO_4 + Na_2CO_3 \longrightarrow Na_2SO_4 + H_2O + CO_2$$
- (A) 2.46 L (B) 24.6 L (C) 1.23L (D) 123
36. 1 g of oleum sample is diluted with water. The solution required 54 ml of 0.4 N NaOH for complete neutralization. The % of free SO_3 in the sample is :
- (A) 74 (B) 26 (C) 20 (D) None of these

Comprehension # 4

Volumetric analysis is based on the principle of equivalence that involves the ratio of their equivalents. At the equivalence point of the reaction, involving the reactants A and B:

Number of gram equivalents of A = Number of gram equivalents of B.

If V_A ml of solution A having normality N_A react just completely with V_B ml of solution B having normality N_B then

$$\frac{N_A V_A}{1000} = \frac{N_B V_B}{1000}; N_A V_A = N_B V_B \quad \dots\dots\dots(i)$$

Equation (1), called normality equation is very useful in numerical of volumetric analysis. Equivalent masses of different substances :

Basically the equivalent mass of a substance is defined as the mass which combines with or displaces 1.0078 parts (≈ 1 part) by mass of hydrogen, 8 parts by mass of oxygen and 35.5 parts by mass of chlorine.

Mass of a substance expressed in gram equal to its equivalent mass is gram equivalent mass. Equivalent mass of a substance is not constant but depends upon the maximum number of electrons which the substance participates.

Equivalent mass of an acid in acid-base reaction is its mass in which one replaceable H⁺ ions (≈ 1.0078 g ≈ 1 g). On the other hand, equivalent mass of a base is its mass in which one replaceable OH⁻ ions. 1 g equivalent mass each of an acid and base combine to form 1 mole of water (= 18 g).

Equivalent mass of an oxidising agent is its mass which gains 1 mole of electrons. It can be obtained by dividing the molecular mass or formula mass by the total decrease in oxidation number of one or more elements per molecule.

On the other hand, equivalent mass of a reducing agent is the mass of the substance which loses 1 mole of electrons. It can be calculated by dividing the molecular or formula mass of the substance by the total increase in oxidation number of one or more elements per molecular or formula mass.

37. When 5.00 g of a metal is strongly heated, 9.44 g of its oxide is obtained. The equivalent mass of the metal is
 (A) 2.22 g (B) 5.00 g (C) 9.00 g (D) 4.44 g
38. How many gram of phosphoric acid (H_3PO_4) would be required to neutralize 58 g of magnesium hydroxide?
 (A) 65.3 g (B) 70.2 g (C) 85.0 g (D) 112.0 g
39. Which of the following solutions, when mixed with 100 ml of 0.05 M NaOH, will give a neutral solution?
 (A) 100 ml of 0.1 M H_2SO_4 (B) 50 ml of 0.05 M H_2SO_4
 (C) 100 ml of 0.05 M CH_3COOH (D) None of these
40. 100 ml of 0.1 M H_3PO_2 is titrated with 0.1 M NaOH. The volume of NaOH needed will be
 (A) 300 ml (B) 200 ml (C) 100 ml (D) None of these
41. 9.8 g of an acid on treatment with excess of an alkali forms salt along with 3.6 g of water. What is the equivalent mass of the acid?
 (A) 98.0 g (B) 49.0 g (C) 24.5 g (D) 73.5 g

Comprehension #5

Molality : It is defined as the moles of the solute present in 1kg of the solvent. It is denoted by 'm'.

$$\text{Molality (m)} = \frac{\text{Number of moles of solute}}{\text{Number of kilo-gram of the solvent}}$$

Let W_A grams of the solute of molecular mass m_A be present in W_B grams of the solvent, then

$$\text{Molality (m)} = \frac{W_A}{m_A \times W_B} \times 1000$$

Relation between mole fraction and Molality :

$$X_A = \frac{n}{N+n} \quad \text{and} \quad X_B = \frac{N}{N+n}$$

$$\frac{X_A}{X_B} = \frac{n}{N} = \frac{\text{Moles of solute}}{\text{Moles of solvent}} = \frac{w_A \times m_B}{w_B \times m_A}$$

$$\frac{X_A \times 1000}{X_B \times m_B} = \frac{w_A \times 1000}{w_B \times m_A} = m \quad \text{or} \quad \frac{X_A \times 1000}{(1-X_A) m_B} = m$$

42. If the ratio of the mole fraction of a solute is changed from $\frac{1}{3}$ to $\frac{2}{3}$ in the 800 g of solvent then the ratio of molality will be :
 (A) 1 : 3 (B) 3 : 1 (C) 4 : 3 (D) 1 : 2
43. The mole fraction of the solute in the 12 molal solution of Na_2CO_3 is :
 (A) 0.822 (B) 0.177 (C) 1.77 (D) 0.0177
44. What is the quantity of water that should be added to 16 gm, methanol to make the mole fraction of methanol as 0.25 –
 (A) 27 gm. (B) 12 gm. (C) 18 gm. (D) 36 gm.
45. A 300 gm, 30% (w/w) NaOH solution is mixed with 500 gm 40% (w/w) NaOH solution. What is % (w/w) NaOH, if density of final solution is 2 gm/ml.
 (A) 72.5 (B) 65 (C) 62.5 (D) None

46. What is the molality of final solution obtained in the above problem
 (A) 1.422 (B) 14.22 (C) 15.22 (D) None

MATRIX MATCH

- 47.
- | Column – I
(Reactions) | Column – II
(Information conveyed by the reactions) |
|---|---|
| (A) Complete reaction of Cuprous Sulphide with acidified Potassium permanganate solution producing a gas which turns lime water milky. | (p) Gases evolved do not have their constituent elements in their maximum possible oxidation states |
| (B) Reaction of Hydrochloric acid with Potassium dichromate solution Producing a gas necessary for The manufacture of Bleaching Powder | (q) Greater than one mole of oxidising agent is consumed for every mole of reducing agent. |
| (C) Reaction of Iron pyrites (FeS ₂) with Oxygen gas producing a gas having Bent shape | (r) The element in oxidant, which undergoes change in oxidation number, is in its maximum possible Oxidation state. |
| (D) Complete reaction of Ferrous oxalate (s) with acidified Potassium dichromate solution producing a gas isoelectronic a gas isoelectronic and isostructural with nitrous oxide. | Moles of reductant consumed is greater ten times the moles of oxidant consumed. |
48. Match the column
- | Column- I | Column- II |
|---|--|
| (A) $\text{CaCO}_3 + \text{H}_3\text{PO}_4 \rightarrow \text{Ca}_3(\text{PO}_4)_2 + \text{CO}_2 + \text{H}_2\text{O}$ | (p) 1 mole of oxidising agent gains more electrons than lost by 1 mole of reducing Agent. |
| (B) $\text{MnO}_2 + \text{HCl} \rightarrow \text{MnCl}_2 + \text{Cl}_2 + \text{H}_2\text{O}$ | (q) No change in oxidation number of any element takes place. |
| (C) $\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{SO}_4$ | (r) All elements (except oxygen) are in their maximum oxidation states on the reactant side. |
| (D) $\text{H}_2\text{O} + \text{F}_2 \rightarrow \text{HF} + \text{O}_2$ (s) | Number of moles of oxidising agent Consumed is less than number of Moles of reducing agent. |
49. [H = 1, C = 12, O = 16, Na = 23, P = 31, S = 32]
- | Column – I | Column – II |
|---|--|
| (A) 4.1 g H ₂ SO ₃ | (p) 200 ml of 0.5 N NaOH is used for complete neutralization |
| (B) 4.9 g H ₃ PO ₄ | (q) 200 millimoles of oxygen atoms |
| (C) 4.5 g oxalic acid (H ₂ C ₂ O ₄) | (r) Central atom has its highest oxidation number |
| (D) 5.3 g Na ₂ CO ₃ | (s) May react with an oxidising agent |
| | (t) Shape around central atom is regular |

50. Match the reacting mixture in column-I with the reagent in column – II

Column – I

- (A) $\text{H}_2\text{C}_2\text{O}_4 + \text{NaHC}_2\text{O}_4$
- (B) $\text{NaHPO}_4 + \text{NaNO}_2$
- (C) $\text{Fe}_2(\text{SO}_4)_3 + \text{FeC}_2\text{O}_4$
- (D) $\text{FeO} + \text{Fe}_2\text{O}_3$

Column – II

- (p) NaOH
- (q) HCl
- (r) KMnO_4
- (s) Zinc dust

51. Match the following

Column – I

- (A) 4.5 m solution of CaCO_3 density 1.45 gm/ml
- (B) 3M 100 ml H_2SO_4 mixed with 1M 300 ml H_2SO_4 solution
- (C) 14.5 m solution of Ca (r) molarity = 4.5
- (D) in 4 M 2 litre solution of NaOH, 40 gm NaOH is added.
- (E) 5m (molal) NaOH solution

Column – II

- (p) mole fraction of solute is 0.2
- (q) mass of the solute is 360 gm
- (s) molarity 1.5
- (t) 16.66% (w/w) of NaOH in solution

INTEGER TYPE

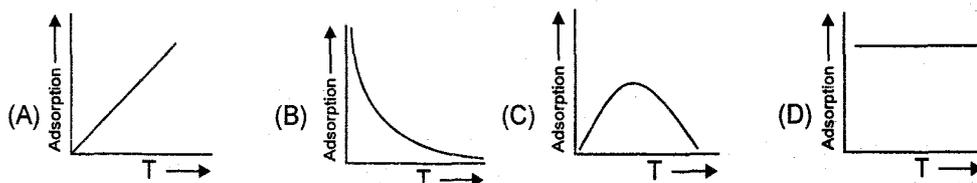
52. Polychlorinated biphenyls, PCBs, known to be dangerous environmental pollutants, are a group of compounds with the general empirical formula $\text{C}_{12}\text{H}_m\text{Cl}_{10-m}$, where m is an integer. What is the value of m, if percentage of carbon atom in the compound is 40 ?
53. 50 ml of water sample, containing temporary hardness only, required 0.1 ml of M/50 HCl for complete neutralisation. Calculate the temporary hardness of water in ppm.
54. A mixture contains 61.2% BaO, 28% CaO and 10.8% (silica) impurities. What volume in lit. of 3.00 M HCl would be required to react completely with 1 g of the mixture ?

SURFACE CHEMISTRY

ONLY ONE OPTION CORRECT

1. Which of the following statements about physical adsorption is not correct?
(A) It is usually monolayer
(B) It is reversible in nature
(C) It involves van der Waals interactions between adsorbent and adsorbate
(D) It involves small value of adsorption

2. Following is the variation of physical adsorption with temperature:



3. Finally divided catalyst has greater surface area and has greater catalytic activity than the compact solid. If a total surface area of 6291456 cm² is required for adsorption of gaseous reaction in a catalysed reaction, then how many splits should be made of cube exactly 1 cm in length.
(A) 60 (B) 80 (C) 20 (D) 22
4. Which of the following is not characteristic of chemisorption?
(A) it is irreversible (B) it is specific
(C) it is multilayer phenomenon (D) heat of adsorption of about – 400 kJ
5. A colloidal solution can be purified following the method of
(A) dialysis (B) peptization (C) filtration (D) oxidation
6. Gold number of a lyophilic sol is such property that:
(A) the larger its value, the greater is the peptising power
(B) the lower its value, the greater is the peptising power
(C) the lower its value, the greater is the protecting power
(D) the larger its value, the greater is the protecting power
7. For the coagulation of 200 mL of As₂S₃ solution, 10 ml. of 1 M NCl₃ is required. What is the coagulating value of NCl₃.
(A) 200 (B) 100 (C) 50 (D) 25
8. At CMC, the surfactant molecules :
(A) Decomposes (B) Become completely soluble
(C) Associate (D) Dissociate
9. Some type of gels like gelatin lose water slowly. The process is known as :
(A) Syneresis (B) Thixotropy (C) Peptisation (D) Imbibition
10. Size of colloidal particles may range from
(A) 1 to 1000 nm (B) 10 to 100 pm (C) 1 to 1001.1M (D) 1 to 10 mm

11. Select correct statement (s) :
- (A) hydrophilic colloid is a colloid in which there is a strong attraction between the dispersed phase and water
 (B) hydrophobic colloid is a colloid in which there is a lack of attraction between the dispersed phase and water
 (C) hydrophobic soils are often formed when a solid crystallises rapidly from a chemical reaction or a supersaturated solution
 (D) all of the above
12. Gold number of haemoglobin is 0.03. Hence, 100 ml. of gold sol will require haemoglobin so that gold is not coagulated by 10 mL of 10% NaCl solution
 (A) 0.03 mg (B) 30 mg (C) 0.30 mg (D) 3 mg
13. Which one of the following statements is correct:
- (A) Brownian movement is more pronounced for smaller particles than for bigger ones
 (B) Sols of metal sulphides are lyophilic
 (C) Schulze-Hardy law states, the bigger the size of the ion, the greater is its coagulating power
 (D) One would expect charcoal to adsorb chlorine more strongly than hydrogen sulphide.
14. What can adsorb larger volume of hydrogen gas :
- (A) Colloidal solution of palladium (B) Finely divided nickel
 (C) Finely divided platinum (D) Colloidal $\text{Fe}(\text{OH})_3$.

ONE OR MORE THAN ONE OPTION CORRECT

15. Which of the following are correct statements
- (A) Spontaneous adsorption of gases on solid surface is an exothermic process as entropy decreases during adsorption
 (B) Formation of micelles takes place when temperature is below Kraft Temperature (T_k) and concentration is above critical micelle concentration (CMC)
 (C) A colloid of $\text{Fe}(\text{OH})_3$ is prepared by adding a little excess (required to completely precipitate Fe^{3+} ions as $\text{Fe}(\text{OH})_3$) of NaOH in FeCl_3 solution the particles of this sol will move more towards cathode during electrophoresis.
 (D) According to Hardy-Schulze rules the coagulation (flocculating) value of Fe^{3+} ion will be more than Ba^{2+} or Na^+
16. Which of the following statements are true for physisorption?
- (A) Extent of adsorption increases with increase in pressure.
 (B) It needs activation energy
 (C) It can be reversed easily (D) It occurs at high temperature.
17. Which of the following are incorrect statements ?
- (A) Hardy schulz rule is related to coagulation
 (B) Brownian movement and Tyndall effect are the characteristic of colloids.
 (C) In gel, the liquid is dispersed in liquid
 (D) Lower the gold number, more is the protective power of lyophilic soils.
18. The origin of charge on colloidal solution is
- (A) Frictional rubbing
 (B) Electron capture during Bredig's arc method
 (C) Selective adsorption of ion on their surface
 (D) It is due to addition of protective colloids

PARAGRAPH BASED QUESTIONS

Comprehension # 1

Adsorption is the presence of excess concentration of any particular component at the surface of liquid or solid phase as compared to bulk. This is due to presence of residual forces at the surface of body. In the adsorption of hydrogen gas over a sample, of charcoal, 1.12cm³ of H₂(g) measured over S.T.P. was found to adsorb per gram of charcoal. Consider only monolayer adsorption. Density of H₂ is 0.07gm/cc. In another experiment same 1 gm charcoal adsorbs 100m³ of 0.5M CH₃COOH to form monolayer and thereby the polarity of CH₃COOH reduces to 0.49.

$$(3 \times 47.73)^{1/3} \times 47t = 2.24 \cdot (2.24)^2 = 5$$

19. Numbers of molecules of hydrogen over 1 gram charcoal are —
(A) 3.01×10^{15} (B) 3.01×10^{13} (C) 3.01×10^{21} (D) 3.01×10^{22}
20. What is the radius of adsorb hydrogen molecule
(A) 2.24×10^{-7} cm (B) 2.24×10^{-5} cm
(C) 2.24×10^{-10} cm (D) 2.24×10^{-15} cm
21. Specific surface area of charcoal is (cm²/gm) —
(A) 4.72×10^3 (B) 4.72×10^4 (C) 4.72×10^5 (D) 4.72×10^6
22. Molecule of acetic acids adsorbed —
(A) 6.023×10^{25} (B) 6.023×10^{21}
(C) 6.023×10^{22} (D) 6.023×10^{23}
23. Surface area of charcoal adsorbed by each molecule of (acetic acid) is —
(A) 7.8×10^{-9} cm² (B) 7.8×10^{-15} cm²
(C) 7.8×10^{-17} cm² (D) 7.8×10^{-16} cm²

MATRIX MATCH

24. Match list I with list II and select the correct answer :
- | List I | | List II |
|----------------|-----|--------------------------|
| Coagulation | (p) | Scattering of light |
| Dialysis | (q) | Washing of precipitates |
| Peptization | (r) | Purification of colloids |
| Tyndall effect | (s) | Electrolyte |
25. Match list I (Colloidal system) with list II (Example) and select the correct answer :
- | List I | | List II |
|-----------------------|-----|--------------------|
| Emulsifies | (p) | Colloidal solution |
| Xerogel | (q) | Soaps |
| Colloidal electrolyte | (r) | Foil of cellophane |
| Purple of Cassius | (s) | Dextrin |

INTEGER TYPE

26. 5ml. of standard gold sol, needs 0.5 mg of gelatin for its protection from coagulation, calculate the gold no. of gelatin.
27. 100 ml of a colloidal solution is completely precipitated by addition of 0.5 ml of 1M NaCl solution, calculate the coagulation value of NCl.
28. On addition of the 1ml. solution of 10% NCl to 10 ml gold sol in the presence of 0.00399 gm of starch, calculate the gold no.
29. Coagulation experiment, 5ml of As_2S_3 is mixed with distilled water and 0.01 M solution of an electrolyte AB so that total volume is 10ml. it was found that all solution containing more than 5 ml of AB coagulate within 5 min. What is the Flocculation value of AB for As_2S_3 sol.

ATOMIC STRUCTURE

- 1.(D) 2.(D) 3.(A) 4.(A) 5.(A) 6.(C) 7.(D)
- 8.(B) 9.(A) 10.(C) 11.(A,C) 12.(A,B,D) 13.(A,B) 14.(B, C, D)
- 15.(A, B) 16.(A, B, C) 17. (A, C, D) 18. (B, C, D) 19.(B) 20.(B) 21.(D)
- 22.(D) 23.(C) 24.(A) 25. (C) 26.(C) 27.(A) 28. (A)
- 29.(A – s), (B – p), (C – p), (D – q) 30.(A – q, r), (B – p, s), (C – s), (D – q)
- 31.(A – r, s), (B – p, s), (C – q, r), (D – p, q) 32.(3) 33.(6eV) 34.(8) 35.(3)
- 36.(6)

GASEOUS STATE

- 1.(B) 2.(D) 3.(B) 4.(B) 5.(B) 6.(B) 7.(A)
- 8.(B) 9.(B) 10.(8) 11.(B) 12.(A) 13.(B) 14.(C)
- 15.(C) 16.(A) 17.(A) 18.(B) 19.(B) 20.(A, B, C) 21.(A, C, D)
- 22.(A, D) 23.(A, C, D) 24.(A, C, D) 25.(A, B, D) 26.(A, D) 27.(B, C) 28.(A)
- 29.(A) 30.(A) 31.(C) 32.(A) 33.(D) 34.(C) 35.(A, B, C, D)
- 36.(D) 37.(A, B) 38.(D) 39.(A) 40.(B) 41.(B) 42.(B)
- 43.(B) 44.(A) 45.(C) 46.(C) 47.(B)
- 48.(A – r), (B – q, r, s), (C – r), (D – p, r). 49.(A – p, r), (B – q, s), (C – r), (D – p, s)
- 50.(A – p, s), (B – p, r, s), (C – q), (D – p, r, s) 51.(A – p, s), (B – r, s, t), (C – r, s, t), (D – p, s)
- 52.(A – s), (B – p), (C – q), (D – r)

SOLID STATE

- 1.(A) 2.(D) 3.(C) 4.(B) 5.(A) 6.(A) 7.(B)
8.(A) 9.(C) 10.(D) 11.(D) 12.(C) 13.(D) 14.(B, C)
15.(B, C) 16.(C) 17.(A, B, C, D) 18.(A, C) 19.(A) 20.(D) 21.(A)
22.(A) 23.(C) 24.(C) 25.(A) 26.(C) 27.(D)
28.(A – p, q, r s), (B – p, q, s), (C – p, q, s), (D – p, q, r)
29.(A – p, q, s), (B – p, q, r), (C – s), (D – p, q, s) 30.(A – r, s), (B – r, s), (C – p), (D – q)
31.(A – p, q, r, s), (B – p, q, r, s), (C – p, q, r), (D – p, q, r). 32.(A – q), (B – s), (C – p), (D – r)
33. (2) 34. (6) 35.(8) 36. (5)

SOLUTION & COLLIGATIVE PROPERTIES

- 1.(C) 2.(C) 3.(D) 4.(C) 5.(B) 6.(A) 7.(C)
8.(A) 9.(B) 10.(D) 11.(C) 12.(A) 13.(B) 14.(B)
15.(A) 16.(D) 17.(B) 18.(A) 19.(A, B, C) 20.(A, C, D) 21.(A, B, C, D)
22.(B) 23.(A) 24.(C) 25.(D) 26.(A) 27.(C) 28.(B)
29.(C) 30.(D) 31.(A) 32.(C) 33.(D) 34.(B) 35.(B)
36.(D) 37.(A – p, s, r), (B – p, q, t), (C – p), (D – p, q, t)
38.(A – q, s), ; (B – q, s), (C – q, s), (D – q, s) 39.(A – q), (B – p), (C – r, s) (D – p)
40.(3.5) 41.(6) 42.(1) 43.(5) 44.(5 PPM)

ELECTROCHEMISTRY

- 1.(B) 2.(B) 3.(A) 4.(B) 5.(A) 6.(A) 7.(D)
8.(C) 9.(B) 10.(A) 11.(A) 12.(A) 13.(A) 14.(B)
15.(A) 16.(B) 17.(B) 18.(B) 19.(A) 20.(A) 21.(A)
22.(B) 23.(A) 24.(B) 25.(A) 26.(A, B, D) 27.(A, C) 28.(A, B, C, D)
29.(B, C, D) 30.(C) 31.(A) 32.(B) 33.(B) 34.(B) 35.(A)
36.(D) 37.(B) 38.(A) 39.(B) 40.(C)
41.(A - p, q, s); (B - r, s); (C - p, q), (D - p, q, s) 42.(A - q), (B - r), (C - s), (D - t), (E - p)
43.(A - p, q, r, s), (B - p, q), (C - p, q, r, s), (D - p, q, r, s) 44.(A - p, s); (B - q, r); (C - p, s); (D - q, s)
45.(A - p, q, r), (B - p, q, r), (C - p, q, r), (D - r)
46. (2) 47.(2) 48.(9) 49.(8) 50.(5)

STOICHIOMETRY

- 1.(C) 2.(D) 3.(A) 4.(C) 5.(B) 6.(A) 7.(B)
8.(D) 9.(A) 10.(B) 11.(B) 12.(A) 13.(D) 14.(D)
15.(C) 16.(D) 17.(C) 18.(B) 19.(B) 20.(A) 21.(A, D)
22.(A, B, C, D) 23.(A, B, C) 24.(A, B, D) 25.(B, C) 26.(A, B, C) 27.(A, B, D) 28.(B)
29.(C) 30.(A) 31.(B) 32.(B) 33.(A) 34.(B) 35.(C)
36.(B) 37.(C) 38.(A) 39.(B) 40.(C) 41.(B) 42.(D)
43.(B) 44.(A) 45.(A) 46.(B) 47.(A - p, q, r), (B - p, r, s), (C - p, q), (D - r).
48.(A - q, r), (B - p, s), (C - q, r), (D - r). 49.(A - p, s), (B - q, r, t); (C - p, q, s, t), (D - r, t)
50.(A - p, q, r), (B - p, q, r, s), (C - r, s), (D - r, s) 51.(A - r); (B - s); (C - p); (D - q, r), (E - t)
52.(40) 53.(2 ppm) 54.(9 mL)

SURFACE CHEMISTRY

1.(A)	2.(B)	3.(C)	4.(C)	5.(A)	6.(C)	7.(C)
8.(C)	9.(A)	10.(A)	11. (D)	12.(C)	13.(A)	14.(A)
15.(A, C)	16.(A, C)	17.(C, D)	18.(A, B, C)	19.(B)	20.(B)	
21.(B)		22.(A)	23.(C)	24.(A – s); (B – r); (C – q); (D – p)		
25.(A – s); (B – r); (C – q); (D – p)			26.(1)	27.(5)	28.(4)	29.(5)