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6

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Managing Editor Mahabir Singh Editor Anil Ahlawat

Corporate Office:

Plot 99, Sector 44 Institutional area, Gurgaon -122 003 (HR). Tel: 0124-6601200 e-mail: info@mtg.in website: www.mtg.in **Regd. Office:**

No. 8

406, Taj Apartment, Near Safdarjung Hospital, New Delhi - 110029.

Class 11 8

- Focus NEET / JEE Be NEET Ready 18
- **Brush Up Your Concepts** 21
 - **Examiner's Mind** 25
 - **CBSE Drill** 31
 - Monthly Tune Up 39
 - **Concept Map** 46

Class 12

- Focus NEET / JEE 42
 - Be JEE Ready 53
- **Brush Up Your Concepts** 56
 - **Examiner's Mind** 60
 - **CBSE Drill** 66
 - Monthly Tune Up 73

Competition Edge

- **Chemistry Musing Problem Set 61** 77
 - You Ask We Answer 79
 - **JEE Workouts Solutions** 80
- **Chemistry Musing Solution Set 60** 84

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Unit-2 : Classification of Elements and Periodicity in Properties | **Chemical Bonding and Molecular Structure**

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

HISTORY OF THE PERIODIC TABLE

Earlier Attempts

Dobereiner's Triads

In the triad of elements, the atomic weight of middle element is the arithmetic mean of other two.

Newland's Law of Octaves

Elements are arranged in increasing order of their atomic weights, the properties of every eighth element are similar to the first one.

Mendeleev's Periodic Table

Elements are arranged such that the properties of the elements are the periodic function of their atomic weights. Table contains 8 groups and 7 periods.

MODERN PERIODIC TABLE

Modern Periodic Law

- The physical and chemical properties of elements are periodic function of their atomic numbers.
- Elements are arranged in order of increasing atomic numbers.
- It has seven horizontal rows known as periods and eighteen vertical columns known as groups.



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Elements in Periodic Table

s-block elements Group-1 to 2

- $E.C.: ns^{1-2}$
- Group-1 elements form M^+ ions.
- Group-2 elements form M^{2+} ions.

p-block elements

- Group -13 to 18
- *E.C.* : $ns^2 np^{1-6}$ (excluding helium)
- Except noble gases and fluorine, all other • elements show variable oxidation states.

d-block elements

- Group 3 to 12
- Lies between *s* and *p*-block elements *E.C.* : $(n 1)d^{1-10}ns^{0-2}$
- Show variable valencies and oxidation states.

f-block elements

- 4f-series : lanthanides
- 5*f*-series : actinides
- *E.C.* : $(n-2) f^{1-14} (n-1) d^{0-1} ns^2$
- Variable oxidation states, most common in +3.



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Periodic Trends

Atomic Radius

- Crystal or metallic radius : It is one-half of the • internuclear distance between the two nearest atoms in the metallic lattice. It is generally used for metals.
- van der Waals' radius : It is one-half of the internuclear distance between the two adjacent identical atoms belonging to two neighbouring molecules of an element.
- Covalent radius : It is one-half of the distance between the centres of the nuclei of two similar atoms joined by a single covalent bond. This is generally used for non-metals.
 - The atomic radii of noble gases or inert gases are, in fact, van der Waals' radii since they do not form molecules.
 - ➢ van der Waals' radius > metallic radius > covalent radius (for an atom)

Ionic Radius

- It is the distance between the nucleus and the point where the nucleus exerts its influence on the electron cloud.
 - Cation is smaller and anion is larger than the parent atom of the element. In case of isoelectronic ions, the size decreases with increase in the nuclear charge.

Ionisation Enthalpy

- It is the energy required to remove an electron from an isolated gaseous atom in its ground state. $M_{(g)} + I.E. \rightarrow M^+_{(g)} + e^-$
- *I.E.* $\propto \frac{1}{\text{size of atom}} \propto \text{Effective nuclear charge}$
 - $\infty \frac{1}{\text{Screening effect}}$
- Completely or half-filled orbital has higher I.E. • because of higher stability.

Electron Gain Enthalpy

- It is the amount of energy released when an electron is added to an isolated gaseous atom. $A_{(g)} + e^- \rightarrow A_{(g)}^-; \Delta_{eg} H$
- $\Delta_{eg}H \propto \frac{1}{\text{Size of atom}} \propto \text{ Effective nuclear charge}$ $\propto \frac{1}{\text{Screening effect}}$



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Electronegativity

- It is the tendency of an atom to attract the shared pair of electrons towards itself in a covalent bond.
- Mulliken scale of electronegativity

$$\chi = \frac{1}{2} \left[\Delta_i H + \Delta_{eg} H \right]$$

Pauling scale of electronegativity

$$\chi_A - \chi_B = 0.1017 \sqrt{\Delta}$$

where,
$$\Delta = E_{A-B} - \frac{1}{2}\sqrt{E_{A-A} + E_{B-B}}$$

Here, E represents bond dissociation enthalpy $(in kJ mol^{-1}).$

Percentage of ionic character

$$= 16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2$$

- If $\chi_A \chi_B = 1.7$, bond is 50% covalent and 50%
- If $\chi_A \chi_B > 1.7$, bond is predominately ionic.
- ► If $\chi_A \approx \chi_B$, A B bond is purely covalent.

SUMMARY OF SOME GENERAL TRENDS





CHEMICAL BONDING AND MOLECULAR STRUCTURE

The phenomenon of union of two or more atoms involving redistribution of electrons, so that each atom involved in bonding acquires stable configuration in order to gain stability is known as chemical bonding.

- Atoms form bonds since it leads to decrease in energy.
- Whenever atoms come close, both attractive and repulsive forces operate and if the magnitude of attractive forces is more than those of repulsive forces, a chemical bond is formed.

Kössel-Lewis Approach to Chemical Bonding

Atoms can combine either by transfer of valence electrons from one atom to another or by sharing of valence electrons in order to have an octet in their valence shell (octet rule).

TYPES OF BOND



Bond Formation

- Nature of bond formed between two atoms depends upon electropositive and electronegative character of bonded atoms.
 - Ionic bond : Electropositive element +

Electronegative element

- Covalent bond : Electronegative element + Electronegative element
- Metallic bond : Electropositive element + Electropositive element

Ionic bond is non-directional in nature while covalent bonds are directional in nature.

IONIC BOND

• The bonds formed between atoms by transferring of valence electrons from one atom to another

is said to be electrovalent or ionic bond, and the compound so formed is an ionic compound.

- Conditions for the formation of electrovalent bond :
 - Number of valence electrons : The atom which changes to a cation must contain 1, 2 or 3 valence electrons and the one changing to anion must contain 5, 6 or 7 valence electrons.
 - Electronegativity difference : Higher the electronegativity difference between the atoms, more ionic will be the bond formed.
 - Low ionisation energy : Ionisation energy of the element forming the cation *i.e.*, metal, should be low.
 - High electron affinity : Electron affinity of the element forming anion *i.e.*, non-metal, should be high.
 - High lattice energy : Higher the lattice energy, greater is the ease of formation of ionic compound.

BORN HABER CYCLE

- Born Haber cycle is based on Hess's law of constant heat summation and it correlates the energy changes taking place in various steps involved in the formation of ionic compounds.
- The steps can be represented in the cycle as :



 $\Delta H_f = \Delta H_s + IE + \frac{1}{2} \Delta H_{diss} + \Delta H_{eg} + U$ where, ΔH_f = Enthalpy of formation, ΔH_s = Enthalpy of sublimation, IE = Ionisation energy, ΔH_{diss} = Enthalpy of dissociation, ΔH_{eg} = Electron gain enthalpy and U = Lattice energy.

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COVALENT BOND

• Bond formed by sharing of electrons between the combining atoms is called covalent bond and the compound so formed is a covalent compound.

COORDINATE BOND

• A covalent bond in which both electrons of the shared pair are contributed by one of the atoms only, is called a coordinate bond or dative bond and the compound is called a coordinate compound.

POLARISATION

• Fajan's rule: In ionic bond, some covalent character is introduced because of the tendency of the cation to polarise the anion. In fact, cation attracts the electron cloud of the anion and pulls electron density between two nuclei.



• According to Fajan's rule :

Smaller the size of cation, larger is its polarising power.

of anion

- Larger the size of anion, more will be its polarisability.
- More the charge on cation and anion, more is the covalent character.
- Cations having 18 electrons in outermost shell bring greater polarisation than the other which have 8 electrons in outermost shell.

IMPORTANT TERMS AND FORMULAE

Formal charge of an atom in a Lewis structure
 = Total no. of electrons in the free atom – Total no. of electrons of lone pairs (non-bonding electrons) –1/2 × Total no. of shared electrons (bonding electrons)

i.e., $F = V - L - \frac{1}{2}S$

• **Bond length :** Equilibrium distance between the nuclei of two bonded atoms in a molecule.

> Bond length \propto size of atoms, $\propto \frac{1}{\text{bond order}}$

• **Bond angle :** Angle between the orbitals containing

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bonding electron pairs around the central atom in a molecule/complex ion.

- **Bond enthalpy :** Amount of energy required to break one mole of bonds between two atoms in a gaseous state.
- **Bond order :** Number of bonds formed between two atoms in a covalent compound.
- **Resonance :** The phenomenon of existence of a molecule in different structural forms, each of which can explain most of the properties of the molecule but none can explain all the properties of the molecule.
- Dipole moment (μ) = Charge × Distance of separation

THEORIES OF COVALENT BONDING

VSEPR Theory (Nyholm and Gillespie)

- The shape of a molecule depends upon the number of valence shell electron pairs (bonded or non bonded) surrounding the central atom.
- Electron pairs tend to occupy such positions in space which minimise repulsions.
- The repulsive interactions of electron pairs decrease in the order : lp - lp > lp - bp > bp - bp

Valence Bond Theory (Pauling)

- A bond is formed between two atoms when the forces of attraction are greater than forces of repulsion.
- A covalent bond is formed between two atoms by pairing of electrons present in the valence shell having opposite spins.
- During bond formation, only valence electrons loose their identity.
- Bond formation is accompanied by release of energy and this accounts for the stability of bond.
- Sigma (σ) bond is formed by the head on overlap of atomic orbitals.
- Pi (π) bond is formed by lateral overlap of half-filled atomic orbitals, perpendicular to internuclear axis.

Molecular Orbital Theory (F. Hund and R.S. Mulliken)

- Molecular orbitals are formed by the linear combination of atomic orbitals.
- The number of molecular orbitals formed is equal to the number of atomic orbitals combined.



- When two atomic orbitals combine they form one bonding molecular orbital of lower energy and one anti-bonding molecular orbital of higher energy.
- The molecular orbitals are filled in accordance with Aufbau principle, Pauli's exclusion principle and Hund's rule.
- Energy order for molecular orbitals upto N₂ is σ1s < σ*1s < σ2s < σ*2s < π2p_x

 $= \pi 2p_y < \sigma 2p_z < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$

• Energy order for molecules beyond N₂ $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x$ $= \pi 2p_y < \pi^* 2p_x = \pi^* 2p_y < \sigma^2 p_z$

• Bond order (B.O.) =
$$\frac{1}{2} \left(N_b - N_a \right)$$

where, N_b is number of electrons present in BMO and N_a is number of electrons present in ABMO

- If $N_b > N_a$; B.O. = +ve, the molecule is stable.
- For $N_b < N_a$; B.O. = -ve, the molecule is unstable or does not exist.

- For $N_b = N_a$; B.O. = 0, the molecule is unstable or does not exist.
- Isoelectronic species have same bond order.

Hybridisation

- Hybridisation is a hypothetical phenomenon. It is introduced to explain shapes of molecules and bonding parameters such as bond angle, strength of bonds.
- The structure of a molecule can be predicted on the basis of hybridisation by using the formula :

$$H = \frac{1}{2}(V + M - C + A)$$

where, H = number of orbitals involved in hybridisation, V = number of electrons in valence shell of the central atom, M = number of monovalent atom, C = charge on cation and A = charge on anion.

IIT-Delhi tops MHRD mandate, enrols 16% girls in all its courses

At a time when engineering institutes are struggling to admit girls. IIT-Delhi has touched an all-time high number of female students this year. The HRD ministry had mandated that all 23 IITs increase the enrolment of girls to 14% in 2018. IIT-Delhi has already recorded a 16% enrolment of girls in every course, before the admission season gets over.

"Our faculty members conducted special interaction sessions with all JEEqualified girl students and their parents both last year and this year to explain the prospects of studying at IIT," said Aditya Mittal, professor and chairman of Joint Entrance Examination-Advanced at IIT-Delhi.

The sessions for two consecutive years are already showing results. In 2016, IIT-D admitted 70 girls, which increased by over 30% to 93 in 2017 and this year it is likely to reach 150 out of a total 851 seats.

The idea behind the initiative was to help qualified female candidates make their choices during the JEE/JoSAA (Joint Seat Allocation Authority) 2018 counselling process. "The session saw over 150 students attending it where not just faculty members, but even student mentors interacted with potential candidates," Mittal said.

Asked why fewer girls enrol in IITs despite getting good ranks, Mittal attributed it to several factors. "Our IIT-Mandi director Timothy Gonsalves in his four-year research found that there are many girls who get good ranks in JEE Advance but don't enrol in IITs. Several parents we interacted with had the perception that engineering sectors like mechanical and chemical are not viable for girl students. Many avoid IITs as they prefer institutes closer to their homes," he added.

There were some parents who didn't agree to send their daughters for specialised preparations as they would do for boys. "The central idea to bring in more girls was based on the IIT ethos that we don't provide literacy but education. It is also because we revise curriculum frequently. While 40% of our curriculum is core, 60% are electives chosen by the students," Mittal said.



"We at IIT-Delhi are vying for more than 14% girl students this year. We want to enrol 17% in 2019 and 20% in 2020. Eventually, we hope that these steps would be enough to encourage more girl students to join the institute," said Mittal.

The chairman of the JEE counselling said that the increase in enrolment will not be radical but gradual. "We have limited space in hostels, laboratories and classrooms and this endeavour will not be affecting the seats already allotted for non-female students," Mittal added.



Courtesy : The Times of India

Type of hybridisation	No. of hybrid orbitals	Shape of molecule	Bond angle	Examples
sp	2	Linear	180°	BeCl ₂ , BeF ₂ , CO ₂
sp ²	3	Trigonal planar	120°	BF ₃ , BCl ₃
sp ³	4	Tetrahedral	109.5°	CH_4 , CCl_4
dsp ²	4	Square planar	90°	${[Ni(CN)_4]}^{2-}$ ${[PtCl_4]}^{2-}$
dsp^3 or sp^3d	5	Trigonal bipyramidal	120° and 90°	PCl ₅ , PF ₅
d^2sp^3 or sp^3d^2	6	Octahedral	90°	SF ₆
d^3sp^3 or sp^3d^3	7	Pentagonal bipyramidal	72° and 90°	IF ₇

MOLECULES HAVING BOND PAIRS ONLY

Molecules having bond pairs and lone pairs

Type of	Urbridication	Rond	Actual	Evamplas
Type of	Hydridisation	Dona	Actual	Examples
molecule		angle	shape	
AB_2L	sp^2	<120°	V-shape	SO ₂ ,
			or Bent	PbCl ₂
AB_2L_2	sp ³	<109°28′	V-shape	Н ₂ О,
			or Bent	Cl ₂ O
AB_2L_3	sp ³ d	180°	Linear	XeF ₂
AB_3L_2	sp ³ d	90°	T-shape	ClF ₃
AB_3L_1	sp ³	<109°28′	Trigonal	NH ₃ ,
	_		pyramidal	PCl ₃
AB_4L_1	sp ³ d	120°, 90°	See saw or	SF_4 , SCl_4
			Distorted	
			tetrahedron	
AB_4L_2	sp^3d^2	90°	Square	XeF ₄
	-		planar	_
AB_5L_1	$sp^{3}d^{2}$	<90°	Square	IF ₅
	-		pyramidal	
AB_6L_1	$sp^{3}d^{3}$	-	Distorted	XeF ₆
	-		octahedral	



- Which of the following geometry is not possible when the central atom is having *sp*³*d*-hybridization?
 (a) Trigonal bipyramidal
 - (a) Trigonal dipyran
 - (b) Trigonal planar
 - (c) Linear (d) T-shaped
- **2.** Five ionization energy values in kJ/mol are listed below:

 $E_1 = 870, E_2 = 830, E_3 = 1010, E_4 = 1290, E_5 = 376.$ These are

- (a) successive ionization energies for the element with atomic number 5
- (b) the first *I.E.* of successive elements in group 15, 16, 17, 18 and 1 respectively
- (c) the first I.E. of elements with atomic number 1 to 5
- (d) successive *I.E.* for transition elements with four electrons in *d*-subshell.
- **3.** Which of the following statements are true (T) or false (F)?
 - In SnCl₂ the bonding takes place in ground state and the bond angle Cl—Sn—Cl is slightly less than 120°.

- (II) The molecular geometry of XeF₇⁺ is pentagonal bipyramidal having two different Xe—F bond lengths.
- (III) In SF_4 , the bond angles, instead of being 90° and 120° are 89° and 117° respectively due to the presence of a lone pair.
- (a) T T T (b) F T T
- (c) T T F (d) T F T
- **4.** Generally, the first ionisation energy increases along a period. But there are some exceptions. The one which is not an exception is
 - (a) Na and Mg (b) Be and B
 - (c) N and O (d) Mg and Al.
- 5. The bonds present in $[Cu(NH_3)_4]SO_4$ are
 - (a) ionic (b) covalent
 - (c) co-ordinate (d) all of these.
- 6. Compare bond angles for the following molecules :



(a)	x > y	(b)	y > x
(c)	x = y	(d)	Cannot be compared

7. Which of the following statements is wrong?

- (a) In *s*-block elements, the 1st ionization energy decreases down the group.
- (b) In *p*-block elements, the decrease in 1^{st} ionization energy is large between 1^{st} and 2^{nd} element but thereafter the decrease is minor.
- (c) In transition elements, the ionization energy decreases regularly down the group from 5th group.
- (d) In a transition series, the 2nd *IP* value is more for Cr and Cu groups compared to the adjacent groups.
- Atomic number of Ag is 47. In the same group, the atomic numbers of elements placed above and below Ag in long form of periodic table will be

 (a) 29, 65
 (b) 39, 79
 (c) 29, 79
 (d) 39, 65
- 9. In a periodic table, the basic character of oxides
 - (a) increases from left to right and decreases from top to bottom
 - (b) decreases from right to left and increases from top to bottom
 - (c) decreases from left to right and increases from top to bottom
 - (d) decreases from left to right and increases from bottom to top.
- 10. Which of the following statements are correct?
 - (I) The hybridisation found in cation of solid PCl_5 is sp^3 .
 - (II) In AB_2L_2 type, the *BAB* bond angle is always greater than the normal tetrahedral bond angle.
 - (III) In ClO₃, NH₃ and XeO₃, the hybridisation and the number of lone pairs on the central atoms are same.
 - (IV) In P_4 molecule, there are six P—P bonds and four lone pairs of electrons.
 - (a) I, II and III only (b) I, III and IV only
 - (c) III and IV only (d) All are correct

Solution Senders of Chemistry Musing

Set - 59

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 - Set 60
- Samaroha Nandi, West Bengal

- 11. In the hypothetical molecule AX_2L_n (where A is central atom, X is surrounding atom L is lone pair, n is the number of lone pair), for which possible value of "n" will the dipole moment of the molecule be zero?
 - (a) Zero (b) 1
 - (c) 2 (d) All of these
- 12. *A*, *B*, *C* are three substances. *A* does not conduct electricity in the solid or solution state. *B* conducts electricity both in the fused and solution states, while *C* conducts electricity only in the solution state. Which of the following statements is false regarding *A*, *B* and *C*?
 - (a) *A* has polar covalent linkage.
 - (b) A has non-polar covalent linkage.
 - (c) *B* has ionic nature.
 - (d) *C* has polar covalent linakge.
- **13.** Using the following data, calculate the electronegativity of fluorine.

 $E_{\rm H-H} = 104.2 \text{ kcal mol}^{-1}, E_{\rm F-F} = 36.6 \text{ kcal mol}^{-1}$

- $E_{\rm H-F} = 134.6 \text{ kcal mol}^{-1}, \chi_{\rm H} = 2.1.$
- (a) 3.87 (b) 3.77
- (c) 3.67 (d) 4.87
- **14.** Consider (i) CO₂, (ii) CCl₄, (iii) C₆Cl₆ and (iv) CO and tell which of the following statements is correct?
 - (a) (i), (ii) and (iii) have zero dipole moment.
 - (b) (i), (ii) and (iv) have zero dipole moment.
 - (c) Only (iv) has zero dipole moment.
 - (d) All have zero dipole moment.
- 15. The electronic configuration of an element is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^3$. What is the atomic number of the element which is just below the given element in the periodic table?
 - (a) 34 (b) 49
 - (c) 33 (d) 31

M	ONTHL	Y TU	NE UF	P CLA	SS XI	A	NSW	ER	KEY
1.	(a)	2.	(b)	3.	(b)	4.	(d)	5.	(b)
6.	(c)	7.	(a)	8.	(b)	9.	(c)	10.	(a)
11.	(b)	12.	(b)	13.	(c)	14.	(a)	15.	(b)
16.	(d)	17.	(a)	18.	(d)	19.	(b)		
20.	(a, b,	c, d)		21.	(b, d)	22.	(a,d)	23.	(b, c)
24.	(5.27	$\times 10^{-1}$	⁻⁶)	25.	(27)	26.	(498.3	3)	
27.	(b)	28.	(d)	29.	(c)	30.	(b)		



- 16. Which of following is the correct order of ionisation enthalpy?
 - (a) $Te^{2^{-}} < I^{-} < Cs^{+} < Ba^{2+}$
 - (b) $I^- < Te^{2-} < Cs^+ < Ba^{2+}$

(c)
$$Te^{2-} < Cs^+ < I^- < Ba^{2+}$$

(d)
$$Ba^{2+} < Cs^+ < I^- < Te^{2-}$$

- 17. Which of the following pairs will have same bond order?
 - (a) F_2 and O_2^{2-} (b) N₂ and CO₂
 (d) N₂ and N⁺₂

(c) O_2 and O_2^-

18. Which of the following statements are correct?

- As the s-character of a hybrid orbital decreases
- (I) the bond angle decreases
- (II) the bond strength increases
- (III) the bond length increases.
- (b) (II) and (III) (a) (I) and (III)
- (c) (I) and (II) (d) All are correct
- 19. Which of the following grouping represents a collection of isoelectronic species?
 - (b) Ca^{2+}, Cs^+, Br^- (d) Na^+, Ca^{2+}, Mg^{2+} (a) N^{3-} , F^- , Na^+
 - (c) Be, Al^{3+} , Cl^{-}
- 20. A sigma bond may be formed by the overlap of two atomic orbitals of atoms A and B. If the bond is formed along the *x*-axis which of the following overlaps is acceptable?
 - (a) *s*-orbitals of *A* and p_z -orbital of *B*
 - (b) p_x -orbitals of A and p_y -orbital of B
 - (c) p_x -orbitals of A and p_z -orbital of B
 - (d) p_x -orbitals of *A* and *s*-orbital of *B*
- 21. The correct order of decreasing polarisability of the ions is
 - (a) $Cl^{-}, Br^{-}, I^{-}, F^{-}$ (b) $F^{-}, I^{-}, Br^{-}, Cl^{-}$ (c) F^{-} , Cl^{-} , Br^{-} , I^{-} (d) I^-, Br^-, Cl^-, F^-

22. Which of the following pairs are not isostructural?

- (a) IO_3^- and XeO_3^- (b) PF_6^- and SF_6
- (c) BH_4^- and NH_4^+ (d) SiF_4 and SF_4
- **23.** If the ionic radii of K^+ and F^- are about 1.34 Å each, then the expected values of atomic radii of 'K' and 'F' should be respectively
 - (a) 1.34 and 1.34 Å (b) 2.31 and 0.64 Å
 - (c) 0.64 and 2.31 Å (d) 2.31 and 1.34 Å
- 24. In which of the following processes the maximum amount of energy is involved?
 - (a) $Cl \rightarrow Cl^{-}$ (b) $Br \rightarrow Br^{-}$
 - (d) $I \rightarrow I^{-}$ (c) $F \rightarrow F^-$

16 CHEMISTRY TODAY | AUGUST '18

- 25. The correct order in which the first ionisation potential increases is
 - (a) K, Be, Na (b) Be, Na, K
 - (c) Na, K, Be (d) K, Na, Be.

SOLUTIONS

- **1.** (b): From sp^3d -hybridization trigonal planar geometry is not possible, because in trigonal planar geometry lone pair electrons will be placed at the axial position, which violates VSEPR theory or Bent's rule.
- 2. (b): I.E. values are increasing gradually and suddenly decreased in the E_5 value indicating a change from noble gas to alkali metal.
- 3. (a)
- (a): Na and Mg is not an exception because there is 4. no half-filled or completely filled orbital in them.
- 5. (d) 6. (a)
- 7. (c): In a transition group (from 5^{th} group) ionization energy decreases from first to second element but from second to third element the ionization energy does not decrease due to lanthanide contraction.
- 8. (c): Silver belongs to fifth period. So, the atomic number of elements placed above and below will be 47 - 18 = 29 and 47 + 32 = 79 respectively.
- 9. (c): As the electronegativity of element increases, acidic character of oxides increases. So, in a group, basic nature increases on moving down and decreases along a period.
- **10.** (b): (I) $[PCl_4]^+ \rightarrow sp^3$



- (II) H H has 104.5° bond angle due to lp-lp repulsion.
- (III) All have sp^3 hybridisation and one lone pair.



12. (a): A is non-polar. So do not ionize.

13. (a):
$$\chi_{\rm F} - \chi_{\rm H} = 0.208 [E_{\rm H-F} (E_{\rm F-F} \times E_{\rm H-H})^{1/2}]^{1/2}$$

 $\chi_{\rm F} - 2.1 = 0.208 [134.6 - (36.6 \times 104.2)^{1/2}]^{1/2}$
 $= 0.208 [134.6 - 61.75]^{1/2} + 2.1$
 $= 0.208 \times 8.53 + 2.1 = 1.77 + 2.1 = 3.87$
14. (a) **15.** (c)

16. (a) : All are isoelectronic species but as number of protons *i.e.*, atomic number increases, the attraction between electron (to be removed) and nucleus increases and thus ionisation enthalpies increase in the order : Te²⁻ (52) < I⁻ (53) < Cs⁺ (55) < Ba²⁺ (56).
17. (a) E and Q²⁻ are inclustenein.

17. (a):
$$F_2$$
 and O_2^- are isoelectronic.
 $F_2: (\sigma 1s^2) (\sigma^* 1s^2) (\sigma 2s^2) (\sigma^* 2s^2) (\sigma 2p_z^2) (\pi 2p_x^2 = \pi 2p_y^2)$
 $(\pi^* 2p_x^2 = \pi^* 2p_y^2)$
B.O. $= \frac{1}{2} \times (10 - 8) = 1$
 $O_2^{2^-}: (\sigma 1s^2) (\sigma^* 1s^2) (\sigma 2s^2) (\sigma^* 2s^2) (\sigma 2p_z^2) (\pi 2p_x^2 = \pi 2p_y^2)$
B.O. $= \frac{10 - 8}{2} = 1$

18. (a): % *s*-character \propto bond angle $\propto \frac{1}{\text{bond length}} \propto \text{bond strength}$

21. (d): Larger the size of anion, greater the polarisability. Thus, $I^- > Br^- > Cl^- > F^-$ (polarisability order).

22. (d): Molecule/ion Hybridisation Actual shape

IO_3^-	sp ³	pyramidal
XeO ₃	sp ³	pyramidal
PF_6^-	sp^3d^2	octahedral
SF ₆	sp^3d^2	octahedral
BH_4^-	sp ³	tetrahedral
NH_4^+	sp ³	tetrahedral
SiF ₄	sp ³	tetrahedral
SF_4	sp ³ d	irregular (see saw)

23. (b)

24. (a): *E.A.* of Cl is maximum.

25. (d): The electronic configuration of the elements are :

$${}_{4}\text{Be} - 1s^2 2s^2; {}_{11}\text{Na} - 1s^2 2s^2 2p^6 3s^1 {}_{19}\text{K} - 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$$

The first ionization energy of Be is maximum because electron is to be drawn from stable (fully filled) orbital. The 1^{st} ionization energy of Na is greater than K because size of K is bigger than Na which facilitates easy removal of electron from its outermost shell. So the sequence is K < Na < Be.

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CHEMDOKU

In this puzzle 5 \times 5 grid is given, your objective is to fill the digits 1-5 so that each appear exactly once in each row and each column.

Notice that most boxes are part of a cluster. In the upper-left corner of each multibox cluster is a value that is addition, subtraction or multiple (as indicated) of its numbers. For example, if that value is $3\times$ for a two-box cluster, you know that only 1 and 3 can go in there. But it is your job to determine which number goes where! A few cluster may have just one box and that is the number that fills that box.

 $\ensuremath{\textbf{Note}}$: Atomic number of the given element to be considered as your answer.

Clues :

(a) A noble gas which do not form clathrate compounds with quinol. In liquid form it is an important cryogenic refrigerant and has 3 times more refrigerating capacity per unit volume than liquid hydrogen. Also used to make high voltage indicator and switching gear.

a+	b×		C+
	d×		
e×		f–	
g×	h+	i+	

(b) It is an important nutrient for animals. Its oxide when mixed with a saturated solution of its chloride sets to a hard mass like cement known as Sorel's cement.

- (c) It is used to provide an unreactive atmosphere. It is used in this way to preserve foods and in the electronic industry during the production of transistors and diodes.
- (d) It is one of three toxic essential trace elements. Its poisoning causes hallucinations, forgetfullness and nerve damage.
- (e) It is a common element and in combined state, it is widely distributed in nature. This metal is used in preference to sodium for the removal of last traces of water from alcohol as it does not react with alcohol.
- (f) In its solid phase it has the lowest density among all crystalline solids that are present on earth and in gas form it was used in first gas balloon flight launched in 1783.
- (g) Traces of this element in the form of organo-metallic compounds have been reported in the animal cells and in snake poison. It is used in Parkes process for the extraction of silver from argentiferous lead.
- (h) Its fibre is very strong material, high stiffness, high in tensile strength but low in weight. It is stronger and stiffer than steel. Thus, this fibre is very popular in many industries such as aerospace, automotive and military.
- (i) It was finally isolated in 1886 by French Chemist Henri Moissan whose own work was interrupted four times by serious poisoning caused by the element he was pursuing. He won the Nobel prize in Chemistry for his work of isolating this element.

Readers can send their responses at editor@mtg.in or post us with complete address. Solution Senders name with their valuable feedback will be published in next issue. Hope our readers will enjoy solving Chemdoku.



Be

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Practicing these MCQs helps to strengthen your concepts and give you extra edge in your NEET preparation

The major product of dehydration of the following 1.



In the absence of Aufbau rule and also assume that 2. each orbital can take maximum of three electrons, then number of elements in different periods are

Period	3	4	5
(a)	18	18	32
(b)	18	32	50
(c)	27	27	48
(d)	27	48	75

On being placed in water, sodium peroxide not 3. only produces an alkaline solution but also some bubbles. If we assume that the peroxide ion picks up two protons from water to produce a compound that can be seen as the dibasic conjugate acid of peroxide ion and then this compound undergoes a redox disproportionation.

Using the above information, identify *X* and *Y*. $Na_2O_{2(s)} + H_2O_{(l)} \longrightarrow X + Y$

- (X) and (Y) are (a) H_2O and O_2 (b) H_2O_2 and NaOH (c) NaOH and O_2 (d) Na₂O and NaOH
- Given the following reactions,

propyne +
$$\operatorname{HCl}_{(g)} \to A$$

$$A + \operatorname{HI}_{(g)} \to B$$

- The compounds A and B are respectively
- (a) 1-chloropropene and 1-chloro-1-iodopropane
- (b) 1-chloropropene and 1-chloro-2-iodopropane
- (c) 2-chloropropene and 2-chloro-2-iodopropane
- (d) 2-chloropropene and 1-iodo-2-chloropropene.
- 5. Consider the following statements :
 - (i) A balanced chemical reaction should follow law of conservation of mass on either side.
 - (ii) 2 moles of $H_{2(g)}$ and 3 moles of $O_{2(g)}$ produce 3 moles of water.
 - (iii) Equal wt. of carbon and oxygen are taken to produce CO_2 , then O_2 is limiting reagent.
 - The above statements (i), (ii), (iii) respectively are (T = True, F = False)
 - (a) TTT (c) FFF (d) TFT (b) FTF
- For the reaction, $CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)}, \Delta H$, 6. and ΔS are -283 kJ and -87 JK⁻¹, respectively. It was intended to carry out this reaction at 1000, 1500,



3000 and 3500 K. At which of these temperatures would this reaction be thermodynamically spontaneous?

- (a) 1500 and 3000 K (b) 1000 and 3500 K (c) 1000, 1500 and 3000 K (d) 1500, 3000 and 3500 K
- 7. Sulphur reacts with chlorine 1 : 2 ratio and forms X. Hydrolysis of X gives a sulphur compound Y. What is the hybridisation state of central atom in the compound?
- (c) sp^2 (b) sp^3 (d) dsp^2 (a) *sp* 8. Standard electrode potentials of redox couples A^{2+}/A , B^{2+}/B , C^{2+}/C and D^{2+}/D are 0.3 V, -0.5 V, -0.75 V and 0.9 V respectively. Which of these is best oxidising agent and reducing agent respectively? (b) B^{2+}/B and D^{2+}/D (d) C^{2+}/C and D^{2+}/D . (a) D^{2+}/D and B^{2+}/B (c) D^{2+}/D and C^{2+}/C
- Identify the incorrect statement from the following 9. (a) Ozone absorbs the intense ultraviolet radiation of the sun.
 - (b) Depletion of ozone layer is because of its chemical reactions with chlorofluoro alkanes.
 - (c) Ozone absorbs infrared radiation.
 - (d) Oxides of nitrogen in the atmosphere can cause the depletion of ozone layer.
- **10.** If the partition is removed the average molar mass of the sample will be (Assume ideal behaviour).

H ₂	D ₂
16.42 L	16.42 L
300 K	300 K
3 atm	6 atm

(a)
$$\frac{1}{2}$$
 g/mol
(b) $\frac{10}{3}$ g/mol
(c) $\frac{3}{2}$ g/mol
(d) $\frac{5}{3}$ g/mol

11. The value of equilibrium constant of a reaction changes with change of temperature and the change

is given by van't Hoff equation, $\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$ $RT^{\overline{2}}$ where enthalpy change, ΔH° is taken as constant in the small temperature range.

If for reaction,
$$A_{(g)} + 3B_{(g)} \rightleftharpoons 2C_{(g)}$$
, a plot of $\ln K_{eq}$ versus for $1/T$ a reaction is shown, then which of the following condition will be $\ln K_{eq}$ $\ln K_{eq}$ $1/T$

- (a) Low temperature and high pressure
- (b) High temperature and high pressure

- (c) High temperature and low pressure
- (d) Low temperature and low pressure
- 12. The number of structural and configurational isomers of a bromo compound, C₅H₉Br, formed by the addition of HBr to 2-pentyne respectively are (a) 2 and 2 (b) 2 and 4
 - (c) 4 and 2 (d) 2 and 1
- 13. Magnetic moments of the following isoelectronic species (24 electrons) are in order Mn⁺, Cr, Fe²⁺, Co³⁺ (a) $Fe^{2+} = Co^{3+} < Mn^+ = Cr$

 - (a) $Fe^{2+} = Cr < Co^{3+} = Mn^+$ (b) $Fe^{2+} = Cr < Co^{3+} = Mn^+$ (c) $Cr < Mn^+ < Fe^{2+} < Co^{3+}$ (d) $Fe^{2+} < Co^{3+} < Mn^+ < Cr$
- 14. The hydride ion, H^- , is a stronger base than the hydroxide ion, OH⁻. Which one of the following reactions will occur if sodium hydride (NaH) is dissolved in water?
 - (a) $H_{(aq)}^{-} + H_2O_{(l)} \longrightarrow OH_{(aq)}^{-} + 2H_{(aq)}^{+} + 2e^{-}$ (b) $H_{(aq)}^{-} + H_2O_{(l)} \longrightarrow OH_{(aq)}^{-} + H_{2(g)}$

 - (c) $H_{(aq)}^{-1} + H_2O_{(l)} \longrightarrow H_3O_{(aq)}^{-1}$ (d) $H_{(aq)}^{-1} + H_2O_{(l)} \longrightarrow$ No reaction
- 15. Beryllium and aluminium exhibit many properties which are similar. But, the two elements differ in
 - (a) exhibiting maximum covalency in compounds
 - (b) exhibiting amphoteric nature in their oxides
 - (c) forming polymeric hydrides
 - (d) forming covalent halides.

SOLUTIONS



2. (d):

Period	Suborbit	Orbitals	Elements	Total
3	3s	1	3	
	3р	3	9	27
	3 <i>d</i>	5	15	



4	4s 4p 4d 4f	1 3 5 7	3 9 15 21	48
5	5s 5p 5d 5f 5g	1 3 5 7 9	3 9 15 21 27	75

(c) : From the given information, we can see that 3. the reaction proceeds via formation of H_2O_2 (which is diabasic conjugate acid of peroxide ion), H₂O₂ then disproportionates into water and oxygen.

$$\begin{split} &\operatorname{Na_2O_{2(s)}} + 2\operatorname{H_2O_{(l)}} \longrightarrow 2\operatorname{NaOH_{(aq)}} + \operatorname{H_2O_{2(aq)}} \\ &\operatorname{H_2O_{2(aq)}} \longrightarrow \operatorname{H_2O_{(l)}} + \frac{1}{2}\operatorname{O_{2(g)}} \\ &\operatorname{Thus, overall reaction is} \\ &\operatorname{Na_2O_{2(s)}} + \operatorname{H_2O_{(l)}} \longrightarrow 2\operatorname{NaOH_{(aq)}} + \frac{1}{2}\operatorname{O_{2(g)}} \end{split}$$

$$CH_{3}-C \equiv CH + HCl \longrightarrow CH_{3} - \stackrel{C}{C} = CH_{2}$$

$$\downarrow H^{+}$$

$$Cl \qquad Cl \qquad Cl$$

$$CH_{3} - \stackrel{I}{C} - CH_{3} \xleftarrow{HI} CH_{3} - \stackrel{I}{C^{+}} = CH_{2}$$

$$(more stable carbocation due to back bonding)$$

 C^{1}

- 5. (d): $2H_2 + O_2 \longrightarrow 2H_2O$ Initial mole 2 3 0 Final mole $0 \quad 3-1=2$ 2 $C + O_2 \longrightarrow CO_2$ w w 12 32 Here, O_2 is limiting reagent.
- (c) : $\Delta G = \Delta H T \Delta S$ 6. For a spontaneous reaction ΔG should be negative $\Delta H = -283 \text{ kJ}, \Delta S = -87 \text{ J K}^{-1}$

Hence, reaction will be spontaneous when $\Delta H > T\Delta S$. Therefore, at 1000, 1500 and 3000 K the reaction would be spontaneous.



Hybridisation of
$$H_2SO_3 = \frac{1}{2}(6 + 2 + 0) = 4(sp^3)$$

- (c) : The redox couple with maximum reduction 8. potential will be best oxidising agent and with minimum reduction potential will be best reducing agent.
- (c) 9.

10. (b): Moles of H₂ =
$$\frac{3 \times 16.42}{0.0821 \times 300} = 2$$

Moles of D₂ = $\frac{6 \times 16.42}{0.0821 \times 300} = 4$
Average molecular weight = $\frac{2 \times 2 + 4 \times 4}{4 + 2} = \frac{10}{3}$

11. (b):Since slope is negative hence reaction is endothermic. So high temperature favours forward reaction similarly high pressure favours forward reaction.

12. (b): Br H

$$C-C=C-C-C-C C - C - C = C-C-C$$

H Br
structural: 1, structural: 1,
geometrical: 2 geometrical: 2
Hence, 2 structural and 4 geometrical isomers.
13. (a): Fe(26): [Ar]4s²3d⁶: $4s^2 3d^6$
Fe²⁺(24): [Ar]4s⁰3d⁶: $4s^2 3d^6$
Fe²⁺(24): [Ar]4s¹4d⁵: $4s^1 3d^5$
 $r(24): [Ar]4s^14d^5: [4s^1 3d^5$
 $r(24): [Ar]4s^23d^5$
Mn⁺(24): $n = 6$
Co(27): [Ar]4s²3d⁷
Co³⁺(24): $n = 4$
Magnetic moment = $\sqrt{n(n+2)}$ BM
Thus, Fe²⁺ = Co³⁺ < Mn⁺ = Cr
14. (b): $H_{(aq)}^{-} + H_2O_{(l)} \longrightarrow OH_{(aq)}^{-} + H_{2(q)}$

$$\begin{array}{c} \Pi_{(aq)} + \Pi_2 O_{(l)} & \longrightarrow O\Pi_{(aq)} + \Pi_{2(g)} \\ \text{base 1} & \text{acid 1} & \text{base 2} & \text{acid 2} \end{array}$$

In this reaction H⁻ acts as Bronsted base as it accepts one proton (H^+) from H_2O and form H_2 .

15. (a) : The maximum valency of beryllium is +2while that of aluminium is +3.

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This specially designed column will help you to brush up your concepts by practicing questions. You can mail us your queries and doubts related to this topic at editor@mtg.com. The queries will be entertained by the author.*

SOME BASIC CONCEPTS OF CHEMISTRY

In continuation with previous article :

- In 1961, ¹²C was taken to decide masses of other atoms. $\left(\frac{1}{12}\right)^{\text{th}}$ the mass of ¹²C-atom was taken as 1 unified mass (u), 1 atomic mass unit (amu), 1 carbon unit, 1 dalton, 1 aston and also 1 avogram. One amu corresponds to the production of 931.48 MeV energy.
- Average mass of all the naturally occurring isotopes of an element was taken its average atomic mass.
- The sum of atomic masses of all atoms of elements present in one molecule or formula unit was considered molecular mass.
- The mass of a compound per pre-decided atom is called its minimum molecular mass (Cannizzaro's view).
- The methodology for calculating number of particles, masses, moles and volumes of substance using chemical equations of reactions is called stoichiometry.
- In a chemical reaction, where two reactants are involved, the one which is completely consumed is called limiting reagent. Calculations of other substances are based on this limiting reagent.
- Most commonly used methods of expressing concentrations of solutions are :
 - (I) Concentration terms which are not affected by temperature.
 - (a) Mass fraction = $\frac{\text{Mass of component}}{\text{Total mass of solution}}$ (b) Mass percent = $\frac{\text{Mass of component}}{\text{Total mass of solution}} \times 10$

(c) ppm by mass =
$$\frac{\text{Mass of component}}{\text{Total mass of solution}} \times 10^6$$

(d) Mole fraction =
$$\frac{\text{Moles of component}}{\text{Total moles in solution}}$$

$$\Rightarrow x_B = \frac{n_B}{n_A + n_B}$$

(e) Molality(m) =
$$\frac{\text{Moles of solute}}{\text{Wt. of solvent in kg}}$$

= $\frac{W_B}{M_B} \times \frac{1000}{W_A(g)}$
= $\frac{1000 \times \text{molarity}}{1000 \times d_{\text{soln}}(\text{g mL}^{-1}) - \text{molarity} \times M_B}$
= $\frac{1000\chi_B}{W_B}$

$$=\frac{\kappa_L}{\chi_A M_A}$$

=

- (II) Concentration terms which are affected by temperature (volume based).
- (a) Strength in g $L^{-1} = \frac{W_B(g)}{V_{\text{soln.}}(L)}$

(b) Molarity
$$(M) = \frac{n_B}{V_{\text{soln}}(L)} = \frac{1000 W_B}{M_B \cdot V_{\text{soln}}(mL)}$$
$$= \frac{1000 md}{1000 + mM_B} = \frac{10 \times x\%(w/w) \times d}{M_B}$$

• **Dilution of solution :** Molarity of final solution (M_f) if V_1 mL of solution of M_1 molarity is diluted by adding x mL of water, then

$$M_f = \frac{M_1 V_1}{V_1 + x}$$

*By **R.C. Grover**, having 45+ years of experience in teaching chemistry.

CHEMISTRY TODAY | AUGUST '18

21

- Mixing of different solutions of the same solute $M_f V_f = M_1 V_1 + M_2 V_2 + \dots$
- O Reactions of two solutions
 - (a) $aA + bB \rightarrow$ Products

$$\frac{(MV)_A}{(MV)_B} = \frac{a}{b}$$

(b) W_B g of a substance of molar mass M_B , if completely reacts with V_A mL of another solution of molarity M_A (n_A and n_B are *n* factors of *A* and *B* respectively).

$$\frac{n_B W_B}{M_B} \times 1000 = M_A V_A n_A$$

- (c) Acid-base reaction: A is for acid and B is for base, b is basicity of acid and a is acidity of base.
- (i) If $b(MV)_A = a(MV)_B$, the final solution is neutral with pH = 7
- (ii) If $b(MV)_A > a(MV)_B$, the final solution is acidic (pH < 7) and molarity of final solution

$$M_f = \frac{b(MV)_A - a(MV)_B}{b(V_A + V_B)}$$

(iii) If $b(MV)_A < a(MV)_B$, the final solution is basic (pH > 7) and molarity of final solution

$$M_f = \frac{a(MV)_B - b(MV)_A}{a(V_A + V_B)}$$

MULTIPLE CHOICE QUESTIONS

One amu corresponds to MeV energy.
 (a) 831.49
 (b) 931.48
 (c) 831.49
 (d) 931.48

(c) 6.6×10^{-34}	(d) 6.022×10^{23}
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- 2. How many molecules of HCl gas will be produced by reacting 112 L of H₂ (0 °C, 1 atm) with 213 g of Cl₂?
 - (a) 3.61×10^{24} (b) 6.13×10^{23}
 - (c) 6.13×10^{24} (d) 1.63×10^{24}
- 20 mL of 0.4 M AgNO₃ (molar mass = 170 g) is reacted with 15 mL of 0.6 M BaCl₂ (molar mass = 208.4 g). The mass of AgCl (molar mass = 143.5 g) produced is
 - (a) 11.48 g (b) 18.14 g
 - (c) 14.18 g (d) 1.148 g
- **4.** 85 g $CaCO_3$ (limestone sample), on heating produces exactly the same amount of CO_2 which converts 30 g of MgO to MgCO₃. The percentage purity of limestone sample is
 - (a) 80% (b) 82.4%
 - (c) 88.24% (d) 84.8%

- 5. Mole fraction of acetic acid in an aqueous sample is
 0.1, the molality of the solution is
 (a) 7.16 (b) 1.67 (c) 6.17 (d) 5.25
- 6. The density of 4 M NaOH solution is 1.6 g mL⁻¹. The molality of the solution is
 (a) 2.77 (b) 14.28 (c) 7.14 (d) 57.14
- 7. Which of the following varies with temperature?
 (a) Molality
 (b) Mole fraction
 (c) Molarity
 (d) Mass per cent
- 8. 1.5 moles of each of XY_2 and XY_3 if weigh 96 g and 120 g respectively. The atomic masses of X and Y respectively are

(a) 4, 8 (b) 8, 16 (c) 32, 16 (d) 32, 64

- 9. Volume of 0.5 M HCl required for complete reaction of 10 g equimolar mixture of Na₂CO₃ (molar mass = 106 g) and NaHCO₃ (molar mass = 84 g) is
 (a) 125 8 mJ
 - (a) 135.8 mL (b) 315.8 mL (c) 831.5 mL (d) 513.8 mL
- 10. KMnO₄ reacts with oxalic acid solution : $2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4$ $\rightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$

What mass of $KMnO_4$ in aqueous solution will suffice to completely react with 100 mL of M/10 oxalic acid solution?

(a)	10.53 g	(b)	0.632 g
(c)	3.105 g	(d)	3.501 g

11. Three samples of NaCl (molar mass = 58.5 g) solutions of molarities 3 M, 5 M and 7 M are mixed in equal volumes. The same volume of water is now added to the solution. The molarity of the final solution is

(a) 3.0 M (b) 5.0 M (c) 2.5 M (d) 7.5 M

- 12. What volume of H_2SO_4 of 98% mass/mass solution of density 1.8 g mL⁻¹ will be used for preparing 5 L of 0.2 M H_2SO_4 ?
 - (a) 11.11 mL (b) 44.44 mL (c) 33.33 mL (d) 55.55 mL
- 13. What mass of a tribasic acid of molar mass 98 g mol⁻¹ will completely neutralise 100 mL of M/2 NaOH solution?
 - (a) 1.633 g (b) 16.33 g (c) 13.63 g (d) 31.36 g
- 14. 200 mL of M/5 dibasic acid is mixed with 150 mL of M/2 monoacid base. The pH of the resulting solution is likely to be
 - (a) more than 7 (b) less than 7
 - (c) equal to 7 (d) uncertain.



15. Which of the following is correct order for number of molecules of 0.56 L of each of the following gases at 25 °C and 2 atm pressure?

(a) $SO_2 > CO_2 > CH_4 > H_2$ (b) $H_2 > CH_4 > CO_2 > SO_2$

(c)
$$SO_2 = CO_2 > CH_4 > H_2$$

- (d) All are equal.
- **16.** If 5 g hydrogen is present in 0.4165 moles of a carbohydrate, its formula is

(a) $C_6H_{12}O_6$ (b) $C_{12}H_{22}O_{11}$ (c) $C_3H_6O_3$ (d) none of these.

- 17. How many grams of zinc (molar mass = 65.3 g) will be reacted with HCl to collect so much of H₂ gas which can convert 280 g ethene to ethane?
 (a) 65.3 g
 (b) 120.6 g
 - (c) 326.5 g (d) 653.0 g
- If 10 L of a mixture of CO and CO₂ that contains 30% of CO₂, is passed over red hot coke, the final volume is
 - (a) 12.0 L (b) 12.5 L (c) 13.0 L (d) 13.5 L
- 19. What is the molarity of 200 g of pure water?(a) 18(b) 55.56(c) 20.0(d) 6.55
- 20. A solution has density 1.2 g mL⁻¹ and molality 2.0 m. If molar mass of the solute is 100 g mol⁻¹, the molarity of the solute is
 (a) 0.5 (b) 1.0 (c) 1.5 (d) 2.0

SOLUTIONS

1. **(b)** (a): 2. $H_{2(g)}$ $2HCl_{(g)}$ $Cl_{2(g)}$ $112 L = \frac{112}{22.4} \text{ moles } 213 \text{ g} = \frac{213}{71}$ = 5 moles = 3 moles Here, $Cl_{2(g)}$ is limiting reagent, 1 Mole $Cl_{2(g)}$ produces $HCl_{(g)}$ = $2 \times 6.022 \times 10^{23}$ molecules 3 Moles $Cl_{2(g)}$ produces $HCl_{(g)}$ = 3 × 2 × 6.022 × 10²³ molecules = 3.61×10^{24} molecules $2AgNO_3 + BaCl_2 \rightarrow 2AgCl + Ba(NO_3)_2$ 3. (**d**): Moles: $\frac{20}{1000} \times 0.4$ $\frac{15}{1000} \times 0.6$ = 0.008 = 0.009 2 moles AgNO₃ reacts with 1 mole of BaCl₂ 0.008 moles AgNO₃ reacts with $\frac{0.008}{2}$

 $= 0.004 \text{ mol } BaCl_2$

Given moles of BaCl₂ are quite high, thus, AgNO₃ is limiting reagent. 2 moles AgNO₃ gives = 2×143.5 g AgCl 0.008 mole AgNO₃ gives AgCl $=\frac{2\times 143.5\times 0.008}{2}=1.148$ g AgCl (c) : MgO + $\underset{40 \text{ g}}{\text{CO}_2}$ + $\underset{44 \text{ g}}{\text{CO}_2}$ \rightarrow MgCO₃ 4. 40g MgO needs $CO_2 = 44$ g 30 g MgO needs $CO_2 = \frac{44 \times 30}{40} = 33 g$ CaCO₃ \rightarrow CaO + CO₂ 44 g 100 g 44 g CO_2 is obtained from $CaCO_3 = 100$ g 33 g CO_2 is obtained from $CaCO_3$ $=\frac{100\times33}{44}=75\,\mathrm{g}$ Percentage purity of CaCO₃ sample $= \frac{75}{85} \times 100 = 88.24\%$ (c) : $x_{\text{CH}_3\text{COOH}} = \frac{n_{\text{CH}_3\text{COOH}}}{n_{\text{CH}_3\text{COOH}} + n_{\text{H}_2\text{O}}}$ $\Rightarrow 0.1 (given) = \frac{1}{1 + 1}$ $w_A = 9 \times 18 = 162 \text{ g} = \frac{162}{1000} \text{ kg}$ Molality = $\frac{n_B}{w_A (\text{kg})} = \frac{1 \times 1000}{162} = 6.17 \text{ mol kg}^{-1}$ Alternatively, $x_{CH_3COOH} = 0.1$ $x_{\rm H_2O} = 1 - 0.1 = 0.9$ Molality = $\frac{1000 x_B}{x_A M_A} = \frac{1000 \times 0.1}{0.9 \times 18} = 6.17 \text{ mol kg}^{-1}$ 1000 M(a) : $m = \frac{1000 M}{1000 d - MM_B} = \frac{1000 \times 4}{(1000 \times 1.6) - (4 \times 40)}$ $=\frac{4000}{1600-160}=\frac{4000}{1440}=2.77 \text{ mol kg}^{-1}$ (c) 7.

JULY 2018 1-e- BREEDER 2-c- PERSPEX 3-f- BLOOMING 4-a- DENATURANTS 5-j- ALESSANDRO VOLTA 6-i- HOESCH REACTION 7-d- SPELTER 8-g- ACONITIC ACID 9-b- INFUSIONS 10-h- PENTALENOLACTONE Winner: Chelsi Singh (Uttar Pradesh), Neelam Waghmare (Maharashtra)

CHEMISTRY TODAY | AUGUST '18

23

- (c) : If atomic weights of X and Y are 'a' and 'b' 8. respectively 1.5 (a + 2b) = 96 and 1.5 (a + 3b) = 120 \Rightarrow a + 2b = 64 and a + 3b = 80On solving, a = 32 and b = 16
- 9. (b): $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$ $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$ Total wt. of Na₂CO₃ and NaHCO₃ (as per equations) = 106 + 84 = 190 gMoles of HCl used = 3190 g mixture, HCl = 3 mol10 g mixture, HCl = $\frac{3 \times 10}{190}$ mol = $\frac{3}{19}$ mol $(MV)_{\text{HCl}} = \frac{3}{10} \implies V_{\text{HCl}(\text{L})} = \frac{3}{10} \times \frac{1}{0.5}$ $V_{\text{HCl(mL)}} = \frac{3}{19} \times \frac{1}{0.5} \times 1000 = 315.8 \text{ mL}$ 10. (b): $\frac{\frac{W_{\text{KMnO}_4}}{M_{\text{KMnO}_4}} \times 1000}{(MV)_{\text{oxalic acid}}} = \frac{2}{5}$ $\frac{W_{\rm KMnO_4}}{158} \times 1000 = \frac{2}{5} \times \frac{1}{10} \times 100$ $W_{\rm KMnO_4} = \frac{2}{5} \times \frac{1}{10} \times 100 \times \frac{158}{1000} = 0.632 \text{ g}$ 11. (c) : Let 1 L of each solution be mixed,
- $$\begin{split} M_f V_f &= M_1 V_1 + M_2 V_2 + M_3 V_3 \\ M_f &= \frac{(3 \times 1) + (5 \times 1) + (7 \times 1)}{1 + 1 + 1 + 3} = \frac{3 + 5 + 7}{6} = \frac{15}{6} = 2.5 \text{ M} \end{split}$$
- **12.** (d): Molarity of concentrated H_2SO_4 $=\frac{10 \times x\% \times d}{M_{P}} = \frac{10 \times 98 \times 1.8}{98} = 18 \text{ M}$ $(MV)_{\text{dil. soln.}} = (MV)_{\text{conc. soln.}}$ $V_{\text{conc. soln.}} = \frac{0.2 \times 5}{18} \text{ L} = \frac{1000}{18} \text{ mL} = 55.55 \text{ mL}$
- 13. (a) : $H_3A + 3NaOH \rightarrow Na_3A + 3H_2O$ $\frac{\frac{W_{\text{acid}}}{M_{\text{acid}}} \times 1000}{(MV)_{\text{NaOH}}} = \frac{1}{3}$

$$\frac{W_{\text{acid}}}{98} \times 1000 = (MV)_{\text{NaOH}} \times \frac{1}{3}$$
$$W_{\text{acid}} = \left(\frac{1}{2} \times 100\right) \times \frac{1}{3} \times \frac{98}{1000} = 1.633 \text{ g}$$

14. (b): $b(MV)_A = 2 \times \frac{1}{5} \times 200 = 80$ millimoles

 $a(MV)_B = 1 \times \frac{1}{2} \times 150 = 75$ millimoles \Rightarrow Acid dominates, pH < 7

- 15. (d): Equal volumes of all the gases under the same conditions of temperature and pressure contain equal number of molecules.
- **16.** (a) :0.4165 moles of carbohydrate has H = 5 g1 mole of carbohydrate has H = $\frac{5}{0.4165}$ g = 12 g \Rightarrow 1 mole of carbohydrate has 12 H atoms. 17. (d): $Zn + 2HCl \rightarrow ZnCl_2 + H_2$
- $C_2H_4 + H_2 \rightarrow C_2H_6$ Add the two equations, $Zn + 2HCl + C_2H_4 \rightarrow ZnCl_2 + C_2H_6$ 28 g 65.3 g 28 g C_2H_4 , for change to C_2H_6 , needs Zn = 65.3 g 280 g C_2H_4 , for change to C_2H_6 needs Zn $=\frac{65.3\times280}{28}=653$ g **18.** (c) : Mixture has 30% CO₂ = $\frac{30}{100} \times 10$ L $= 3 L CO_2$ \Rightarrow Volume of CO = 10 - 3 = 7 L $CO_2 + C \rightarrow 2CO$ 2 volumes 1 volume
- 19. (b): Whatever be the volume of pure water, its molarity is fixed,

6 L

Final volume, only CO gas = 7 + 6 = 13 L

1000 mL H₂O = 1000 g = $\frac{1000}{18}$ mol = 55.56 mol **20.** (d): Molarity = $\frac{1000md}{1000 + mM_B}$ $=\frac{1000\times2\times1.2}{1000+2\times100}=\frac{2400}{1000+200}=\frac{2400}{1200}=2$ M

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The questions given in this column have been prepared on the basis of pattern of Previous Years' Questions asked in JEE (Main & Advanced)/NEET/AIIMS exams.

SOME BASIC CONCEPTS OF CHEMISTRY

SECTION - I

- Only One Option Correct Type
- 1. Which of the following statements indicates that law of multiple proportion is being followed?
 - (a) Sample of carbon dioxide taken from any source will always have carbon and oxygen in the ratio 1 : 2.
 - (b) Carbon forms two oxides namely CO₂ and CO, where masses of oxygen which combine with fixed mass of carbon are in the simple ratio 2:1.
 - (c) When magnesium burns in oxygen, the amount of magnesium taken for the reaction is equal to the amount of magnesium in magnesium oxide formed.
 - (d) At constant temperature and pressure, 200 mL of hydrogen will combine with 100 mL of oxygen to produce 200 mL of water vapour.
- 2. A compound of iron and chlorine is soluble in water. An excess of silver nitrate was added to precipitate the chloride ion as silver chloride. If a 134.8 mg of the compound gave 304.8 mg of AgCl, what is the formula of the compound?
 - (a) FeCl₆ (b) FeCl₃
 - (c) $FeCl_2$ (d) $FeCl_4$
- 3. At 300 K and 1 atm, 15 mL of a gaseous hydrocarbon requires 375 mL air containing 20% O_2 by volume for complete combustion. After combustion the gases occupy 330 mL. Assuming that the water formed is in liquid form and the volumes were measured at the same temperature and pressure, the formula of the hydrocarbon is

(a)
$$C_{3}H_{6}$$
 (b) $C_{3}H_{8}$
(c) $C_{4}H_{8}$ (d) $C_{4}H_{10}$
(*JEE Main, 2016*)

4. When burnt in air, 14.0 g mixture of carbon and sulphur gives a mixture of CO_2 and SO_2 in the volume ratio of 2 : 1, volume being measured at the same conditions of temperature and pressure. Number of moles of carbon in the mixture is

(a) 0.75 (b) 0.5 (c) 0.4 (d) 0.25

- 5. The density of 3 M sodium thiosulphate is 1.25 g mL^{-1} . Identify the correct statement among the following.
 - (a) % by weight of sodium thiosulphate is 37.92.
 - (b) The mole fraction of sodium thiosulphate is 0.065.
 - (c) The molality of Na⁺ is 7.74 and $S_2O_3^{2-}$ is 3.87.
 - (d) All of the above.

SECTION - II

Paragraph Type

Paragraph for Questions 6 and 7

An empirical formula represents the simplest whole number ratio of various atoms present in a compound whereas the molecular formula shows the exact number of different types of atoms present in a molecule of a compound.

If the mass per cent of various elements present in a compound is known, its empirical formula can be determined. Molecular formula can further be obtained if the molar mass is known.

6. 0.30 g of an organic compound containing C, H and O on combustion gave 0.44 g CO_2 and 0.18 g H_2O . If 1 mole of compound weighs 60, then molecular formula of the compound is

(a)
$$C_2H_4O_2$$
 (b) CH_2O

(c)
$$C_3H_8O$$
 (d) C_4H_{12}



- 7. In a compound C, H and N are present in 9 : 1 : 3.5 by weight. If molecular weight of the compound is 108, then the molecular formula of the compound is
 (a) C₂H₆N₂
 (b) C₃H₄N
 - (c) $C_6H_8N_2$ (d) $C_9H_1N_3$

Paragraph for Ouestions 8 and 9

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately 6.023×10^{23}) are present in a few grams of any chemical compound varying with their atomic/ molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (atomic mass: Na = 23, Hg = 200; 1 faraday = 96500 coulombs).

8. The total number of moles of chlorine gas evolved is

(a)	0.5	(b)	1.0
(c)	2.0	(d)	3.0

9. The total charge (coulombs) required for complete electrolysis is

(a) 24125 (b)	48250
---------------	-------

(c) 96500

(d) 193000

(*IIT JEE*, 2007)

SECTION - III

Assertion Reason Type

Assertion Reason type MCQs having only one option correct. Mark the correct choice as :

(a) If both assertion and reason are true and reason is the correct explanation of assertion.

- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.
- 10. Assertion : 12 parts by mass of carbon in CO and CO_2 molecules combine with 16 and 32 parts by mass of oxygen.

Reason : A given compound always contains exactly the same proportion of elements by weight.

- 11. Assertion : The molality of a solution does not change with change in temperature.Reason : The molality is expressed in units of moles per 1000 g of solvent.
- **12. Assertion :** Mass numbers of most of the elements are fractional.

Reason : Mass numbers are obtained by comparing with mass number of carbon taken as 12.

SECTION - IV

Numerical Value Type

- **13.** 1.325 g of anhydrous sodium carbonate is dissolved in water and the solution made upto 250 mL. On titration 25 mL of this solution neutralise 20 mL of a solution of sulphuric acid. How much water should be added to 450 mL of this acid solution to make it exactly *N*/12 ?
- 14. A sample of pure Cu (3.18 g) heated in a stream of oxygen for sometime gains weight with the formation of black oxide of copper (CuO). The final weight is 3.92 g. The percentage of copper that remains unoxidised is
- 15. A compound H_2X with molar weight of 80 g is dissolved in a solvent having density of 0.4 g mL⁻¹. Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is

(JEE Advanced, 2014)

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

SECTION - I

Only One Option Correct Type

1. The electronic configuration of the four elements are $P : 1s^2$; $Q : 1s^2$, $2s^2$, $2p^2$; $R : 1s^2$, $2s^2$, $2p^5$; $S : 1s^2$, $2s^2$, $2p^6$. The tendency to form electrovalent bond is maximum in

(a)	Р	(b)	Q
(c)	R	(d)	S

- 2. Identify the incorrect statement.
 - (a) The first ionisation potential of Al is less than the first ionisation potential of Mg.
 - (b) The second ionisation potential of Mg is greater than the second ionisation potential of Na.
 - (c) The first ionisation potential of Na is less than the first ionisation potential of Mg.
 - (d) The third ionisation potential of Mg is greater than that of Al.

- 3. Elements X, Y and Z have atomic numbers 19, 37 and 55 respectively. Which of the following statements is true about them?
 - (a) Their ionization potential would increase with increasing atomic number.
 - (b) *Y* would have an ionization potential between those of *X* and *Z*.
 - (c) *Z* would have the highest ionization potential.
 - (d) *Y* would have the highest ionization potential.
- 4. Al^{3+} has a lower ionic radius than Mg^{2+} ion because
 - (a) Mg atom has less number of neutrons than Al
 - (b) Al^{3+} has higher nuclear charge than Mg^{2+}
 - (c) their electronegativities are different
 - (d) Al has lower ionization potential than Mg atom.
- The element Z = 114 has been discovered recently. It 5. will belong to which of the following family/group and electronic configuration?
 - (a) Carbon family, [Rn] $5f^{14} 6d^{10} 7s^2 7p^2$
 - (a) Carbon family, [Rn] $5f^{14} 6d^{10} 7s^2 7p^4$ (b) Oxygen family, [Rn] $5f^{14} 6d^{10} 7s^2 7p^4$ (c) Nitrogen family, [Rn] $5f^{14} 6d^{10} 7s^2 7p^5$ (d) Halogen family, [Rn] $5f^{14} 6d^{10} 7s^2 7p^5$

(NEET, 2017)

SECTION - II

More than One Options Correct Type

- 6. Which of the following are correct statements?
 - (a) The electron affinity of Si is greater than that of P.
 - (b) Penetrating power of *p*-orbital is more than s-orbital.
 - (c) The numerical value of electronegativity of an atom depends on its ionisation potential and electron affinity.
 - (d) All of the above.
- 7. Which of the following is not true for the long form of periodic table?
 - (a) It reflects the sequence of filling the electrons in *s*, *p*, *d* and *f*-orbitals.
 - (b) It helps to predict the stable valency of elements.
 - (c) It does not reflect trends in physical and chemical properties.
 - (d) It helps to predict the relative ionic character of the bond between two elements.
- 8. The values of two lattice energies are given below: NaF – 915 kJ mol⁻¹; MgO – 3933 kJ mol⁻¹ Which of the following correct statements help to explain the difference between these two values?
 - (a) In each of these compounds, the ions are isoelectronic.
 - (b) The attraction between doubly charged ions

is about four times than that between singly charged ions.

- (c) The interionic distance in NaF is greater than that in MgO.
- (d) The interionic distance in NaF is smaller than that in MgO.
- 9. In which of the following species the octet rule is not applicable?
 - (a) BrF₅ (b) SF_6 (c) IF_7 (d) PCl_5
- **10.** The option(s) with only amphoteric oxides is(are) (a) Cr_2O_3 , BeO, SnO, SnO₂
 - (b) ZnO, Al₂O₃, PbO, PbO₂
 - (c) NO, B_2O_3 , PbO, SnO₂
 - (d) Cr₂O₃, CrO, SnO, PbO (*JEE Advanced*, 2017)

SECTION - III

Assertion Reason Type

Assertion Reason type MCQs having only one option correct. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.
- 11. Assertion : Lithium having maximum negative *E*° value is the strongest reducing agent amongst all alkali metals in solution. Reason: Lithium is the lightest metal in the periodic table.
- 12. Assertion : If the five successive ionization energies of an element are 700, 2145, 3478, 30450 and 38748 kJ mol⁻¹ respectively, the number of valence electrons is three.

Reason : Ionization energy increases abruptly at fourth ionization energy.

13. Assertion : Helium has the highest value of ionisation energy among all the elements known. Reason : Helium has the highest value of electron affinity among all the elements known. ATTN (C. 2010)

							(7	IIMS	5, 2010)
MO	NTHLY	TUN	E UP	CLAS	SS XII	A	NSW	ER	KEY
1.	(c)	2.	(d)	3.	(b)	4.	(b)	5.	(b)
6.	(b)	7.	(d)	8.	(c)	9.	(a)	10.	(c)
11.	(a)	12.	(a)	13.	(b)	14.	(a)	15.	(b)
16.	(c)	17.	(b)	18.	(c)	19.	(b)	20.	(a,b)
21.	(a,c)	22.	(b,c)	23.	(a,b,d)	24.	(525)	25.	(0.154)
26.	(1.064)	27.	(a)	28.	(b)	29.	(c)	30.	(a)



SECTION - IV

Numerical Value Type

- 14. The electron affinity of chlorine is 3.7 eV. How much energy in kcal is released when 2 g of chlorine is completely converted to Cl⁻ ion in a gaseous state?
- **15.** The periodic table consists of 18 groups. An isotope of copper, on bombardment with protons, undergoes a nuclear reaction yielding element *X* as shown below. To which group, element *X* belongs in the periodic table?

SOLUTIONS

6.

SOME BASIC CONCEPTS OF CHEMISTRY

- 1. (b): Law of multiple proportions states that 'if two elements can combine to form more than one compound, then the mass of one element that combines with a fixed mass of the other element, is in the ratio of small whole numbers.
- **2.** (c) : Let the formula of iron chloride be FeCl_x

 $\operatorname{FeCl}_{x} + x\operatorname{AgNO}_{3} \rightarrow x\operatorname{AgCl} + \operatorname{Fe(NO}_{3})_{x}$ $(56 + 35.5 x) \text{ g} \qquad 143.5 x \text{ g}$ $\frac{\text{wt. of FeCl}_{x}}{\text{wt. of AgCl}} = \frac{\text{mol. wt. of FeCl}_{x}}{\text{mol wt. of AgCl}(x \text{ unit})}$ $\frac{134.8}{304.8} = \frac{56 + 35.5 x}{143.5 x} \Rightarrow x = 2$

Hence, the formula of iron chloride is FeCl₂.

3. (b): Chemical equation for the combustion of hydrocarbon is

$$C_{x}H_{y(g)} + \left(x + \frac{y}{4}\right)O_{2(g)} \rightarrow xCO_{2(g)} + \frac{y}{2}H_{2}O_{(l)}$$

Initial 15 mL 15 $\left(x + \frac{y}{4}\right)$ mL 0
Final 0 0 15x mL

Now, volume of O₂ in air $=\frac{20}{100} \times 375 = 75$ mL

$$\therefore 75 = 15\left(x + \frac{y}{4}\right) \implies x + \frac{y}{4} = 5$$

Out of given four options, C_3H_8 will satisfy the above equation.

4. (b): Let weight of C be x g, then weight of S will be (14 - x) g in a mixture.

$$\frac{x/12}{(14-x)/32} = \frac{2}{1} \quad (\because V \propto n)$$

$$\Rightarrow x = 6 \text{ g}$$

$$\therefore \text{ Moles of } C = \frac{6}{12} = 0.5$$

5. (d): $M = \frac{M \operatorname{ass} \% \times d \times 10}{M_2}$



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$$3 = \frac{\text{Mass } \% \times 1.25 \times 10}{158} [\because M_{\text{Na}_2\text{S}_2\text{O}_3} = 158 \text{ g mol}^{-1}]$$

$$\text{Mass } \% = \frac{3 \times 158}{1.25 \times 10} = 37.92$$

$$\text{Also, } \frac{1}{m} = \frac{d}{M} - \frac{M_2}{1000}; \frac{1}{m} = \frac{1.25}{3} - \frac{158}{1000}$$

$$\Rightarrow m = \frac{3000}{776} = 3.87$$
Thus, molality of Na⁺ ions = 2 × 3.87 = 7.74 m
and molality of S₂O₃²⁻ ions = 3.87 m

and molality of S₂O₃²⁻ ions = 3.87 m \therefore Moles of Na₂S₂O₃ in 1000 g of water = 3.87 Moles of solvent = $\frac{1000}{18}$ = 55.55 Mole fraction of Na₂S₂O₃ = $\frac{n_2}{n_1 + n_2}$ = $\frac{3.87}{3.87 + 55.55}$ = $\frac{3.87}{59.42}$ = 0.065

(a): Weight of carbon =
$$12 \times \text{moles of CO}_2$$

= $\frac{12 \times 0.44}{44} = 0.12 \text{ g}$

Weight of hydrogen = $2 \times \text{moles of H}_2\text{O}$

$$=\frac{2\times0.18}{18}=0.02$$
 g

Weight of oxygen = 0.30 - (0.12 + 0.02) = 0.16 g

Element	С	Н	0
Weight ratio	0.12	0.02	0.16
Mole ratio	$\frac{0.12}{12} = 0.01$	$\frac{0.02}{1} = 0.02$	$\frac{0.16}{16} = 0.01$

Simple ratio = 1:2:1

Empirical formula = CH_2O

Molecular weight = $n \times$ Empirical formula weight 60 = $n \times 30 \implies n = 2$

 \therefore Molecular formula = C₂H₄O₂

7. (c):

Element	Weight ratio	Atomic mass	Molar ratio	Simplest ratio
Carbon	9	12	$\frac{9}{12} = 0.75$	3
Hydrogen	1	1	$\frac{1}{1} = 1$	4
Nitrogen	3.5	14	$\frac{3.5}{14} = 0.25$	1

- :. Empirical formula of the compound = C_3H_4N $n(12 \times 3 + 1 \times 4 + 14 \times 1) = 108$
- or, $54n = 108 \implies n = 2$
- \therefore Molecular formula of the compound = C₆H₈N₂
- (b): 500 mL of 4.0 molar NaCl solution contains 2 moles of NaCl. The chlorine content of this sample will be evolved as chlorine gas.

The number of moles of NaCl = Number of moles

of
$$Cl^- = 2$$
 mole $\left(4 \times \frac{1}{2}\right)$

 \therefore Number of moles of Cl_2 gas evolved

$$=\frac{2}{2}=1 \text{ mole } (2\text{NaCl} \rightarrow \text{Cl}_2)$$

9. (d): $Na^+ + e^- \rightarrow Na$

Moles of Na^+ discharged at cathode = 2

 \therefore The number of electrons required for this purpose = 2

- $\therefore \quad \text{Total charge required} = 2 \text{ Faradays} \\ = 2 \times 96500 = 193000 \text{ Coulombs}$
- **10.** (b): The masses of oxygen (*i.e.*, 16 g and 32 g) which combine with a fixed mass of carbon (*i.e.*, 12 g) bear a simple ratio, *i.e.* 16 : 32 or 1 : 2. This is in accordance with the law of multiple proportions.

11. (a)

12. (d): Mass numbers are whole numbers, atomic masses are fractional.Atomic masses are obtained by comparing with

Atomic masses are obtained by comparing with mass of C-12 atom taken as 12.

13. (225): Eq. mass of Na₂CO₃ = $\frac{\text{Mol. mass}}{2} = \frac{106}{2} = 53$ 250 mL of the sodium carbonate solution contains = 1.325 g

1000 mL of the sodium carbonate solution contains

$$\frac{1.325}{250} \times 1000 = 5.3 \,\mathrm{g}$$

Normality of Na₂CO₃ solution

$$= \frac{\text{Strength}(g/L)}{\text{Eq. mass}} = \frac{5.30}{53} = \frac{1}{10} \text{ N}$$

Applying,
$$N_1V_1 = N_2V_2$$
$$(Na_2CO_3) (H_2SO_4)$$
$$\frac{1}{10} \times 25 = N_2 \times 20 \Rightarrow N_2 = \frac{25}{10 \times 20} = \frac{1}{8}$$
Applying,
$$N_BV_B = N_AV_A$$
Before dilution After dilution
$$\frac{1}{8} \times 450 = \frac{1}{2} \times V_A \Rightarrow V_A = \frac{450 \times 12}{8} = 675 \text{ mL}$$
Water to be added for dilution
$$= (675 - 450) = 225 \text{ mL}$$

14. (7.5): 63.6 g of Cu gives (63.6 + 16) g of CuO So, *a* g of Cu will give $\frac{(63.6+16)}{63.6}a$ g of CuO Thus, final weight = $(3.18-a) + \frac{(63.6+16)a}{63.6} = 3.92$ $\Rightarrow a = 2.94$ g Thus, % of Cu left unoxidised

$$=\frac{(3.18-2.94)}{3.18} \times 100 = 7.5$$
(8): Mass of 1 L solvent = 0.4 g mL⁻¹ × 10³ mL

15. (8): Mass of 1 L solvent =
$$0.4 \text{ g mL}^{-1} \times 10^3 \text{ mL}$$

= 400 g = 0.4 kg

So, molality (m) =
$$\frac{\text{Moles of solute}}{\text{Mass of solvent (kg)}} = \frac{3.2}{0.4}$$

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

- 1. (c) : *R* forms anion readily by gaining one electron only.
- 2. (b): IE_2 of Na is higher than that of Mg because in case of Na, the second electron has to be removed from the noble gas core while in case of Mg, removal of second electron gives a noble gas core.
- 3. (b): Elements X, Y and Z with atomic numbers 19, 37, 55 lie in group 1 (alkali metals). Within a group, *IE* decreases from top to bottom. Therefore, *IE* of Y could be between X and Z.

- 5. (a): The electronic configuration of the element with Z = 114 (flerovium) is $[\text{Rn}]5f^{14} 6d^{10}7s^27p^2$. Hence, it belongs to carbon family which has the same outer electronic configuration.
- 6. (a, c) : (a) is correct because the electronic configuration of P is exactly half-filled *i.e.*, more stable.

(b) is incorrect because *s*-orbital is closer to nucleus than *p*-orbital.



(c) is correct because, electronegativity

= (I.P. + E.A.)/2

- 7. (b, c)
- 8. (b, c) : Higher magnitude of charge and smaller interionic radius of MgO are responsible for higher lattice energy.
- **9.** (**a,b,c,d**) : BrF₅ (12 electrons), SF₆ (12 electrons), IF_7 (14 electrons) and PCl_5 (10 electrons).
- **10.** (a, b) : Amphoteric oxides are : Cr₂O₃, BeO, SnO, SnO₂, ZnO, Al₂O₃, PbO and PbO₂ Whereas, NO is a neutral oxide, B₂O₃ is an acidic oxide and CrO is a basic oxide.
- 11. (b)
- 12. (a): Ionization energy increases abruptly at fourth ionization energy *i.e.* $IE_4 >>> IE_3$ and as the 4th electron requires very-very high energy for its removal as this electron is to be knocked out from

the noble gas core. Hence, the number of valence electron is three.

13. (c): He contains fully filled $1s^2$ orbital which has more penetrating effect and is very close to the nucleus and hence has highest value of ionisation energy. Chlorine has highest electron affinity amongst all the elements known, not helium.

14. (4.8) : $Cl + e^- \rightarrow Cl^- + 3.7 \text{ eV}$ 35.5 3.7 × 23.06 kcal

> Energy released for conversion of 2 g gaseous *:*. chlorine into Cl⁻ ions

$$= \frac{3.7 \times 23.06}{35.5} \times 2 = 4.8 \text{ kcal}$$

15. (8): ${}^{63}_{29}Cu + {}^{1}_{1}H \rightarrow 6 {}^{1}_{0}n + {}^{4}_{2}He(\alpha) + 2{}^{1}_{1}H + {}^{52}_{26}X$ Atomic number 26 represents Fe which belongs to group 8.

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Scientist of the Month



Erich Armand Arthur Joseph Hückel (9 August, 1896 - 16 February, 1980)

Early life and Education

Erich Armand Arthur Joseph Hückel was a German physicist and physical chemist.

Hückel was born in the Charlottenburg suburb of Berlin. He studied physics and mathematics from 1914 to 1921 at the University of Göttingen.

On receiving his doctorate, he became an assistant at Göttingen, but soon became an assistant to Peter Debye at Zürich. It was there that he and Debye developed their theory (the Debye-Hückel theory, in 1923) of electrolytic solutions, elucidating the behavior of strong electrolytes by considering interionic forces, in order to account for their electrical conductivity and their thermodynamic activity coefficients.

After spending 1928 and 1929 in England and Denmark, working briefly with Niels Bohr, Hückel joined the faculty of the Technische Hochschule in Stuttgart. In 1935, he moved to Phillips University in Marburg, where he finally was named Full Professor a year before his retirement 1961. He was a member of the International Academy of Quantum Molecular Science.

Contributions

He is known for two major contributions:

- The Debye–Hückel theory of electrolytic solutions.
- The Hückel method of approximate molecular orbital (MO) calculations on π -electron systems.

In 1930 he proposed a σ/π separation theory to explain the restricted rotation of alkenes (compounds containing a C=C double bond). This model extended a 1929 interpretation of the bonding in triplet oxygen by Lennard-Jones. According to Hückel, only the ethene σ -bond is axially symmetric about the C-C axis, but the π -bond is not; this restricts rotation. In 1931 he generalized his analysis by formulating both valence bond (VB) and molecular orbital (MO) descriptions of benzene and other cycloconjugated hydrocarbons. Although undeniably a cornerstone of organic chemistry, Hückel's concepts were undeservedly unrecognized for two decades. His lack of communication skills contributed.

The famous Hückel 4n + 2 rule for determining whether ring molecules composed of C=C bonds would show aromatic properties was first stated clearly by Doering in a 1951 article on tropolone.

In 1936, Hückel developed the theory of ϖ -conjugated biradicals (non-Kekulé molecules). The first example, known as the Schlenk-Brauns hydrocarbon, had been discovered in the same year.

In 1937 Hückel refined his MO theory of pi-electrons in unsaturated organic molecules. This is still used occasionally as an approximation, though the more precise PPP Pariser-Parr-Pople method succeeded it in 1953. "Extended Hückel MO theory" (EHT) applies to both sigma and pi-electrons, and has its origins in work by William Lipscomb and Roald Hoffmann for nonplanar molecules in 1962.

Award

1965 Otto Hahn Prize for Chemistry and Physics.





Chapterwise practice questions for CBSE Exams as per the latest pattern and marking scheme issued by CBSE for the academic session 2018-19.

- **GENERAL INSTRUCTIONS**
- (i) All questions are compulsory.

Time Allowed : 3 hours

- (iii) Q. no. 6 to 12 are short answer questions and carry 2 marks each.
- (v) Q. no. 25 to 27 are long answer questions and carry 5 marks each.
- (ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each. (iv) Q. no. 13 to 24 are also short answer questions and carry 3 marks each.
- (vi) Use log tables if necessary, use of calculators is not allowed.

Maximum Marks: 70

Classification of Elements and Periodicity in Properties **Chemical Bonding and Molecular Structure**

- 1. Why do elements in the same group have similar chemical properties?
- 2. An element 'X' belongs to the third period of the *p*-block. It has four electrons in the outermost shell. Deduce the atomic number of element '*X*'.
- 3. How many resonance structures are possible for an SO_4^{2-} ion with a formal charge of (i) + 1 and (ii) + 2 on S?
- 4. Which has higher value (negative) of lattice enthalpy, NaCl or MgO?
- 5. In terms of period and group where would you locate the element with Z = 114?
- 6. Why is NaCl a bad conductor of electricity in the solid state though it has ions present?
- 7. Explain why cations are smaller and anions are larger in radii than their parent atoms.
- 8. The C = O and $C \equiv O$ bond lengths are generally 121 and 110 pm respectively. The actual C—O bond

length in CO₂ is 115 pm. What does this suggest regarding the Lewis structure of CO₂?

9. Apart from tetrahedral geometry, another possible geometry for CH₄ is square planar with the four H-atoms at the corners of the square and the C-atoms at its centre. Explain why CH₄ is not sqaure planar.

Although geometries of NH₃ and H₂O molecules are distorted tetrahedral, bond angle in H₂O is less than that of NH₃. Discuss.

- 10. Use the periodic table to answer the following questions.
 - (i) Identify an element with five electrons in the outer subshell.
 - (ii) Identify an element that would tend to lose two electrons.
 - (iii) Identify an element that would tend to gain two electrons.
 - (iv) Identify the group having element with metallic lustre, non-metal, liquid as well as gas at the room temperature.



- 11. All transition elements are *d*-block elements, but all d-block elements are not transition elements. Explain.
- **12.** Which of the following will have the most negative electron gain enthalpy and which have the least negative? P, S, Cl and F
- 13. How many electron pairs available in the valence shell of (i) N in NH₃ (ii) P in PCl₃ (iii) C in CO₂ (iv) N in NH_4^+ (v) P in PCl_5 (vi) S in H_2S
- 14. Which of the following pairs of elements would have a higher negative electron gain enthalpy? (i) O or F (ii) F or Cl (iii) N or O Give reasons.
- **15.** (i) Find the total number of σ -and π -bonds and lone pair of electrons in a molecule of CH₂COOH.
 - (ii) Predict the state of hybridisation of the central atom in (a) IF_5 and (b) CO_2 .

Also, predict the shape of these molecules.

16. (i) Define electronegativity. How does it differ from electron gain enthalpy.

- (ii) State diagonal relationship.
- 17. What are the various factors due to which the ionization enthalpy of the main group elements tends to decrease down a group?

OR

Among the second period elements the actual ionization enthalpies are in the order Li < B < Be < C < O < N < F < Ne. Explain why

- (i) Be has higher $\Delta_i H$ than B
- (ii) O has lower $\Delta_i H$ than N and F.
- **18.** (i) Explain why BeH_2 molecule has zero dipole moment although Be-H bonds are polar.
 - (ii) Arrange the following in increasing order of ionic character:

C—H, H—Cl, H—Br, K—F, Na—I

- (iii) The percentage ionic character in a certain bond between A and B is 75% and the bond distance A - B is 155 pm. What is the dipole moment of AB molecule?
- 19. Compare the relative stability of the following species and indicate their magnetic properties:

 O_2 , O_2^+ , O_2^- (superoxide ion), O_2^{2-} (peroxide ion)

20. The formation of $F_{(g)}^{-}$ from $F_{(g)}$ is exothermic whereas that of $O_{(g)}^{2-}$ from $O_{(g)}$ is endothermic. Explain.



32 CHEMISTRY TODAY | AUGUST '18

- 21. Among the elements B, Al, C and Si:
 - (i) Which has the highest first ionization enthalpy?
 - (ii) Which has the most negative electron gain enthalpv?
 - (iii) Which has the most metallic character? Give reasons.
- 22. (i) Use molecular orbital theory to explain why Be₂ molecule does not exist.
 - (ii) What is the significance of plus and minus signs when representing an orbital?
 - (iii) The experimentally determined N-F bond length in NF₃ is greater than the sum of the single covalent radius of N and F. Explain.
- 23. (i) Using VSEPR theory, draw the shape of PCl₅ and BrF₅.
 - (ii) Describe the change in hybridisation (if any) of Al atom in the following reaction:

$$AlCl_3 + Cl^- \longrightarrow AlCl_4^-$$

- 24. (i) Explain why $\Delta_i H_1$ of Na is lower than that of Mg but $\Delta_i H_2$ of Na is higher than that of Mg.
 - (ii) The first, second and third ionization enthalpies of an element *E* are 419, 3069 and 4400 kJ mol⁻¹. To which group of the periodic table does E belong?
- 25. Ionisation enthalpies of elements of second period are given below:

Ionisation enthalpy/kcal mol⁻¹: 520, 801, 899, 1086, 1314, 1402, 1681, 2080.

Match the correct enthalpy with the elements and complete the graph given in figure.



OR

Which elements have the following electronic configuration?

- (ii) [Ar] $4s^2 3d^{10} 4p^1$ (iv) [Xe] $6s^2 5d^1 4f^7$ (i) $1s^2 2s^2 2p^5$ (iii) [Xe] 6s² [Ar] $4s^1 3d^{10}$ (v)
- The H-O-H bond angle in the water 26. (i) molecule is 105°. The H-O bond distance is

0.94 Å. The dipole moment of the molecule is 1.85 D. Calculate the charge on oxygen atom.

(ii) In SF_4 molecule, the lone pair of electrons occupies an equatorial position in the overall trigonal bipyramidal arrangement in preference to an axial position. Why?

OR

Discuss the shapes of following molecules using VSEPR model : BeCl₂, BCl₃, SiCl₄, AsF₅, H₂S

- 27. (i) Explain why the chemcial reactivity increases in the order Li < Na < K < Rb < Cs in group 1 but decreases in the order F > Cl > Br > I in group 17.
 - (ii) Arrange the given elements in the correct order of their chemical reactivities. F, Cl, O and N?
 - (iii) Arrange HClO₄, HClO₂, HClO and HClO₃ in order of acidic nature.

- (i) Arrange the elements Na, Mg, K, Cs, Al and B in order of decreasing metallic character. Explain briefly.
- (ii) Which of the following atoms / ions are isoelectronic? Al³⁺, F, Cl⁻, O²⁻, Na, Mg²⁺

Arrange the isoelectronic ions in decreasing order of their sizes.

(iii) Is the second electron gain enthalpy of O expected to be positive, more negative or less negative than the first?

SOLUTIONS

Due to same valence shell configuration. 1.

'X' has four valence electrons and belongs to 3rd 2. period hence, it is silicon with atomic number 14.



4. MgO has higher negative value of lattice enthalpy because both Mg^{2+} and O^{2-} have two units of charges, hence greater attractive forces between the ions.

5. The outermost electronic configuration of element $(_{114}Z)$ is [Rn] $5f^{14} 6d^{10}7s^27p^2$. It has n = 7, so period $\rightarrow 7$ It belongs to *p*-block so, group number = 10 + 4 = 14.

6. In solid state of NaCl, Na⁺ and Cl⁻ ions occupy fixed positions in the crystal lattice and there are strong electrostatic forces of attraction between the ions and hence, ions are unable to move under the influence of external EMF and therefore, it does not conduct electricity.

7. A cation is smaller than its parent atom because it has fewer electrons while its nuclear charge remains the same. The size of an anion will be larger than that of the parent atom because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge.

The C—O bond length in CO_2 is in between the 8. C = O and $C \equiv O$ lengths. This suggest that the actual structure of CO₂ is a resonance hybrid of the canonical forms containing double and triple bonds between C and O.

$$\ddot{\mathbf{O}} = \mathbf{C} = \ddot{\mathbf{O}} \longleftrightarrow \dot{\mathbf{O}} \equiv \mathbf{C} - \ddot{\ddot{\mathbf{O}}} \longleftrightarrow \ddot{\mathbf{O}} = \mathbf{C} \equiv \ddot{\mathbf{O}}$$

For tetrahedral geometry, the bond angle is 109°28' 9. but for square planar geometry, the bond angle is 90°. If CH₄ molecule is square planar, bond angle would be 90° and there would be more repulsion between bond pairs, resulting in less stability. Therefore, CH₄ is not square planar.

OR

In NH₃ and H₂O, the central atoms N and O both have four pairs of electrons. In NH₃, there is only one lone pair but H₂O has two lone pairs of electrons. As *lp-lp* repulsion is more than *lp-bp* thereby, decreasing tetrahedral angle to 104.5° in HOH than in case of ammonia where the HNH bond angle is 107°.

10. (i) Fluorine (ii) Magnesium (iii) Oxygen (iv) Group 17 (Halogens) : F, Cl – Non metals and gases Br - Non metal and liquid I – Shows metallic lustre

11. According to the definition of transition metals, the element should have incomplete penultimate (n - 1)d shell. But few d-block elements have completely filled penultimate shell, these are not considered as transition metals, e.g., $Zn(3d^{10} 4s^2)$, $Cd(4d^{10}, 5s^2)$ and $Hg(5d^{10} 6s^2)$.

12. Electron gain enthalpy generally becomes more negative across a period as we move from left to right while becomes less negative down the group. However, adding an electron to the 2p-orbital leads to greater repulsion than adding an electron to the larger 3p-orbital. Hence, the element with most negative electron gain enthalpy is chlorine, the one with the least negative electron gain enthalpy is phosphorus.



13. (i) N has 5 electrons in its valence shell and obtains 3 from three H atoms and thus attains a total of 8 electrons, *i.e.*, 4 electron pairs.

(ii) P has 5 electrons in its valence shell and gets 3 from three Cl atoms, thus attaining a total of 8 electrons, *i.e.*, 4 electron pairs.

(iii) C has 4 electrons in its valence shell, gets four from the O atoms so attains total of 8 electrons, *i.e.*, 4 pairs of electrons.

(iv) N has 5 electrons in its valence shell, obtains 4 from the four H atoms and loses 1 due to positive charge, thus attaining 9 - 1 = 8, *i.e.*, 4 pairs of electrons.

(v) P has 5 electrons in its valence shell and gets 5 from five Cl atoms, thus attaining total of 10 electrons *i.e.*, 5 electron pairs.

(vi) S has 6 electrons in its valence shell and gets 2 from two H atoms, thus attaining total of 8 electrons *i.e.*, 4 electron pairs.

14. (i) F has more negative electron gain enthalpy than O due to smaller size, higher nuclear charge and greater possibility of attaining the nearest noble gas configuration by gaining one electron.

(ii) Cl has more negative electron gain enthalpy because in F the incoming electron is added to the smaller n = 2quantum level and suffers significant repulsion from the other electrons present in this level. In Cl, the added electron goes to n = 3 quantum level and occupies a larger region of space and electron-electron repulsion experienced is far less.

(iii) O has higher electron gain enthalpy than N as N has less tendency to accept electron due to its stable half filled configuration.

15. (i) Lewis structure of CH₃COOH:

$$H = \frac{H}{C} = C$$

$$H = \frac{G}{C} = C$$

$$H = \frac{G}{C} = \frac{G}{C}$$

$$H = \frac{G}{C} = \frac{G}{C}$$
Number of σ -bonds = 1
Number of lone pairs of electrons = 4
(ii) (a) Lewis structure of IF₅:

$$F = \frac{F}{F} = F$$

The valence shell of the central atom, *i.e.*, I in IF₅ has 6 pairs of electrons. Hence, state of hybridisation is sp^3d^2 . Out of these 6 pairs, five are bond pairs and one is lone pair of electrons. Therefore, the shape is square pyramidal.



(b) Lewis structure of CO_2 :

$$\ddot{\Omega} = \frac{\pi}{\sigma} C = \frac{\pi}{\sigma} \ddot{\Omega}$$

The central atom carbon has 4 pairs of electrons but we shall count them as 2 pairs because π -electrons do not take part in hybridisation. Therefore, hybridisation is *sp* and shape of the molecule is linear.

16. (i) A qualitative measure of the ability of an atom in a chemical compound to attract shared electrons towards itself is called electronegativity.

	Electron gain enthalpy	Electronegativity
1.	It provides a measure of the ease with which an atom adds an electron to form an anion.	It is a qualitative measure of the ability of an atom in a chemical compound to attract shared electrons to itself.
2.	It has an absolute value.	It is not a measurable quantity.
3.	Its periodicity is not regular in a period or in a group.	The periodicity is regular in a period but not so regular in a group.
4.	Its units are eV/atom or kJ/mole.	It has no units but is merely a number.





17. Consider two factors : (i) the attraction of electrons towards the nucleus and (ii) the repulsion of electrons from each other. The effective nuclear charge experienced by a valence electron in an atom will be less than the actual charge on the nucleus because of shielding or screening of the valence electron from the nucleus by the intervening core electrons. As we descend the group, the outermost electron being increasingly farther from the nucleus, there is an increased shielding of the nuclear charge by the electrons in the inner levels. The increase in shielding outweighs the increasing nuclear charge and the removal of the outermost electron requires less energy down a group.

OR

(i) In beryllium, the electron removed during the ionization is an *s*-electron whereas the electron removed during ionization of boron is a *p*-electron. The



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CHEMISTRY TODAY | AUGUST '18 35

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penetration of a 2s-electron to the nucleus is more than that of a 2*p*-electron therefore, it is easier to remove the 2p-electron from boron as compared to the removal of a 2s-electron from beryllium. Thus, boron has a smaller first ionization enthalpy than beryllium.

(ii) O has lower ionisation energy than N because N $(1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1)$ has extra stable electronic configuration then O $(1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1)$. O has lower ionisation energy than F because O has larger size than F.

18. (i) The molecule BeH_2 is linear (H-Be-H). The Be-H bond moments are equal and opposite and hence cancel out. Therefore, BeH2 is nonpolar (zero dipole moment).

(ii)
$$C-H < H-Br < H-Cl < Na-I < K-F$$

(iii) If bond were 100% ionic, then

 $\mu_{\text{ionic}} = 1.602 \times 10^{-19} \times 155 \times 10^{-12} = 248.31 \times 10^{-31} \text{ C m}$ $\mu_{\text{obs}} = \frac{\% \text{ ionic character} \times \mu_{\text{ionic}}}{100} = \frac{75 \times 248.31 \times 10^{-31}}{100}$ $= 1.86 \times 10^{-29} \text{ C m}$

19. The molecular orbital description and bond order of these species are as follows:

$$O_{2} = KK(\sigma 2s)^{2} (\sigma^{2}2s)^{2} (\sigma 2p_{z})^{2} (\pi 2p_{x})^{2} (\pi 2p_{y})^{2} (\pi^{*}2p_{x})^{1}$$

$$(\pi^{*}2p_{y})^{1}; BO = 2$$

$$O_{2}^{+} = KK(\sigma 2s)^{2} (\sigma^{*}2s)^{2} (\sigma 2p_{z})^{2} (\pi 2p_{x})^{2} (\pi 2p_{y})^{2} (\pi^{*}2p_{x})^{1};$$

$$BO = 2.5$$

$$O_{2}^{-} = KK(\sigma 2s)^{2} (\sigma^{*}2s)^{2} (\sigma 2p_{z})^{2} (\pi 2p_{x})^{2} (\pi 2p_{y})^{2} (\pi^{*}2p_{x})^{2}$$

$$(\pi^{*}2p_{y})^{1}; BO = 1.5$$

$$O_{2}^{2-} = KK(\sigma 2s)^{2} (\sigma^{*}2s)^{2} (\sigma 2p_{z})^{2} (\pi 2p_{x})^{2} (\pi 2p_{y})^{2} (\pi^{*}2p_{x})^{2}$$

$$(\pi^{*}2p_{y})^{2}; BO = 1$$

Therefore, relative stability is given as follows: $O_2^+ > O_2 > O_2^- > O_2^{2-}$

O₂ has two unpaired electrons = Paramagnetic

 O_2^+ has one unpaired electron = Paramagnetic O_2^- has one unpaired electron = Paramagnetic O_2^{2-} has no unpaired electron = Diamagnetic

20. The addition of an electron to a neutral atom is an exothermic process.

 $F + e^- \longrightarrow F^- + energy$ $O + e^- \longrightarrow O^- + energy$

...(i) The addition of second electron to a monovalent anion,

O⁻ is difficult because both have the same charge and experience a lot of repulsion. Thus, the addition of an electron to O⁻ requires energy to overcome the force of repulsion.

 $O^- + e^- + energy \longrightarrow O^{2-}$...(ii) The energy absorbed in (ii) step is more than the energy released in the (i) step. Hence, the formation of O^2 from O is endothermic in nature.

36 CHEMISTRY TODAY | AUGUST '18

21. (i) Carbon has highest first ionisation enthalpy. Ionisation enthalpy increases across a period and

decreases down the group. (ii) Carbon has most negative electron gain enthalpy as

electron gain enthalpy increases across a period (due to more effective nuclear charge) and decreases down the group (due to larger size).

(iii) Aluminium has the most metallic character.

Metallic character increases down the group and decreases in a period. Hence, the order is : C < Si < B < Al.

22. (i) Be(Z = 4) atom has 4 electrons. The molecule Be₂ would have 8 electrons and MO configuration would be $(\sigma_{1s})^{2} (\sigma_{1s})^{2} (\sigma_{2s})^{2} (\sigma_{2s})^{2}$

Bond order = 1/2(4 - 4) = 0

As the bond order is zero, Be₂ molecule does not exist.

(ii) An orbital is pictorial representation of wave function. The value of wave function can be positive or negative. Plus and minus signs have nothing to do with electric charges, it simply refers to the sign of the wave function.

(iii) Both N and F atoms are small in size and their electron density is high. Both N and F repel the bond pair and as a result N-F bond length is larger than the sum of the atomic radii of N and F atoms.



(ii) Electronic configuration of Al (Z = 13) in excited state is $1s^2 2s^2 2p^6 3s^1 3p_x^1 3p_y^1$. In AlCl₃, it undergoes sp^2 hybridisation to give planar triangular structure. In the formation of AlCl⁻, the empty p_z -orbital is also involved and the hybridisation changes to sp^3 , giving AlCl₄⁻ a tetrahedral shape.

24. (i) The ionization steps can be shown as follows :

$$\begin{array}{c} \operatorname{Na}_{(g)} \xrightarrow{\Delta_{i}H_{1}} \operatorname{Na}_{(g)}^{+} \xrightarrow{\Delta_{i}H_{2}} \operatorname{Na}_{(g)}^{2+} \\ \operatorname{[Ne]} 3s^{1} \qquad \operatorname{[Ne]} \\ \operatorname{Mg}_{(g)} \xrightarrow{\Delta_{i}H_{1}} \operatorname{Mg}_{(g)}^{+} \xrightarrow{\Delta_{i}H_{2}} \operatorname{Mg}_{(g)}^{2+} \\ \operatorname{[Ne]} 3s^{2} \qquad \operatorname{[Ne]} 3s^{1} \qquad \operatorname{[Ne]} \end{array}$$

It is easier to take out an electron from an incomplete 3s-orbitals of Na than from the filled 3s-orbital of Mg. So, $\Delta_i H_1$ of Na < $\Delta_i H_1$ of Mg.

However, it is more difficult to take out an electron from the noble gas(Ne) configuration of Na⁺ than from the incomplete 3s-orbital of Mg⁺.

So, $\Delta_i H_2$ of Na > $\Delta_i H_2$ of Mg.
(ii) The large gap between the first and the second ionisation enthalpies suggests that the element has the configuration [noble gas] ns^1 . Thus, element belongs to group 1 of the periodic table.

25. We know that as we move from left to right across a period, the ionisation enthalpy keeps on increasing due to increased nuclear charge and simultaneous decrease in atomic radius. However, there are some exceptions also.

(i) In spite of increased nuclear charge, the first ionisation enthalpy of B is lower than that of Be. This is due to the reason that in case of Be, the outermost electron lies in the 2*s*-orbitals but in case of B, it is present in a 2*p*-orbital. Since, the electrons in 2*s*-orbital are more tightly held by the nucleus than those present in 2*p*-orbital, therefore, ionisation enthalpy of B is lower than that of Be.

(ii) The first ionisation enthalphy of N is higher than that of O though the nuclear charge of O is higher than that of N. This is due to reason that in case of N, the electron is to be removed from a more stable exactly half-filled electronic configuration $(1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1)$ but in case of O $(1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1)$, it is not so. Therefore, the first ionisation enthalpy of N is higher than that of O. The symbols of elements along with their ionisation enthalpy are given in the graph.





(i) The outer electronic configuration of $1s^2 2s^2 2p^5$ is $2s^2 2p^5$. Therefore, this element is a *p*-block element and belongs to the second period and group 17. Thus, the element is fluorine, F.

(ii) The outer electronic configuration of [Ar] $4s^2$ $3d^{10} 4p^1$ is $4s^2 4p^1$, therefore, it is a *p*-block element. It belongs to the fourth period and group 13. Therefore, the element is gallium, Ga.

(iii) The outer electronic configuration of $[Xe] 6s^2$ is $6s^2$, therefore, it is a *s*-block element. It belongs to the sixth period and group 2 of the periodic table. Therefore, the element is barium, Ba.

(iv) In the electronic configuration [Xe] $6s^2 5d^1 4f^7$ the electrons add to 4f-shell, therefore it is a *f*-block element and belongs to the sixth period and third group. Thus, the element is gadolinium, Gd.

(v) The outer electronic configuration of [Ar] $4s^1 3d^{10}$ is $4s^1 3d^{10}$, therefore, it is *d*-block element and belongs to the fourth period and group 11. Thus, the element is copper, Cu.

26. (i) Since H_2O has two vectors of O—H bond acting at 105°, the dipole moment of H_2O , *i.e.*, μ_{H_2O} , is as follows:



$$\mu_{\rm H_2O} = \sqrt{\mu_{\rm O-H}^2 + \mu_{\rm O-H}^2 + 2\mu^2 \cos(105^\circ)}$$

:.
$$1.85 = \sqrt{2a^2(1 + \cos 105^\circ)}$$

Presuming that dipole moment of O—H bonds is 'a'. \therefore (1.85)² = 2a²(1 - 0.2588)

- *a*, *i.e.*, $\mu_{H-O} = 1.52$ debye = 1.52×10^{-18} esu cm
- But μ_{H-O} = Charge (δ) × d \therefore 1.52 × 10⁻¹⁸ esu cm = δ × (0.94 × 10⁻⁸ cm)

$$\therefore \quad \delta = 1.617 \times 10^{-10} \text{ esu}$$

Since O-atom acquires 2 δ charge, one δ charge from each bond, therefore,

charge on O-atom = $2 \times 1.617 \times 10^{-10} = 3.23 \times 10^{-10}$ esu cm



In figure (a) the lone pair of electrons is on axial position which has 3 lp-bp repulsions at 90°. In figure (b) the lone pair is on equatorial position and there are only two lp-bp repulsions. Hence in (b) lesser repulsions occur and hence figure (b) has a more stable arrangement than figure (a). Figure (b) results distorted tetrahedron or folded square or see saw structure.



mathematics nor natural science.

Albert Einstein



OR

According to VSEPR theory, the shape of a molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) around the central atom. (i) BeCl₂ : The central atom Be has only 2 valence electrons which are bonded to Cl, so there are only 2 bond pairs and no lone pairs. It is of the type AB_2 and hence, the shape is linear.

$$Cl - Be - Cl$$

(ii) BCl_3 : The central atom B has only 3 valence electrons which are bonded with three Cl atoms, so it contains only 3 bond pairs and no lone pair. It is of the type AB_3 and hence, the shape is trigonal planar.

$$Cl - B \begin{pmatrix} Cl \\ C \end{pmatrix}$$

(iii) $SiCl_4$: Similarly, the central atom Si has only 4 bond pairs and no lone pair. It is of the type AB_4 and hence, the shape is tetrahedral.



(iv) AsF_5 : The central atom As has only 5 bond pairs and no lone pair. It is of the type AB_5 and hence, the shape is trigonal bipyramidal.



(v) H_2S : The central atom S has 2 bond pairs and 2 lone pairs. It is of the type AB_2L_2 and hence, the shape is bent or V-shaped.



27. (i) Having the lowest ionisation enthalpies and the lowest electronegativities, the group 1 elements are characterized best as reducing agents and their chemical reactivity will be directly related to their reducing power. As the ionization energy as well as the electronegativity decreases down the group, the reducing power of the elements increases in the same order and so does the chemical reactivity. Thus, in group 1, chemical reactivity follows the order : Li < Na < K < Rb < Cs.

Having the highest negative electron gain enthalpies and the highest electronegativities, the group 17 elements are characterized best as oxidizing agents

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and their chemical reactivity will be directly related to their oxidizing power. As the negative electron gain enthalphy as well as the electronegativity decreases down a group, the oxidizing power of an element also decreases in that order and so does the chemical reactivity. Thus, in group 17 chemical reactivity follows the order : F > Cl > Br > I.

(ii) For electronegative elements reactivity is given as oxidizing power and as electronegativity increase left to right hence, chemical reactivity also increases. Between Cl and O, Cl $(3s^2 3p^5)$ is a more powerful oxidizing agent than O because it has much higher negative electron gain enthalpy than O $(2s^2 2p^4)$, though the electronegativity of Cl (3.0) is lower than that of O (3.5). Therefore, chemical reactivity follows the order : N < O < Cl < F

(iii) On the basis of the oxidation states of Cl in these acids, the order of acidic nature is as follows :

$$HClO < HClO_2 < HClO_3 < HClO_4$$

OR

(i) The trend in the metallic character with reference to the position of these elements in the periodic table should be as shown :



So, the order of decreasing metallic character is Cs > K > Na > Mg > Al > B

(ii) The number of electrons in these atoms or ions are: Ion or atom Al^{3+} F $Cl^ O^{2-}$ Na Mg^{2+} No. of electrons 10 9 18 10 11 10 Thus, Al^{3+} , O^{2-} and Mg^{2+} are isoelectronic ions because all the three ions have ten electrons. Now nuclear charge in Al^{3+} is +13, in O^{2-} is +8 and in Mg^{2+} is +12. With increase in nuclear charge (electrons remain same), size will decrease. Consequently, the size follows the order: $O^{2-} > Mg^{2+} > Al^{3+}$.

(iii) The second electron gain enthalpy of O is expected to be positive. This is because the nuclear charge remaining the same, electron-electron repulsion in the principal quantum shell 2 increases enormously.

۵.

Class XI



hese practice problems enable you to self analyse your extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Performance analysis table given at the end will help you to check your readiness.

Structure of Atom

Time Taken : 60 Min.

Total Marks : 120

NEET / AIIMS

Only One Option Correct Type

- 1. In two elements $_{Z_1}X^{M_1}$ and $_{Z_2}Y^{M_2}$, $M_1 \neq M_2$ and $Z_1 \neq Z_2$ but $M_1 Z_1 = M_2 Z_2$. These elements are (a) isotonic (b) isobaric
 - (c) isotopic (d) isoprotonic.
- 2. Of the given quantum state designations which does not describe an allowed state for an electron in an atom?

(I) $n = 3, l = 2, m_l = -2$ (II) $n = 3, l = 1, m_l = 0$ (III) n = 3, l = 0, $m_l = -1$ (IV) n = 3, l = 2, $m_l = 0$ (V) $n = 3, l = 3, m_l = -2$ (b) III and V (a) I and III

- (c) II and V (d) I and V
- 3. Visible spectrum of hydrogen shows that it exists in two different forms which are based on direction of spin of the
 - (a) molecule of hydrogen
 - (b) nuclei of hydrogen atoms
 - (c) electrons of hydrogen
 - (d) atoms of hydrogen molecule.
- 4. The number of 2*p* electrons having spin quantum number s = -1/2 are

- 5. The electronic configuration of an element is $1s^22s^22p^63s^23p^63d^54s^1$. This represents its
 - (a) excited state (b) ground state
 - (d) cationic form. (c) anionic form

The two electrons have the following sets of quantum numbers :

X: 3, 2, -2, +1/2 and Y: 3, 1, 0, +1/2

- The true statement for *X* and *Y* is
- (a) *X* and *Y* have same energy
- (b) *X* and *Y* represent same electron
- (c) energy of *X* is higher than that of *Y*
- (d) energy of *Y* is higher than that of *X*.
- 7. Which of the following arrangements of electrons is most stable?

(a)
$$\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$$
 (b) $1 \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$
(c) $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \downarrow$ (d) $\uparrow \uparrow \uparrow \uparrow \uparrow \downarrow$

8. For two particles X and Y, \sqrt{V} against de-Broglie wavelengths curves are plotted, where V is the potential on the particles. Which of the following relation is correct about the mass of particles?

(a)
$$m_X = m_Y$$
 (b) $m_X > m_Y$
(c) $m_X < m_Y$ (d) $m_Y \le m_X$

- Uncertainty in the position of an electron 9. (mass = 9.1×10^{-31} kg) moving with a velocity 300 m s^{-1} , accurate upto 0.001% will be
 - (a) 19.3×10^{-2} m (b) 3.76×10^{-2} m
 - (c) 1.93×10^{-2} m (d) 5.84×10^{-2} m
- **10.** Which of the following is not correct for the velocity of electron?

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11. The orbital diagram in which both Pauli's exclusion principle and Hund's rule are violated is

(a)	11/	1⊬ ↑	(b) 🌵	<u> 1/ ↑↑ </u>
(c)	1	$ \downarrow \downarrow $	(d) 🎼	1↓1↓↑

12. For which of the following sets of four quantum numbers, an electron will have the highest energy?

	n	l	m	S
(a)	3	2	1	-1/2
(b)	4	2	-1	+1/2
(c)	4	1	0	+1/2
(d)	5	0	0	-1/2

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.
- **13.** Assertion : $3d_{xy}$, $4d_{xy}$, $5d_{xy}$, all have the same shape *i.e.*, the double dumb-bell. Reason : The size of orbitals are independent of the principal quantum number.
- 14. Assertion : The electronic configuration of nitrogen

	$1s^2$	$2s^2$		2p-	, 	
atom is represented as	11/	11/	1	1	\uparrow	and
not as 1/ 1/ 1/ 1						

Reason : The electronic configuration of the ground state of an atom is the one which has the greatest multiplicity.

15. Assertion : Angular momentum of the electron in the orbit which has four subshell is $2h/\pi$.

Reason: Angular momentum of electron is quantised.

JEE MAIN / ADVANCED

Only One Option Correct Type

16. Light of wavelength λ shines on a metal surface with intensity X, and the metal emits *n* electrons per second of average energy E. What will happen to n and *E* if *X* is doubled?



40 CHEMISTRY TODAY | AUGUST '18

- (a) *n* will be doubled and *E* will become half.
- (b) *n* will remain same and *E* will be doubled.
- (c) Both *n* and *E* will be doubled.
- (d) *n* will be doubled but *E* will remain same.
- 17. Magnetic moment of M^{x+} (Z = 26) is $\sqrt{24}$ B.M. Hence, number of unpaired electrons and value of xrespectively are

(a)
$$4, 2$$
 (b) $2, 4$ (c) $3, 1$ (d) $0, 2$

18. The energies of three different energy levels I, II and III of a certain atom are E, 4E/3 and 2E respectively. A photon of wavelength λ is emitted during a transition from III to I. What will be the wavelength of emission for transition II to I?

(a)
$$\lambda/2$$
 (b) λ (c) 2λ (d) 3λ

19. The frequency of light emitted for the transition n = 4 to n = 2 of He⁺ is equal to the transition in H atom corresponding to which of the following? (a) n = 3 to n = 1(b) n = 2 to n = 1

(c)
$$n = 3$$
 to $n = 2$ (d) $n = 4$ to $n = 3$

More than One Options Correct Type

- 20. In a sample of H-atoms, electrons are de-excited from 4th excited state to ground state. Which is/are correct statement?
 - (a) Total ten lines observed in spectrum.
 - (b) Four lines in UV-region and three lines in visible region observed.
 - (c) One line observed in Brackett series.
 - (d) No line observed in Pfund series.
- **21.** The alpha particle scattering
 - (a) is due to nuclear forces
 - (b) is due to coulomb forces
 - (d) path is hyperbola. (c) path is parabola
- 22. For the given transitions in hydrogen like atoms, select the correct relations.

$$n = 3$$

$$n = 2$$

$$n = 1$$

$$(a) \quad v_3 = v_1 + v_2$$

$$(b) \quad \lambda_3 = \lambda_1 + \lambda_2$$

$$(c) \quad v_3 = \frac{v_1 v_2}{v_1 + v_2}$$

$$(d) \quad \lambda_3 = \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2}$$

- 23. Which of the following statements are correct for an electron that has n = 4 and m = -2?
 - (a) The electron may be in a *p*-orbital.
 - (b) The electron is in the fourth principal electronic shell.
 - (c) The electron may be in a *d*-orbital.
 - (d) The electron must have the spin quantum number = -1/2.

Numerical Value Type

- 24. A dust particle having mass equal to 10^{-11} g, diameter of 10^{-4} cm and velocity 10^{-4} cm sec⁻¹. The error in measurement of velocity is 0.1%. Calculate uncertainty in its position.
- **25.** How many elements would be in the third period of the periodic table if the spin quantum number m_s could have the value -1/2, 0 and +1/2?
- **26.** Photochemical dissociation of oxygen results in the production of two oxygen atoms, one in the ground state and one in the excited state.

$$O_2 \xrightarrow{hv} O + O^*$$

The maximum wavelength (λ) needed for this is 174 nm. If the excitation energy O \rightarrow O^{*} is 3.15×10^{-19} J. How much energy in kJ mol⁻¹ is needed for the dissociation of one mole of oxygen into normal atoms in ground state?

Comprehension Type

The set of an electron is described by a set of four quantum numbers.

- (i) Principal quantum number (*n*) gives the size of the shell and the energy of the electron.
- (ii) Azimuthal quantum number or subsidiary quantum number (*l*) gives the subshell and shape of the orbital for the electron.
- (iii) Magnetic quantum number (*m*) determines the preferred orientations of orbitals in space.
- (iv) Spin quantum number (*s*) represents the spin of the electron.
- 27. Which combination of quantum numbers *n*, *l*, *m* and *s* for the electron in an atom does not provide a permissible solution of the wave equation?
 - (a) 3, 2, -2, +1/2 (b) 3, 3, 1, -1/2
 - (c) 3, 2, 1, +1/2 (d) 3, 1, 1, -1/2
- **28.** In a multi-electron atom, which of the following orbitals, described by the three quantum numbers, will have the same energy in the absence of magnetic field and electric fields?

(i) $n = 1, l = 0, m$	= 0 (ii)	n = 2, l = 0, m = 0
(iii) $n = 3, l = 1, m$	= 1 (iv)	n = 3, l = 2, m = 1
(v) $n = 3, l = 2, m$	= 0	
(a) (i) and (ii)	(b)	(ii) and (iii)
(c) (iii) and (iv)	(d)	(iv) and (v)

Matrix Match Type

29. Match Column I with Column II and choose the correct answer using the codes given below :

	Column I			Column II
А.	$n_1 \rightarrow n_\infty$ in	H-atom	p.	Visible region
B.	$n_4 \rightarrow n_2$ in	He^+ ion	q.	Energy numerically
				equal to Rydberg energy
C.	$n_{\infty} \rightarrow n_1$ in	hHe ⁺ ion	r.	Called ionisation energy
D.	$n_4 \rightarrow n_2$ in	H-atom	s.	Ultraviolet
Coc	les :			
	Α	В	С	D
(a)	p, q, r	q, s	p, q	p, s
(b)	q, r	S	q, r	p, q, s
(c)	q, r, s	s	q, s	р
(d)	p, q, s	q, s	р	q, r

30. Match Column I with Column II and choose the correct answer using the codes given below :

	Column I		C	Column II
А.	Number of or	bitals in the	p.	2(2l+1)
B.	Maximum nu	mber of	q.	п
	electrons in a	subshell	r.	2l + 1
C.	Number of su	bshell in <i>n</i> th	s.	n^2
P	shell	1		
D.	Number of or subshell	bitals in a		
Codes	:			
Α	В	С	D	
(a) p	q	r	S	
(b) s	р	q	r	
(c) q	r	S	р	
(d) r	S	р	q	

41

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UNIT - 2 : Electrochemisty | Chemical Kinetics | Surface Chemistry

ELECTROCHEMISTRY

ELECTROCHEMICAL CELL

(Converts chemical energy into electrical energy in a redox reaction or vice-versa)

	+	\
	Galvanic cell	Electrolytic cell
Anode	Oxidation, negative	Oxidation, positive
	(–) terminal	(+) terminal
Cathode	Reduction, positive	Reduction, negative
	(+) terminal	(–) terminal

Electrode Potential

• It is defined as the tendency of an electrode to gain or lose electrons when it is in contact with the solution of its own ions.

Nernst Equation

$$M_{(aq)}^{n+} + ne^{-} \longrightarrow M_{(s)}$$

 $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \frac{[M_{(s)}]}{[M_{(aq)}^{n+}]}$

For pure solid or liquid or gas at 1 atm pressure, the molar concentration is taken as unity; [M] = 1

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303RT}{nF} \log \frac{1}{[M_{(aq)}^{n+}]}$$
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M_{(aq)}^{n+}]}$$



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- The electrode potential difference between the two half-cells is known as electromotive force (EMF) of the cell or cell potential or cell voltage.
- EMF can be calculated from the values of electrode potentials of the two half-cells constituting the cell using following methods :
 - $\triangleright E_{cell}^{o} = E_{ox}^{o} (anode) + E_{red}^{o} (cathode)$
 - When only reduction potential is taken into account,

 $E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} (\text{cathode}) - E_{\text{red}}^{\circ} (\text{anode}) = E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ}$

When only oxidation potential is taken into account,

 $E_{\text{cell}}^{\circ} = E_{\text{ox}}^{\circ} (\text{anode}) - E_{\text{ox}}^{\circ} (\text{cathode})$

Applications

• To calculate electrode potential of a cell : $aA + bB \xrightarrow{ne^-} xX + yY$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[X]^{x} [Y]^{y}}{[x]^{a} [D]^{b}}$$

- $n \quad [A]^{a} [B]^{c}$ To calculate equilibrium constant : At equilibrium, $E_{cell} = 0$ $E_{cell}^{\circ} = \frac{0.0591}{n} \log K_{c}$ at 298 K
- Relation between electrochemical cell and Gibbs energy

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}, \Delta G^{\circ} = -2.303 RT \log K_{c}$$

CONDUCTANCE

The reciprocal of the electric resistance is called the conductance. It is usually represented by *G*. Thus, G = 1/R.

Property	Specific conductance	Equivalent conductance	Molar conductance
Definition	Reciprocal of specific resistance or conductance of solution of	Conductance produced by all the ions of 1 g equivalent	Conduction produced by all the ions of 1 mol electrolyte
	1 cm length and 1 cm ² area of cross-section.	electrolyte in a given solution.	in a given solution.
Representation	к (kappa)	Λ_{eq} (lambda)	Λ_m (lambda)
Formula	$\kappa = \frac{1}{\rho} = \frac{l}{Ra} = G\frac{l}{a}$	$\Lambda_{eq} = \kappa \times V = \kappa \times \frac{1000}{\text{Normality}}$	$\Lambda_m = \kappa \times V = \kappa \times \frac{1000}{\text{Molarity}}$
Units	$ohm^{-1} cm^{-1}$	$ohm^{-1} cm^2 eq^{-1}$	$ohm^{-1} cm^2 mol^{-1}$
SI units	S m ⁻¹	$\mathrm{S} \mathrm{m}^2 \mathrm{eq}^{-1}$	S m ² mol ⁻¹

Variation of G, κ , Λ_m and Λ_{eq} with dilution :

- On dilution, as no. of ions increases, conductance (*G*) increases.
- On dilution as no. of ions per cm³ decreases, specific conductance (κ) decreases.
- On dilution, though specific conductance decreases but volume (V) increases much more hence, equivalent conductance (Λ_{eq}) or molar conductance (Λ_m) increases.
- When concentration approaches zero *i.e.*, at infinite dilution, the molar conductivity is known as limiting molar conductivity (Λ_m°).

Variation of molar conductance with concentration (C) :

• For strong electrolytes, Λ_m increases slowly with dilution and can be represented by the equation : $\Lambda_m = \Lambda_m^\circ - AC^{1/2}$ (Debye—Huckel Onsager equation)

Plot of Λ_m against $C^{1/2}$ is a straight line with intercept equal to Λ_m° and slope equal to '-A'.



Thus, Λ_m^c decreases linearly with \sqrt{C} , when C = 0, $\Lambda_m^c = \Lambda_m^\circ$ and Λ_m° can be determined experimentally.

• For weak electrolytes, Λ_m^c increases as *C* decreases but does not reach a constant value even at infinite dilution. Hence, there Λ_m° cannot be determined experimentally.

Kohlrausch's Law

The limiting molar conductivity of an electrolyte is the sum of the limiting ionic conductivities of the cation and the anion each multiplied with the number of ions present in one formula unit of the electrolyte.

$$\Lambda_{m}^{\circ} = \lambda_{+}^{\circ} + \lambda_{-}^{\circ}$$

 λ°_{+} and λ°_{-} are called ionic conductivities of cation and anion at infinite dilution respectively.

$$A_x B_y \longrightarrow x A^{y^+} + y B^{x^-}; \ \Lambda_m^\circ = x \lambda_A^\circ y^+ + y \lambda_B^\circ x^-$$

Applications

• Calculation of molar conductivity of weak electrolytes at infinite dilution :

$$\Lambda_{m (CH_{3}COOH)}^{*} = \Lambda_{CH_{3}COO^{-}}^{*} + \Lambda_{H^{+}}^{*}$$

• The above equation can be obtained as $\Lambda_{m (CH_3COOH)}^{\circ}$ = $\Lambda_{m (CH_3COONa)}^{\circ} + \Lambda_{m (HCl)}^{\circ} - \Lambda_{m (NaCl)}^{\circ}$

$$=\lambda_{CH_{3}COO^{-}}^{\circ}+\lambda_{Na^{+}}^{\circ}+\lambda_{H^{+}}^{\circ}+\lambda_{Cl^{-}}^{\circ}-\lambda_{Na^{+}}^{\circ}-\lambda_{Cl}^{\circ}$$

Calculation of degree of dissociation : Degree of dissociation (α) = $\frac{\Lambda_m^c}{m}$

- Degree of dissociation (α) = $\frac{\Lambda_m^c}{\Lambda_m^\circ}$
- Calculation of dissociation constant of a weak electrolyte :

Dissociation constant
$$(K_c) = \frac{C\alpha^2}{1-\alpha}$$

• Calculation of solubility of a sparingly soluble salt solutions are considered saturated at infinite dilution so, $\Lambda_m = \Lambda_m^\circ$ and molarity = solubility.

Thus,
$$\Lambda_m^{\circ} = \frac{\kappa \times 1000}{\text{molarity}}$$

or Solubility (mol⁻¹) = $\frac{\kappa \times 1000}{\Lambda_m^{\circ}}$



ELECTROLYSIS

It is the process of decomposition of an electrolyte by passing electricity through its aqueous solution or molten state.

• Faraday's first law of electrolysis : The amount of chemical reaction which occurs at any electrode during electrolysis is proportional to the quantity of electricity passed through the electrolyte.

 $w \propto Q$ or $w = ZQ = Z \times I \times t$

where, Z is electrochemical equivalent of the substance deposited.

 $Z = \frac{\text{Eq. wt. of substance}}{96500}$.

• Faraday's second law of electrolysis : The amounts of different substances liberated by the

same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights.

 $\frac{w_1}{w_2} = \frac{E_1}{E_2}$ where *E* is the equivalent weight.

Some Commercial Cells

- **Primary cells :** Cells once exhausted cannot be used again *e.g.*, dry cell and mercury cell.
- **Secondary cells :** Rechargeable cells which can be used again and again *e.g.*, nickel-cadmium storage cell and lead storage battery.
- Fuel cells : Cells which can convert the energy of combustion of fuels such as H₂, CO, CH₄ etc., into electrical energy *e.g.*, H₂ O₂ fuel cell.

CHEMICAL KINETICS

RATE OF CHEMICAL REACTION

• The rate of reaction is the change in the concentration of any one of the reactants or products per unit time.





Negative sign shows decrease in concentration with time and positive sign shows increase in concentration with time.

• Units :

$$Rate = \frac{Concentration}{Time} = \frac{mol/litre}{sec}$$
$$= mol litre^{-1}sec^{-1}$$



RATE LAW AND RATE CONSTANT (LAW OF MASS ACTION)

The rate of reaction is proportional to the product of effective concentrations of the reacting species, each raised to a power which is equal to the corresponding stoichiometric number of the molecules appearing in the chemical reaction.

$$aA + bB \longrightarrow cC + dD$$

$$r \propto [A]^a [B]^b$$
 or $r = k[A]^a [B]^b$

k is the constant of proportionality.

Rate of reaction at unit concentration of reactants is called rate constant.

ORDER AND **MOLECULARITY** OF THE REACTION

- The sum of powers of the concentration of the reactants in the rate law expression is called the order of reaction. For the rate law equation, Rate = $k[A]^{x}[B]^{y}$ x + y gives the overall order of a reaction. Order of a reaction can be 0, 1, 2, 3 and even a fraction.
- The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

Order	Rate law	Integrated rate law	Half-life	Unit of rate constant	Graph
0	Rate = $k[A]^0$	$[A]_t = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$	$mol L^{-1} s^{-1}$	[A] vs t; slope = -k
1	Rate = $k[A]^1$	$\ln[A]_t = -kt + \ln[A]_0$	$t_{1/2} = 0.693/k$	s ⁻¹	$\ln[A]$ <i>vs t</i> ; slope = $-k$
2	Rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$t_{1/2} = 1/k \ [A]_0$	$L \text{ mol}^{-1} \text{ s}^{-1}$	1/[A] <i>vs t</i> ; slope = k
n	Rate = $k[A]^n$	$(n-1)kt = \frac{1}{[A]^{n-1}} - \frac{1}{[A_0]^{n-1}}$	$t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}}$	$(mol L^{-1})^{1-n} s^{-1}$	$\frac{1}{\left[A\right]^{n-1}} \text{ vs } t;$ slope = k

FOR REACTIONS OF DIFFERENT ORDERS

Some typical linear plots for reactions of different orders :



TEMPERATURE DEPENDENCE OF THE RATE OF A **REACTION**:

For a chemical reaction with rise in temperature by 10 °C, the rate constant is nearly doubled.

Arrhenius equation

 $k = Ae^{-E_a/RT}$ where A is pre-exponential factor (Arrhenius factor or frequency factor), E_a is activation energy and $e^{-E_a/RT}$ corresponds to the fraction of molecules that have kinetic energy equal to or greater than E_a .

$$\ln k = -\frac{E_a}{RT} + \ln A \text{ or } \log k = -\frac{E_a}{2.303RT} + \log A$$

The plot of log k vs 1/T gives a straight line with slope

$$= -\frac{E_a}{2.303 R} \text{ and intercept} = \log A$$
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

where, k_1 and k_2 are the values of rate constant at temperatures T_1 and T_2 respectively.

COLLISION THEORY

Reactions occur when molecules collide with appropriate orientation and sufficient energy, not



iranchembook.ir/edu CONCEPT MAP

GENERAL ORGANIC CHEMISTRY

Nomenclature

Rules for nomenclature of branched chain alkanes

- First of all, the longest carbon chain in the molecule is identified.
- The numbering is done in such a way that the branched carbon atoms get the lowest possible numbers.
- If the two substituents are found in equivalent positions, the lower number is given to the one coming first in the alphabetical listing.
- While writing the trivial names of substituents' in alphabetical order, the prefixes *iso*-and *neo*-are considered to be the part of the fundamental name of alkyl group. The prefixes *sec*- and *tert*- are not considered to be the part of the fundamental name.

Rules for nomenclature of organic compounds with functional groups

- The longest chain of carbon atoms containing the functional group is numbered in such a way that the functional group is attached at the carbon atom possessing lowest possible number in the chain.
- In the case of polyfunctional compounds, one of the functional groups is chosen as the principal functional group and the compound is then named on that basis.
- The order of decreasing priority for some functional groups is :
 -COOH, -SO₃H, -COOR (R = all grop , -COCl, -CONH₂, -CN₇-C HO,> C=O,-O H₇-N H₂> C=C<₇C ≡ C-

 $\begin{array}{c} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ CH_3 - CH - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3 \\ I & I \\ CH_3 & CH_2 - CH_3 \\ 6 - Ethyl - 2 - methyl nonane \end{array}$

$$\begin{array}{c}1&2&3&4&5&6&7&8\\ CH_{3}-CH_{2}-CH-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{3}\\ I&I\\ OH&CH_{3}\\ 6-Methyloctan-3-ol\end{array}$$

$$\begin{array}{c} O\\ \parallel\\ CH_3-C-CH_2-CH_2-CH_2-COOH\\ 6 & 5 & 4 & 3 & 2 & 1\\ & & 5-Oxohexanoic acid \end{array}$$

 Different compounds have same molecular formula but different structural formula.
 Compounds have different IUPAC name.

- Compounds have different IUPAC name.
 - Chain(Nuclear/Skeleton) : Difference in the nature of the carbon chain.
 - Position : Difference in the position of the substituent atom/group or an unsaturated linkage in the same C-chain.
 - **Ring-chain** : Difference in mode of linkage of C-atoms.
 - Functional : Difference in the nature of functional group.
 - Metamerism : Difference in the nature of alkyl groups attached on either side of the same functional group.
 - Tautomerism : Isomers exist in dynamic equilibrium.





all molecular collisions result successfully in the formation of product.

- For any successful collision :
 - > Particles must collide with sufficient energy > E_a .
 - They need to have correct alignment (collision geometry) to keep E_a as low as possible.
- To account for effective collision, another factor P, called orientation factor or steric factor or probability factor is introduced.

 $k = P Z_{AB} e^{-E_a/RT}$

where, Z_{AB} represents the collision frequency of reactants *A* and *B*.

SURFACE CHEMISTRY

Adsorption

- The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid.
- Spontaneous, exothermic and leads to lowering of entropy.

Types of Adsorption

Physisorption

- Molecules are held by weak van der Waals' forces.
- Low heat of adsorption and non specific.
- No compound is formed.
 - Decreases with increase in temperature.
 - Forms multimolecular layer and is reversible.

Chemisorption

- Molecules are held by strong chemical bonds.
- High heat of adsorption and specific.
- Surface compounds are formed.
- Increases with increase in temperature.
- Forms unimolecular layer and is irreversible.

Adsorption Isotherms





$\frac{x}{m} = k.P^{1/n} (n > 1)$	$\frac{P}{(x/m)} = \frac{1}{k'} + \left(\frac{k}{k'}\right)P$
$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$	$\frac{x}{m} = \frac{k'P}{1+kP}$
Slope = $1/n$ 1 1 1 1 1 1 1 1	$ \begin{array}{c c} & B \\ & B \\ & Slope = \frac{k}{k'} \\ & A \\ & Intercept = \frac{1}{k'} \\ & 0 \\ & Pressure (P) \longrightarrow \end{array} $
The factor $1/n$ can have values between 0 and 1.	When pressure is very high then $1 + kP \approx kP$ $\Rightarrow \frac{x}{m} = \frac{k'P}{kP} = \text{constant}$
When $1/n = 0$, x/m = constant which shows that adsorption is independent of pressure.	When pressure is very high then $1 + kP \approx 1$ $\Rightarrow x/m = k'P$
When $1/n = 1$, $x/m = kP$, the adsorption varies directly with pressure.	When pressure is moderate then $x/m = kP^{1/n}$, $1/n$ lies between 0 and 1.

CATALYSIS

- The phenomenon of enhancing the rate of a chemical reaction by using a catalyst.
- Activity : Capacity to increase the speed of the chemical reaction.
- **Selectivity** : Ability of a catalyst to direct the reaction to yield a particular product.

Homogeneous catalysis : When the reactants and catalyst are in the same phase e.g., oxidation of SO₂ to SO₃ in presence of NO as catalyst (lead chamber process).

Heterogeneous catalysis : When the reactants and catalyst are in different phases e.g., manufacture of NH₃ from N₂ and H₂ using Fe as catalyst (Haber's process).

Autocatalysis : One of the products formed itself acts as a catalyst e.g., titration of oxalic acid with KMnO₄ in presence of dil. H₂SO₄.

Induced catalysis : One reaction influences the rate of other reaction, which does not occur under ordinary conditions e.g., oxidation of sodium arsenite is induced by oxidation of sodium sulphite.

Enzymes

Types of Catalysis

- Bio-chemical catalysts.
- Highly efficient and specific in nature.

Preparation of Colloidal Solutions

- Highly active under optimum temperature and pH.
- Activity increases in the presence of activators and co-enzymes.
- Activity inhibited by inhibitors and poisons.

COLLOIDS

Suspension, colloid and true solution :					
Suspension	Colloid	True solution			
Size : $> 10^{-5}$ cm	10^{-7} to 10^{-5} cm	$< 10^{-7} \text{ cm}$			
Visible with	Visible with	Not visible by			
naked eyes	ultramicroscope	any optical			
		means			
Does not	Diffuses very	Diffuses			
diffuse	slowly	rapidly			
Settles under	Only under	Does not settle			
gravity	centrifugation.				
Heterogeneous	Heterogeneous	Homogeneous			
Opaque	Generally clear	Clear			



are then dispersed in colloidal graphite and ink.



Substances like oil, mercury, sulphur, oxides of metals can be dispersed into colloidal state with the help of ultrasonic waves.

The dispersion of a freshly precipitated material into colloidal solution by the action of an electrolyte in the solution is termed as peptization and electrolyte used is called a peptizing agent.



CHEMISTRY TODAY | AUGUST '18

49

Purification of Colloidal Solutions

Dialysis : It is the process of separating the particles of colloidal dimensions by means of diffusion through a suitable membrane.



Electrodialysis : In this process, electric field is applied during dialysis.

- Ultrafiltration : Separation of colloidal particles from crystalloids by filtration using ultrafilter papers.
- Ultra-centrifugation : In this process, colloidal • particles settle down at the bottom of tube whereas crystalloids remain in the solution.

Important Properties

- Tyndall effect : Scattering of light by the colloidal particles.
- Brownian movement : Continuous zig-zag movement of colloidal particles.
- Coagulation : Settling of colloidal particles.
- Zeta potential : Potential difference between the fixed layer and the diffused layer of opposite charges, also called electrokinetic potential.
- Colloidal particles possesses electrical charge, positive or negative, which are responsible for their stability.

RACTICE

1. If $E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = x_1 V$, $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = x_2 V$, what is the $E_{\rm Fe}^{\rm o}{}^{3+}/{\rm Fe}$?

(a)
$$\frac{2x_1 + x_2}{4}$$
 (b) $\frac{2x_1 + x_2}{3}$
(c) $\frac{2x_1 + x_2}{2}$ (d) $2x_1 + x_2$

- 2. The rate constant, activation energy and Arrhenius parameter of a chemical reaction at 25 °C are $3.0 \times 10^{-4} \text{ s}^{-1}$, 104.4 kJ mol⁻¹ and $6.0 \times 10^{14} \text{ s}^{-1}$ respectively. The value of the rate constant as $T \rightarrow \infty$ is
 - (a) $2.0 \times 10^{18} \text{ s}^{-1}$ (b) $6.0 \times 10^{14} \, \text{s}^{-1}$ (d) $3.6 \times 10^{30} \, \mathrm{s}^{-1}$ (c) infinity
- 3. The rate of a first order reaction is 1.8×10^{-3} mol L^{-1} min⁻¹ when the initial concentration is $0.3 \text{ mol } L^{-1}$. The rate constant is

(a)
$$1 \times 10^{-2} s^{-1}$$
 (b) $1 \times 10^{-4} s^{-1}$
(c) $6 \times 10^{-2} s^{-1}$ (d) $4 \times 10^{-4} s^{-1}$

- **4.** What is the value of 1/n, in Freundlich adsorption isotherm?
 - (a) Between 2 and 4 in all cases
 - (b) Between 0 and 1 in all cases
 - (c) 1 in case of chemisorption
 - (d) 1 in case of physical adsorption

5. Following two half cells form a complete cell which has ΔG° (in kJ) value

- $2H^+ + 1/2 O_2 + 2e^- \rightarrow H_2O; \quad E^\circ = +1.23 V$ $\mathrm{Fe}^{2+} + 2e^- \rightarrow \mathrm{Fe}_{(s)};$ $E^{\circ} = -0.44 \text{ V}$ (a) -122 (b) -222 (c) -322 (d) -422
- 6. Zinc is used to protect iron from rusting. This is because
 - (a) E_{red}^{o} of Zn is greater than that of Fe
 - (b) E_{ox}^{o} of Zn is greater than that of Fe
 - (c) E_{red}° of Zn is nearly equal to that of Fe
 - (d) Zn is cheap.
- 7. Which of the following is not correct?
 - (a) Rate of zero order reaction depends upon initial concentration of reactant.
 - (b) Rate of zero order reaction does not depend upon initial concentration of reactant.
 - (c) $t_{1/2}$ of first order reaction is independent of initial concentration of reactant.
 - (d) $t_{1/2}$ of zero order reaction is dependent of initial concentration of reactant.
- 8. When the concentration of an adsorbate is higher on the surface of adsorbent than in the adjoining bulk, the phenomenon is called
 - (a) chemisorption (b) physisorption
 - (c) positive adsorption (d) negative adsorption.

- 9. If a homogeneous colloid placed in dark is observed in the direction of light, it appears clear and if it is observed from a direction at right angles to the direction of light beam, it appears perfectly dark. This is known as
 - (a) Brownian effect (b) Hardy Schulze effect
 - (c) Einstein effect (d) Tyndall effect.
- **10.** Which of the following relation is correct for zero order reaction?
- (b) $t_{3/4} = 1.5 t_{1/2}$ (a) $t_{3/4} = 2t_{1/2}$ (c) $t_{3/4} = \frac{1}{2} t_{1/2}$ (d) $t_{3/4} = \frac{1}{3}t_{1/2}$ **11.** Li^+ / Li = -3.05 V; Ba^{2+} / Ba = -2.73 V;
 - $Mg^{2+}/Mg = -2.37 V$ The correct order as per reducing power is

(a) Li > Ba > Mg

- (b) $Li^+ > Ba^{2+} > Mg^{2+}$ (d) $Mg^{2+} > Ba^{2+} > Li^+$ (c) Mg > Ba > Li
- **12.** In the sequence of reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$

 $k_3 > k_2 > k_1$, then the rate determining step of the reaction is:

- (a) $A \rightarrow B$ (b) $B \rightarrow C$ (c) $C \rightarrow D$ (d) $A \rightarrow D$
- 13. Which one of the following is wrong about physical adsorption?
 - (a) It involves only van der Waals' forces of attraction.
 - (b) It has low heat of adsorption.
 - (c) It is reversible in nature.
 - (d) It forms a unimolecular layer on the surface of the adsorbent.
- 14. Λ° ClCH₂COONa = 224 ohm⁻¹ cm² g eq⁻¹, Λ° NaCl $= 38.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ g eq}^{-1}, \Lambda^{\circ}\text{HCl} = 203 \text{ ohm}^{-1} \text{ cm}^2$ g eq⁻¹, what is the value of Λ °ClCH₂COOH?
 - (a) $288.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ g eq}^{-1}$ (b) $289.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ g eq}^{-1}$ (c) $388.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ g eq}^{-1}$ (d) $59.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ g eq}^{-1}$
- **15.** Given : $Zn^{2+}/Zn = -0.76$ V, $Mg^{2+}/Mg = -2.37$ V, then the correct statement about the reaction $Zn_{(s)} + MgCl_{2(aq)} \rightarrow$
 - (a) solid zinc dissolves
 - (b) zinc chloride precipitates
 - (c) magnesium chloride precipitates
 - (d) no reaction takes place.
- **16.** The rate law for a reaction between the substances A and B is given by $r = k[A]^n [B]^m$. On doubling the concentration of A and halving the concentration

of *B*, the ratio of the new rate to the earlier rate of reaction will be

(a)
$$\frac{1}{2^{(m+n)}}$$
 (b) $m+n$ (c) $n-m$ (d) $2^{(n-m)}$

- 17. On addition of 1 mL solution of 10% NaCl to 10 mL gold sol in the presence of 0.0250 g of starch, the coagulation is just prevented. Starch has the gold number
 - (a) 0.025 (b) 0.25 (c) 2.5 (d) 25
- **18.** For a cell reaction involving two electron change, the standard EMF of the cell is 0.295 V at 25 °C. The equilibrium constant of the reaction at 25 °C will be (a) 29.5×10^{-2} (b) 10 (d) 2.95×10^{-10} (c) 1×10^{10}
- **19.** If the rate of a reaction at 50 °C is 2.6×10^{-3} mol L^{-1} s⁻¹, then what will be rate of reaction at 80 °C? (Given that the temperature coefficient is 3.) (a) 7.02×10^{-2} (b) 7.025×10^{-3} (c) 7.8×10^{-3} (d) None of these
- **20.** Reactant (*A*) forms two products :
 - $A \xrightarrow{k_1} B$ Activation energy, E_{a_1} $A \xrightarrow{k_2} C$ Activation energy, E_{a_2} If $E_{a_2} = 2E_{a_1}$, then k_1 and k_2 are related as (a) $k_2 = k_1 e^{E_{a_1}/RT}$ (b) $k_2 = k_1 e^{E_{a_2}/RT}$ (c) $k_1 = Ak_2 e^{E_{a_1}/RT}$ (d) $k_1 = 2k_2 e^{E_{a_2}/RT}$
- 21. According to adsorption theory of catalysis, the speed of the reaction increases because
 - (a) the concentration of the reactant molecules at the active centres of the catalyst becomes high due to adsorption
 - (b) in the process of adsorption, the activation energy of the molecules becomes large
 - (c) adsorption produces heat which increases the speed of the reaction
 - (d) adsorption lowers the activation energy of the reaction
- 22. The half cell potential of a hydrogen electrode at pH = 10 will be
 - (b) 0.59V (a) -0.50V
 - (c) 0.059V (d) none of these
- 23. A radioactive element gets spilled over the floor of a room. Its half-life period is 30 days. If the initial activity is 10 times of the permissible value, after how many days it will be safe to enter the room?
 - (a) 1000 days (b) 300 days
 - (c) 10 days (d) 100 days



- 24. Which one of the following is an example for homogeneous catalysis?
 - (a) Manufacture of ammonia by Haber's process
 - (b) Manufacture of sulphuric acid by contact process
 - (c) Hydrogenation of oil
 - (d) Hydrolysis of sucrose in presence of dilute hydrochloric acid
- 25. All colloidal dispersions have
 - (a) very high osmotic pressure
 - (b) low osmotic pressure
 - (c) no osmotic pressure
 - (d) high osmotic pressure.

SOLUTIONS

1. (b):
$$Fe^{2+} + 2e^- \rightarrow Fe$$
; $E_{Fe^{2+}/Fe}^{\circ} = x_1 V$
 $\Delta G_1 = -nFE_1 = -2x_1F$
 $Fe^{3+} + e^- \rightarrow Fe^{2+}$; $E_{Fe^{3+}/Fe^{2+}}^{\circ} = x_2 V$
 $\Delta G_2 = -nFE_2 = -1x_2F$
 $Fe^{3+} + 3e^- \rightarrow Fe$; $E_{Fe^{3+}/Fe}^{\circ} = ?$
 $\Delta G_3 = \Delta G_1 + \Delta G_2$
 $-nFE_3 = -2x_1F - x_2F \implies -3E_3 = -2x_1 - x_2$
 $E_3 = \left(\frac{2x_1 + x_2}{3}\right)$

- 2. (b)
- 3. (b): Rate = k[A] $1.8 \times 10^{-3} \text{ mol } L^{-1} \text{ min}^{-1} = k \times 0.3 \text{ mol } L^{-1}$ $\therefore \quad k = \frac{1.8 \times 10^{-3}}{0.3 \times 60} = 1 \times 10^{-4} \text{ s}^{-1}$
- 4. (b)
- 5. (c) : $\Delta G^0 = -nFE^0 = -2 \times 96500 \times [1.23 (-0.44)] J$ = -322310 J = -322.31 kJ
- 6. (b): The oxidation potential of Zn is high as compared to oxidation potential of iron.
- 7. (a)
 8. (c)
 9. (d)
 10. (b)

 11. (a)
 12. (a)
 13. (d)
- 14. (c) : $\Lambda^{\circ}(\text{ClCH}_2\text{COOH})$
- = $\Lambda^{\circ}(\text{ClCH}_2\text{COONa}) + \Lambda^{\circ}(\text{HCl}) \Lambda^{\circ}(\text{NaCl})$ = 224 + 203 - 38.2 = 388.8 ohm⁻¹ cm² g equiv⁻¹
- **15.** (d): Magnesium is more electropositive than zinc.

16. (d):
$$\frac{r_{new}}{r} = \frac{k[2A]^n \left[\frac{1}{2}B\right]^m}{k[A]^n [B]^m} = 2^n \times \frac{1}{2^m} = 2^{(n-m)}$$

- 17. (d)
- 18. (c) : According to Nernst equation,

$$E = E^{\circ} - \frac{0.059}{n} \log Q \text{ at } 25 \text{ }^{\circ}\text{C}$$



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At equilibrium,
$$E = 0$$
, $Q = K$
 $\therefore \quad 0 = E^{\circ} - \frac{0.059}{n} \log K \implies E^{\circ} = \frac{0.059}{n} \log K$
 $\log K = \frac{E^{\circ} \times n}{0.059} \implies \log K = \frac{0.295 \times 2}{0.059}$
 $K = \operatorname{antilog} \frac{0.295 \times 2}{0.059} \implies K = 1 \times 10^{10}$
19. (a): $n = \frac{80 - 50}{10} = 3$; $\frac{r_{\text{new}}}{r_{\text{old}}} = (3)^n$
New rate $= 2.6 \times 10^{-3} \times 3^3 = 70.2 \times 10^{-3}$
 $= 7.02 \times 10^{-2} \mod L^{-1} \text{ s}^{-1}$
20. (c): $k_1 = A_1 e^{-E_{a_1}/\text{RT}}$; $k_2 = A_2 e^{-E_{a_2}/\text{RT}}$
 $\frac{k_1}{k_2} = \left(\frac{A_1}{A_2}\right) e^{\frac{-E_{a_1} + E_{a_2}}{RT}}$
Now, $\frac{A_1}{A_2}$ = constant and $E_{a_2} = 2E_{a_1}$
 $\frac{k_1}{k_2} = A e^{\frac{-E_{a_1} + 2E_{a_1}}{RT}} \implies \frac{k_1}{k_2} = A e^{\frac{E_{a_1}/\text{RT}}{RT}}$
or $k_1 = Ak_2 e^{\frac{E_{a_1}}{RT}}$

21. (d)

1 -

- **22.** (b): $pH = 10 \Rightarrow -log [H^+] = 10$ $E^\circ = 0.059 log [H^+] = -0.59 volt$
- **23.** (d): A radioactive disintegration reaction is always of 1st order. $[A]_0 = 10[A]$; $t_{1/2} = 30$ days

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30}$$

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]} = \frac{2.303}{0.693} \times 30 \times \log \frac{10[A]}{[A]}$$

$$= 99.7 \approx 100 \text{ days}$$



A Chemist, a Physicist & a Biologist go to the beach. The Physicist, intrigued by the waves, walks into the ocean & drowns. The Biologist, intrigued by the sea life, walks into the ocean & drowns. The Chemist writes in her notebook :





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1. For this graph which option is correct?

Be



- (a) At less than 1500 °C Mg acts as reducing agent for SiO₂.
- (b) At more than 1500 °C Si acts as reducing agent for MgO.

HBr

• (D)

(c) Both (a) and (b) (d) None of these

2.
$$\langle \bigcirc - CH = CH - \langle \bigcirc -NO_2 - []{}^{-\bigcirc -\bigcirc -}(P)$$

P and *Q* are

- (a) position isomers (b) geometrical isomers
- (c) optical isomers (d) chain isomers.
- 3. The unit cell length of NaCl is observed to be 0.5627 nm by X-ray diffraction studies, the measured density of NaCl is 2.164 cm⁻³. Calculate % of missing Na^+ and Cl^- ions.

(a)	0.882%	(b)	0.920%
(c)	0.775%	(d)	0.351%

If $\Delta_0 < P$, the correct electronic configuration for d^4 4. system will be (a) $t_{2\alpha}^4 e_{\alpha}^0$ (b) $t_{2\alpha}^3 e_{\alpha}^1$ (c) $t_{2\alpha}^0 e_{\alpha}^4$ (d) $t_{2\alpha}^2 e_{\alpha}^2$

5. What is *D* in the following sequence of reactions?

$$O \xrightarrow{\text{NaBH}_4} A \xrightarrow{\text{HBr}} B \xrightarrow{(i) Mg, Et_2O} C$$

(a) CH₃OH (b)
$$H_2C = O$$

(ii) $H_2C = O$
(iii) H_3O^+
 $\frac{PCC}{CH_2Cl_2} \rightarrow D$
(c) OH (d) CH₃
(d) OH

- The vapour pressure of the solution of two liquids 6. $A(p^{\circ} = 80 \text{ mm})$ and $B(p^{\circ} = 120 \text{ mm})$ is found to be 100 mm of Hg when $X_A = 0.4$. The result shows that
 - (a) solution exhibits ideal behaviour
 - (b) $\Delta H_{\text{solution}} < 0$
 - (c) solution shows positive deviation
 - (d) solution will show positive deviation for lower concentration and negative deviation for higher concentration.
- Reagent used to distinguish H₂O₂ and O₃ is 7.
 - (a) PbS (b) potassium iodide
 - (d) bleaching powder. (c) $KMnO_4$
- The end product of the following reaction sequence 8. is



- 9. Zn gives H_2 gas with H_2SO_4 and HCl but not with HNO₃ because
 - (a) Zn acts as an oxidising agent when reacts with HNO₃
 - (b) HNO₃ is weaker acid than H₂SO₄ and HCl
 - (c) in electrochemical series Zn is above hydrogen
 - (d) NO_3^- ion is reduced in preference to hydronium ion.
- 10. An undergraduate student made a Daniell cell using 100 cm^3 of $0.100 \text{ M} \text{ CuSO}_4$ and $0.100 \text{ M} \text{ ZnSO}_4$ solution respectively. The two compartments are connected by suitable salt bridge.

A labmate of the student asked her for some solid $CuCl_2$. While she was lifting the bottle from a shelf, the lid of the bottle slipped and some amount of $CuCl_2$ fell in the $CuSO_4$ compartment at constant volume. She measured the emf of the cell again and found that it had increased by 9 mV. Calculate the mass of $CuCl_2$ that had spilled into the Daniell cell?

(Given:
$$E_{Cu^{2+}/Cu}^{\circ} = 0.34 \text{ V}, \ E_{Zn^{2+}/Zn}^{\circ} = -0.76 \text{ V}$$
)

(a)
$$1.35 g$$
 (b) $13.5 g$ (c) $27 g$ (d) $2.7 g$

- 11. Three separate samples of a solution of a single salt gave these results. One formed a white precipitate with excess ammonia solution, one formed a white precipitate with dil. NaCl solution and one formed a black precipitate with H₂S. The salt could be
 - (a) $AgNO_3$ (b) $Pb(NO_3)_2$
 - (c) $Hg(NO_3)_2$ (d) $MnSO_4$



12. The product (*C*) obtained in the following sequence of reactions is



13. A 1 L reaction vessel which is equipped with a movable piston is filled completely with a 1 M aqueous solution of H_2O_2 . The H_2O_2 decomposes to $H_2O_{(l)}$ and $O_{2(g)}$ in a first order process with half life 5 hrs at 300 K. As gas formed, the piston moves up against constant external pressure of 1 atm. What is the net work done by the gas from the start of sixth hour till the end of 10 hrs?

(a) 25 cal (b) 150 cal (c) 75 cal (d) 100 cal

14. $2CuSO_4 + 2NaCl + SO_2 + 2H_2O \longrightarrow$ Compound + $Na_2SO_4 + 2H_2SO_4$

Compound *X* gradually turns green on exposure in air due to oxidation. Incorrect statement about compound *X* is

- (a) compound *X* is CuCl
- (b) compound *X* forms black ppt. with H_2S
- (c) compound *X* is insoluble in aq. NH_3 solution
- (d) compound *X* is soluble in excess of HCl.
- **15.** How many of the following quantities show increase in their value on increasing temperature?
 - (i) Extent of physisorption of gases on solids
 - (ii) Electrical conductivity of metals
 - (iii) Electrical conductivity of an electrolyte solution
 - (iv) Ionic product of water
 - (v) Vapour pressure of a pure liquid
 - (vi) Vapour pressure of an ideal solution which follows Raoult's law, (keeping composition same)(vii) Solubility of gases in liquids
 - (viii)Reducing power of carbon monoxide for extraction of metals
 - (a) 5 (b) 4 (c) 6 (d) 3

SOLUTIONS

1. (c)
2. (a)
$$: P = \bigcirc -CH_2 - CH_2 - OH_2 - OH_2$$

3. (c) : Density (
$$\rho$$
) = $\frac{z \times M}{N_0 \times a^3}$
= $\frac{4 \times 58.5}{6.023 \times 10^{23} \times (0.5627 \times 10^{-7})^3}$ = 2.1806 g/cm³

 $6.023 \times 10^{-5} \times (0.5627 \times 10^{-5})^{-5}$ Observed density = 2.164 g/cm^3 which is less than calculated density because some ions are missing. Acutal units per unit cell can be calculated as

$$z = \frac{\rho \times N_0 \times a^3}{M}$$
$$= \frac{2.164 \times 6.023 \times 10^{23} \times (0.5627 \times 10^{-7})^3}{58.5} = 3.969$$

Missing units = 4 - 3.969 = 0.031

4.

:. % of missing Na⁺ and Cl⁻ =
$$\frac{0.031}{4} \times 100 = 0.775\%$$

(b)

5. (a) :
$$O \xrightarrow{\text{NaBH}_4} O \xrightarrow{\text{HBr}} O \xrightarrow{$$

CAPSUL COMIC

Who will tell the chemical formula of water?





What is this ???

Mam, yesterday you told us that it is H to O!!

(b) : $P_{\text{Total}} = 0.4 \times 80 + 0.6 \times 120 = 104$ 6. As $p_A + p_B < p_A^{\circ} X_A + p_B^{\circ} X_B$ Thus, solution shows negative deviation and for negative deviation $\Delta H_{\text{mix}} < 0$.

7. (c) : The pink colour of $KMnO_4$ is decolorised by H_2O_2 and not by O_3 . $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O$ +50

$$H_2O_2 + O \longrightarrow H_2O + O_2$$

8.

- (d): NO_3^- ions are reduced by nascent hydrogen. 9. Metal + HNO₃ \longrightarrow Metal nitrate + H $HNO_3 + H \longrightarrow N_2O + H_2O$
- **10.** (a) : 1.109 = 1.100 $\frac{0.059}{2}\log\frac{0.1}{[Cu^{2+}]}$ $[Cu^{2+}] = 0.2 M$ $\Delta n = 0.2 \times 0.1 - 0.1 \times 0.1 = 0.01$ $w = 0.01 \times 135 = 1.35$ g

12. (c) 11. (b)

13. (c) : At the end of 5 hours, $A_{t,1} = A_0/2$ At the end of 10th hours, $A_{t,2} = A_0/4$ $A_{t,2} - A_{t,1} = A_0/2 - A_0/4 = A_0/4 = 0.25 A_0$ Amount decayed = 0.25 molMoles of O_2 formed = 0.25/2 = 1/8 $w = -P\Delta V = -nRT = -(1/8) \times 300 \times 2$ cal = 75 cal 15. (b)

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BRUSH YOUR CONCEPTS

This specially designed column will help you to brush up your concepts by practicing questions. You can mail us your queries and doubts related to this topic at editor@mtg.com. The queries will be entertained by the author.*

In continuation with previous article.

SOLID STATE (CRYSTALLOGRAPHY)

• Radius ratio $\left(\frac{r^+}{r^-} \text{ or } \frac{r}{R}\right)$, Coordination number (C.N.) and Geometry

S. No.	<i>r</i> / <i>R</i> ratio	C.N.	Geometry	Examples
1.	0.225 to	4	Tetrahedral	ZnS, HgS,
	0.414			CuX, etc.
2.	0.414 to	6	Octahedral,	NaCl,
	0.732		square	$[PtCl_4]^{2-}$,
			planar	MgO, etc.
3.	0.732 to	8	bcc	CsBr, CsCl,
	1.0			etc.
4.	1.0	12	ccp or fcc	Mg, Zn, etc.

• Structures of Ionic Crystals

I. АВ-Туре

(i) Rock salt or NaCl type : fcc of A^+ and B^- penetrate

into each other with C.N. of 6, 6, $\frac{r}{r^{-}}$ ratio 0.414 to 0.732. Per unit cell of *AB* type, one ion has 14 locations and other 13 locations. *Z*-value is 4 *i.e.*, 4*AB* units per cell.

Next neighbours of Na⁺ in NaCl, w.r.t. body centre location.

1 st	2 nd	3 rd
8 Cl ⁻ at faces	12 Na ⁺ at edge	8 Cl ⁻ at corners
	centres	

(ii) CsCl type : A^+ is located at body centre and B^- at corners.

C.N. of 8, 8, $\frac{r^+}{r^-}$ ratio 0.732 to 1.0. *Z* value is 1, *i.e.*, one

AB unit per unit cell.

Next neighbouring of Cs⁺ in CsCl.

1 st	2 nd
8 Cl [−] at corners	6 Cs ⁺ at centres of six cubes joined on faces.

(iii) Zinc Blende or Sphalerite or ZnS type : S^{2-} forms *fcc* and Zn²⁺ are located at centres of alternate tetrahedra, dividing a cube into 8 sub-cubes.

C.N. of 4, 4, $\frac{r^+}{r^-}$ ratio 0.225 to 0.414. Z-value is 4, *i.e.*,

4 *AB* units per unit cell.

II. Fluoride $CaF_2 - AB_2$ type

Cations form *ccp* and anions occupy all tetrahedral voids. C.N. $A^{2+}: B^- = 8: 4$. One unit cell has $4 AB_2$ formula units (*Z*-value)

III. Antifluorite Na₂O or Li₂O – A₂B-type

Anions forms *ccp* and cations occupy all tetrahedral voids. C.N. A^+ : $B^- = 4$: 8. One unit cell has 4 formula units (*Z*-value).

- Rock salt system (NaCl-system), C.N. = 6:6 changes to CsCl system, C.N. = 8:8 under pressure and reverse is observed on heating.
- In CaF₂ packing, two F⁻ ions (at tetrahedral locations) are separated by a distance of $\frac{a}{2}$, $\frac{\sqrt{2}a}{2}$ and $\frac{\sqrt{3}a}{2}$.
- In Na₂O packing, two Na⁺ ions (at tetrahedral locations) are separated by a distance of

$$\frac{a}{2}$$
, $\frac{\sqrt{2}a}{2}$ and $\frac{\sqrt{3}a}{2}$.

 Diamond has ZnS-packing where, all positions of Zn²⁺ and S²⁻ are occupied by C-atoms. Thus 8C-atoms are present in one cubic cell. The packing efficiency is 34%.

*By R.C. Grover, having 45+ years of experience in teaching chemistry.

O Bragg Equation

For n^{th} order of diffraction of a crystalline substance, using X-rays of wavelength λ , when diffraction angle is 20. The interplanar distance d is calculated by using the formula, $n\lambda = 2d\sin\theta$



O Imperfections in Crystalline Solids

Stoichiometric Defects I.

(i) In non-ionic solids

- (a) Vacancy defect : Here, lattice sites are vacant. This decreases density.
- (b) Interstitial defect : Here, extra atoms or molecules occupy interstitial sites. This increases density.
- (ii) In ionic solids
- (a) Frenkel defect : This defect occurs in ionic crystals having low radius ratio, *i.e.*, smaller size of cation and low C.N. Here, shift of some cations to interstitial sites takes place. Electrical conductivity increases. Density remains the same. Examples : ZnS, CaF₂, AgBr, etc.
- (b) Schottky defect : This defect occurs in ionic crystals having high C.N. like NaCl, CsCl, AgBr, etc. Here, some cations and anions leave the crystals. Electrical conductivity increases but density decreases.

1 cm³ NaCl, on an average, has 10⁶ and 10²² ionic pairs *i.e.*, one Schottky defect per 10^{16} ionic pairs.

II. Non-Stoichiometric Defects

(i) Metal excess defect (Anion vacancy) : These are present in those ionic compounds where Schottky defect occurs.

- (a) F-centre defect : When alkali metal halide is heated in vapours of metal, some halide ions shift to surface and electrons from metal (vapour) occupy their sites. These sites are called F-centres and the defect as F-centre defect, from German word Farbenzenter meaning colour. KCl acquires violet colour due to absorption of yellow part of visible spectrum by electrons.
- (b) In some ionic compounds, simple heating causes the removal of some anions from the crystal leaving the extra electrons. These entrapped electrons and the excess metal ions shift to nearby interstitial sites. The substance gains some colour because of absorption of some part of visible region. ZnO gains yellow colour on heating.

(ii) Metal deficiency defect (Cation vacancy)

This defect occurs when a metal cation of higher charge enters and replaces metal ions of lower charge but maintains electrical neutrality. In Fe₃O₄, ions Fe²⁺ and Fe^{3+} are present in the ratio 1 : 2 but the charge of all O^{2-} ions is balanced.

(iii) Impurity defect or Doping defect

NaCl is doped by SrCl₂ and creates one cation vacancy per Sr²⁺ ion.

O Semiconductors

These are network covalent crystalline substances whose conductivity increases by increase in temperature. e.g. Ge, Si, etc. Doping by elements of group 13th creates holes in Si and Ge to give *p*-type semiconductors. '*p*' stands for hole density.

Doping by elements of group 15^{th} creates *n*-type semiconductor where every new atom is giving one extra electron for conductivity.

Compounds of 12th group and 13th group with 16th group and 15th group respectively also work as semiconductors. e.g., CdSe, GaAs, etc.

O Conductivity of Solids

27 orders of magnitude of conductivity 10^{-20} to 10^7 S m⁻¹ have been proposed.

- (a) Metallic conductors have overlapping of occupied orbital bands and empty bands where electrons can easily shift. Their conductivities are between 10^4 to 10^7 S m⁻¹.
- (b) In semiconductors there is small energy gap between occupied and empty bands where electrons may jump. Their conductivity ranges between 10^{-6} to 10^4 S m⁻¹.
- (c) In insulator, the conductivity range is between 10^{-20} to 10^{-10} S m⁻¹.

Magnetic Properties

- (a) Diamagnetic substances like NaCl, Zn, etc, do not have unpaired electrons. These feel weak repulsion in magnetic field and weigh less.
- (b) Paramagnetic substances like O₂, Cu²⁺, etc., have unpaired electrons. These feel attraction by magnetic field and weigh more.
- (c) Ferromagnetic substances like CrO₂, Co, Fe, etc., can be magnetised permanently where their magnetic domains (groups of ions or kernels) align in one direction.
- (d) Ferrimagnetic substances like Fe₃O₄, MgFe₂O₄, etc., show a small magnetic moment due to higher alignment of magnetic domains in one direction and less in opposite direction. These

substance become paramagnetic on heating above a temperature called Curie point.

(e) Antiferromagnetic substances like MnO, MnO₂, etc., have zero net magnetic moment due to 50-50 opposite alignments of magnetic domains.

MULTIPLE CHOICE QUESTIONS

- **1.** A solid PQ has rock salt structure with radius Q^{-} as 200 pm. The ideal radius of P^+ is
 - (a) 73.2 pm (b) 41.4 pm
 - (c) 82.8 pm (d) 146.4 pm
- A solid XY has rock salt structure. The third nearest neighbours of X^+ are
 - (a) $6 Y^{-}$ at faces (b) $12 X^+$ at edges
 - (c) 8 Y^- at corners
 - (d) $6X^+$ at centres of cubes sharing the faces.
- **3.** A solid *AB* has radii of cation A^+ and anion B^- as 80 pm and 200 pm. What is the distance between two nearest A^+ cations if 'a' = 497.73 pm?
 - (a) 152 pm (b) 252 pm
 - (c) 352 pm (d) 452 pm
- **4.** A crystalline solid PQ_2 has fluorite type packing. What is the distance between two Q^- ions if 'a' is edge length?
 - (b) $a/\sqrt{2}$ (a) *a*/2 (d) All of these (c) $\sqrt{3a/2}$
- Diamond has exactly ZnS packing of carbon atoms. How many C-atoms are present in one unit cell? (a) 4 (b) 6 (c) 8 (d) 12
- 6. What is the interplanar distance in the packing of a metal if X-rays if wavelength 65 pm scatter at an angle of 16° (sin $8^{\circ} = 0.14$) for second order diffraction?

(a)	464.28 pm	(b)	353.17 pm
(c)	364.82 pm	(d)	446.82 pm

- Which of the following is not correct w.r.t. Frenkel 7. defect?
 - (a) Radius ratio is low. (b) C.N. is low.
 - (c) Equal number of cations and anions balancing the charge are missing from their sites.
 - (d) Electrical conductivity increases.
- Select the correct statement w.r.t. F-centre defect. 8.
 - (a) The defect appears in silver halides only.
 - (b) Electrons coming from outside into the crystal are positioned in voids.
 - (c) The colour appears due to absorption of a part of visible region.
 - (d) This defect is related with Frenkel defect.



- The conductivity range of semiconductors is 9.
 - (a) 10^4 to 10^7 S m⁻¹ (b) 10^{-6} to 10^4 S cm⁻¹ (c) 10^{-20} to 10^{-10} S cm⁻¹

 - (d) 10^{-6} to 10^{-4} S cm⁻¹.
- 10. In which type of substance all magnetic domains are aligned in one direction to help it for becoming permanent magnet?
 - (a) Ferrimagnetic substances
 - (b) Ferromagnetic substances
 - (c) Antiferromagnetic substances
 - (d) Diamagnetic substances
- 11. Solid CO_2 (dry ice or dricold) is an example of
 - (a) covalent solid (b) metallic solid
 - (c) ionic solid (d) molecular solid.
- **12.** The number of unit cells in 15 g of 60 Co having *ccp* system is

(a) $N_A/2$ (b) $8N_A$ (c) $N_A/8$ (d) $N_A/16$

- 13. What is the percentage of Fe^{3+} by mass of wustite $Fe_{0.93} O_{1.0}$? (At. wt. of Fe = 56) (a) 10.53% (b) 11.52% (c) 64.98% (d) 23.04%
- 14. A crystalline solid XY has rock salt structure. The maximum size (radius) of Y⁻ ion for radius of X^+ being 150 pm, is
 - (a) 336.2 pm (b) 233.6 pm (d) 623.3 pm (c) 362.3 pm
- 15. Density and edge length of a *ccp* crystal respectively are 5 g cm⁻³ and 200 pm. The number of unit cells in its 8 gram is
 - (b) 5×10^{23} (a) 2×10^{23} (c) 8×10^{23} (d) 1.6×10^{23}
- 16. Calculate the ratio of edge lengths of packing of KCl to that of NaCl, if

 $r_{\text{Na}^+} / r_{\text{Cl}^-} = 0.5 \text{ and } r_{\text{Na}^+} / r_{\text{K}^+} = 0.7.$ (a) 1.18 (b) 1.14 (c) 2.28 (d) 2.36

17. Match the following and select the correct option.

(Column	-I	Column-II			
(Substance)			(Magnetic behaviour)			
(p)	O_2 mol	ecule	(i)	Fer	rimagne	tic
(q)	Zn met	al	(ii)	Fer	romagne	etic
(r)	CrO_2		(iii)	Para	amagnet	tic
(s)	Fe ₃ O ₄		(iv)	Ant	iferrom	agnetic
(t)	MnO_2		(v)	Dia	magneti	ic
	р	q		r	S	t
(a)	(iv)	(v)		(i)	(ii)	(iii)
(b)	(iii)	(i)		(ii)	(v)	(iv)
(c)	(iii)	(v)		(ii)	(i)	(iv)
(d)	(iii)	(v)		(i)	(iv)	(ii)

- 18. We can increase or develop *p*-type semiconductor conduction by
 - (a) increasing temperature of semiconductor
 - (b) adding electron rich element in semiconductor
 - (c) adding electron deficient element in semiconductor
 - (d) all of these.
- 19. One of the reasons of flame test of metal salts is
 - (a) Frenkel defect (b) Schottky defect
 - (c) metal excess defect (d) metal deficiency defect.
- **20.** If AgCl is doped with 10^{-5} mol % of CdCl₂. The concentration of cation vacancies is
 - (a) 6.02×10^{28} (b) 6.02×10^{18}
 - (c) 6.02×10^{17} (d) 6.02×10^{16}

SOLUTIONS

1. (c) : For ideal radius, $r^+/r^- = 0.414$ (Rock salt packing)

Radius of
$$P^+ = 0.414 \times \text{radius of } Q^-$$

= 0.414 × 200 = 82.8 pm

- 2. (c) : In Na⁺Cl⁻ types solid $X^{+}Y^{-}$, 1st nearest neighbours of X^+ (at centre) are $6Y^-$ at face centres, 2^{nd} are $12X^+$ at centres of edges and 3^{rd} are $8Y^-$ at corners.
- 3. (c): $\frac{r^+}{r^-} = \frac{80}{200} = 0.4 \implies \text{ZnS type packing}$ $2r^+ = \frac{\sqrt{2a}}{2}$ (for centres of alternate 8 sub-cubes) $=\frac{1.414}{2} \times 497.73 \text{ pm} = 351.9 \text{ pm}$
- (d): $P^+(Q^-)_2$ has CaF₂ system. Centres of all 8-sub-**4**. cubes are occupied by Q^- . Hence, $Q^- - Q^-$ distance can be $\frac{a}{2}$, $\frac{\sqrt{2}a}{2}$ and $\frac{\sqrt{3}a}{2}$.
- (c) : ZnS packing has 4 Zn^{2+} and 4 S^{2-} ions in unit 5. cell. All 8 ions are now exchanged by C-atoms.

6. (a)
$$:n\lambda = 2d\sin\theta$$

 $\theta = \frac{16^{\circ}}{2} = 8^{\circ}, \sin 8^{\circ} = 0.14, n = 2, \lambda = 65 \text{ pm}$
 $d = \frac{2 \times 65}{2 \times 0.14} = 464.28 \text{ pm}$
7. (c) 8. (c) 9. (b)

12. (d): Number of unit cells = $\frac{x \times N_A}{Z \times M} = \frac{15 \times N_A}{4 \times 60} = \frac{N_A}{16}$

13. (b): Let Fe^{3+} ions = x, so, Fe^{2+} ions = (0.93 - x) On balancing charge $3x + (0.93 - x) \times 2 - 2 = 0$ $3x - 2x = 0.14 \implies x = 0.14$ Wt. of 0.14 $\text{Fe}^{3+} = 0.14 \times 56 = 7.84$ Molar mass of $Fe_{0.93}O = (0.93 \times 56) + 16 = 68.08 \text{ g}$ Mass percent of Fe^{3+} of $Fe_{0.93}O$ $=\frac{7.84}{68.08}\times100=11.52\%$ 14. (c): $\frac{r^+}{r^-}$ (rock salt system) = 0.414 - 0.732 For maximum radius of Y⁻, $\frac{r^+}{r^-} = 0.414$ $r^- = \frac{r^+}{0.414} = \frac{150}{0.414} = 362.3 \text{ pm}$ 15. (a) : Number of unit cells in $x = \frac{x \times 10^{30}}{d \times a^3}$ = $\frac{8 \times 10^{30}}{5 \times (200)^3} = 2 \times 10^{23}$ 16. (b): $\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = 0.5 \Rightarrow r_{\text{Na}^+} = 0.5 \times r_{\text{Cl}^-}$...(i) $\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} + 1 = 1 + 0.5 \Rightarrow \frac{r_{\text{Na}^+} + r_{\text{Cl}^-}}{r_{\text{Cl}^-}} = 1.5$...(ii) Also, $\frac{r_{\text{Na}^+}}{r_{\text{K}^+}} = 0.7 \implies \frac{r_{\text{K}^+}}{r_{\text{Na}^+}}$, *i.e.*, $\frac{r_{\text{K}^+}}{0.5 r_{\text{Cl}^-}} = \frac{1}{0.7}$ [from (i)] $\Rightarrow \quad \frac{r_{\mathrm{K}^+}}{r_{\mathrm{Cl}^-}} = \frac{0.5}{0.7} \quad \Rightarrow \quad \frac{r_{\mathrm{K}^+}}{r_{\mathrm{Cl}^-}} + 1 = \frac{5}{7} + 1$ $\frac{r_{\rm K^+} + r_{\rm Cl^-}}{r_{\rm Cl^-}} = \frac{12}{7}$...(iii)

From (ii) and (iii),

$$\frac{r_{\rm K^+} + r_{\rm Cl^-}}{r_{\rm Na^+} + r_{\rm Cl^-}} = \frac{12}{7 \times 1.5} = 1.14$$

- 17. (c) 18. (c)
- **19.** (c) : Anion may leave the crystal site and electron may get entrapped that gets excited by energy of the flame and while returning to its normal state electron may release light in the visible spectrum.
- **20.** (d): Presence of one Cd^{2+} creates one vacancy as it replaces two Ag⁺ ions. 100 moles AgCl have vacancies = 10^{-5} mole 1 mole AgCl has vacancies = $\frac{10^{-5}}{100} \times 6.02 \times 10^{23}$ $= 6.02 \times 10^{16}$ vacancies ، ا



The questions given in this column have been prepared on the basis of pattern of Previous Years' Questions asked in JEE (Main & Advanced)/NEET/AIIMS exams.

SOLID STATE

(a) MgCl₂

(c) $H_2O(ice)$

(d) Diamond

(a) NaCl

(a)

8.

(b) I₂

SECTION - II

More than One Options Correct Type Which of the following are correctly matched?

7. In which of the following compounds, cations are

(b) Na_2O (c) ZnS

Which of the following statements are not true?

Vacancy defect results in a decrease in the

(b) Interstitial defect results in an increase in the

(c) Impurity defect has no effect on the density of

(d) Frenkel defect results in an increase in the

:

present in tetrahedral voids?

density of the substance.

density of the substance.

the substance.

Molecular crystal

Molecular crystal

Covalent network crystal

Covalent network crystal

(d) CaF_2

1. Schottky defect occurs mainly in electrovalent compounds where

SECTION - I

Only One Option Correct Type

- (a) positive ions and negative ions are of different size
- (b) positive ions and negative ions are of same size
- (c) positive ions are small and negative ions are big
- (d) positive ions are big and negative ions are small.
- 2. An element (at. wt. = 50) crystallises in fcclattice, with a = 0.50 nm. What is the density of unit cell if it contains 0.25% Schottky defect $(\text{use } N_A = 6 \times 10^{23})?$
 - (a) 2.0 g/cc (b) 2.66 g/cc
 - (d) None of these (c) 3.06 g/cc
- 3. The number of formula units in the crystal of NaCl, (...

ZnS and MgO
$$\left(\frac{r_c}{r_a} = 0.5\right)$$
 will have the ratio
(a) 4:6:2 (b) 4:4:4 (c) 4:2:6 (d) 6:6

4. Which of the following formulae is consistent with the unit cell of the rhenium oxide compound shown below?

(a)
$$\operatorname{ReO}_3$$

(b) Re_2O_3

(c)
$$\text{ReO}_6$$

5. Structure of a mixed oxide is cubic close packed (ccp). The cubic unit cell of mixed oxide is composed of oxide ions. One fourth of the tetrahedral voids are occupied by divalent metal A and the octahedral voids are occupied by a monovalent metal B. The formula of the oxide is

(a)
$$ABO_2$$
 (b) A_2BO_2
(c) $A_2B_3O_4$ (d) AB_2O_2

(AIPMT 2012)

density of the substance. :4 For the orthorhombic crystal system (a) no two sides are equal *i.e.*, $a \neq b \neq c$ (b) all crystallographic angles are equal to 90° *i.e.*,

Oxygen

Rhenium

- $\alpha = \beta = \gamma = 90^{\circ}$ (c) three kinds of unit cells are found, these are primitive, body centred and face centred
- (d) all the four unit cells are found.

10. Ferroelectricity is exhibited by

- (a) barium titanate ($BaTiO_3$)
- (b) potassium tartrate (Rochelle salt)
- (c) potassium dihydrogen phosphate (KH₂PO₄)
- (d) lead zirconate ($PbZrO_3$).

SECTION - III Paragraph Type

Paragraph for Questions 11, 12 and 13

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. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these spheres touches three spheres of the bottom layer. Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be 'r'.

11. The number of atoms in this HCP unit cell is

- (d) 17 (a) 4 (b) 6 (c) 12 **12.** The volume of this HCP unit cell is
 - (b) $16\sqrt{2}r^3$ (a) $24\sqrt{2}r^3$
 - (d) $\frac{64}{3\sqrt{3}}r^3$ (c) $12\sqrt{2}r^3$
- 13. The empty space in this HCP unit cell is (b) 47.6% (c) 32% (a) 74% (d) 26% (*IIT JEE 2008*)

SECTION - IV

Matching List Type

14. Match the substances given in List I with their magnetic properties given in List II and select the correct answer from the codes given below the lists :

	List I				List II
P.	CrO_2			1.	Anti-ferromagnetic
Q.	V_2O_5			2.	Ferromagnetic
R.	V_2O_3			3.	Paramagnetic
S.	TiO			4.	Diamagnetic
	Р	Q	R	S	
(a)	2	4	1	3	
(b)	4	2	3	1	
(c)	2	4	3	1	
(d)	4	2	1	3	

15. Match the List I with the List II and select the correct answer using the code given below the lists : List I I ist II

cial parameters)	(C	rystal system)
$a \neq b \neq c$,	1.	Triclinic
$\alpha = \beta = \gamma = 90^{\circ}$		
$a \neq b \neq c$,	2.	Hexagonal
$\alpha \neq \beta \neq \gamma \neq 90^{\circ}$		
$a = b \neq c$,	3.	Orthorhombic
$\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$		
$a \neq b \neq c$,	4.	Monoclinic
$\alpha = \gamma = 90^{\circ} \neq \beta$		
	tial parameters) $a \neq b \neq c,$ $\alpha = \beta = \gamma = 90^{\circ}$ $a \neq b \neq c,$ $\alpha \neq \beta \neq \gamma \neq 90^{\circ}$ $a = b \neq c,$ $\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}$ $a \neq b \neq c,$ $\alpha = \gamma = 90^{\circ} \neq \beta$	cial parameters)(C $a \neq b \neq c$,1. $\alpha = \beta = \gamma = 90^{\circ}$ $a \neq b \neq c$,2. $\alpha \neq \beta \neq \gamma \neq 90^{\circ}$ $a = b \neq c$,3. $\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}$ $a \neq b \neq c$,4. $\alpha = \gamma = 90^{\circ} \neq \beta$

Р	Q	R	S
(a) 1	4	2	3
(b) 2	3	4	1
(c) 3	2	4	1
(d) 3	1	2	4

SECTION - V

Assertion Reason Type

Assertion Reason type MCQs having only one option correct. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.
- 16. Assertion : Hexagonal close packing is more closely packed than cubic close packing. Reason : Hexagonal close packing has coordination number 12 whereas cubic close packing has coordination number 8.
- 17. Assertion: On heating ferromagnetic or ferrimagnetic substances, they become paramagnetic. **Reason**: The electrons change their spin on heating.
- 18. Assertion : The presence of a large number of Schottky defects in NaCl lowers its density.

Reason : In NaCl, there are approximately 10^6 Schottky pairs per cm³ at room temperature.

(AIIMS 2013)

SECTION - VI

Numerical Value Type

- 19. The compound CuCl has ZnS structure and the edge length of the unit cell is 500 pm. Calculate its [Atomic mass of Cu = 63 u, Cl = 35.5 u] density.
- 20. A crystalline solid of a pure substance has a facecentred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8 g cm^{-3} , then the number of atoms present in 256 g of the crystal is $N \times 10^{24}$. The value of N is

(JEE Advanced 2017)



GENERAL PRINCIPLES OF ISOLATION OF ELEMENTS

SECTION - I

Only One Option Correct Type

- 1. A sulphide ore is generally roasted to the oxide before reduction, because
 - (a) the enthalpy of formation of CO_2 is more than that of CS₂
 - (b) a metal sulphide is generally more stable than the metal oxide
 - (c) no reducing agent is found suitable for reducing a sulphide ore
 - (d) a sulphide ore cannot be reduced at all.
- 2. In blast furnace, iron oxide is reduced by
 - (a) silica (b) carbon monoxide
 - (c) carbon dioxide (d) limestone.
- 3. Carbon cannot be used in the reduction of Al_2O_3 because
 - (a) the enthalpy of formation of CO_2 is more than that of Al₂O₃
 - (b) pure carbon is not easily available
 - (c) the enthalpy of formation of Al_2O_3 is very high
 - (d) it is an expensive proposition.
- 4. Identify the statement that is not correct for Ellingham diagrams.
 - (a) These are the plots of $\Delta_f G^\circ vs T$.
 - (b) Each plot is a straight line unless phase change occurs.
 - (c) These plots tell about the kinetics of reduction process.
 - (d) These plots are based on thermodynamic concepts.
- 5. Which one of the following ores is best concentrated by froth floatation method?
 - (a) Magnetite (b) Siderite
 - (c) Galena (d) Malachite

(JEE Main 2016)

SECTION - II

More than One Options Correct Type

- 6. Which of the following ores represent the ore of iron?
 - (a) Cassiterite (b) Limonite
 - (c) Haematite (d) Magnetite

- Which of the following are correct? 7. (a) $Fe_2O_3 + CO \xrightarrow{Blast furnace} Fe$
 - (b) $ZnO + C \xrightarrow{1200^{\circ}C} Zn$
 - (c) $Ca_3(PO_4)_2 + C \xrightarrow{\Delta} P$
 - (d) MgO + C $\xrightarrow{2000^{\circ}C}$ Mg
- Which of the following are not methods for refining metals?
 - (a) Poling
 - (b) Cupellation
 - (c) Goldschmidt aluminothermic process
 - (d) Smelting
- 9. The metals obtained by hydrometallurgy are (a) Ag (b) Au (c) Hg (d) Fe
- **10.** Upon heating with Cu₂S, the reagent(s) that give copper metal (is) are
 - (a) CuFeS₂ (b) CuO
 - (c) Cu_2O (d) $CuSO_4$
 - (JEE Advanced 2014)

SECTION - III

Matching List Type

11. Match the List I with List II and select the correct answer using the codes given below the lists :

I	List I		List II				
(Element)			(Method of extraction)				
P.	Cu	1.	Direct reduction of sulphide by				
			heating	g			
Q.	Sn	2.	Electro	olysis of fused chloride and			
			fluorid	le			
R.	Hg	3.	Partial	l oxidation of sulphide ore			
S.	Ca	4.	Reduc	tion of oxide with carbon			
	Р	Q	R	S			
(a)	3	1	2	4			
(b)	3	4	1	2			
(c)	1	3	2	4			

- (d) 4 2 3 1
- 12. Match the List I with the List II and select the correct answer using the codes given below the lists:

List I			List II			
(M	etal)		(Procedure of extraction)			
P.	Gold	1.	Carbon reduction method			
Q.	Lead	2.	Self-reduction			
R.	Copper	3.	Thermite process			
S.	Chromium	4.	Hydrometallurgical process			



	Р	Q	R	S
(a)	1	2	3	4
(b)	4	1	2	3
(c)	1	2	4	3
(d)	2	3	1	4

13. Match the List I with List II and select the answer using the codes given below the lists:

	0		0		
	List I				List II
(Ar	nionic s	pecie	es)		(Ore)
P.	Carbo	nate		1.	Siderite
Q.	Sulph	ide		2.	Malachite
R.	Hydro	oxide	•	3.	Bauxite
S.	Oxide	:		4.	Calamine
				5.	Argentite
	Р	Q	R	S	
(a)	1,2,4	5	2,3	3	
(b)	2, 3, 4	5	3,4	1	
(c)	2, 1, 3	4	3,5	5	
(d)	2, 4, 5	1	2,5	3	
					(JEE Advanced 2015)

SOLID STATE

1. (b)

2. **(b)**:
$$d = \frac{Z \times M}{a^3 \times N_A}$$

For fcc, $Z = 4$

$$d = \frac{4 \times 50}{(0.50 \times 10^{-9})^3 \times 6 \times 10^{23}} = 2.66 \times 10^6 \text{ g m}^{-3}$$

If it contains 0.25% Schottky defects, then

$$d' = 2.66 \times 10^{6} \times \frac{0.25}{100} = 6.65 \times 10^{3} \text{ g m}^{-3}$$
$$d'' = d - d' = 2.66 \times 10^{6} - 6.65 \times 10^{3} \text{ g m}^{-3}$$
$$\approx 2.65 \times 10^{6} \text{ g m}^{-3} = 2.65 \text{ g cm}^{-3}$$

- 3. (b): In NaCl crystal, Na⁺ ions are present at 12 edge centres and one at the centre
 - \therefore No. of Na⁺ ions = $\left(12 \times \frac{1}{4}\right) + 1 = 4$

and Cl⁻ ions are present at 8 corners and 6 face centres:

No. of
$$\operatorname{Cl}^-$$
 ions = $\left(\frac{1}{8} \times 8\right) + \left(\frac{1}{2} \times 6\right) = 4$

 \therefore Formula units of NaCl/unit cell = 4 In ZnS, Zn²⁺ ions are present at four tetrahedral sites of *fcc* made by S^{2-} ions. Formula units of ZnS = 4

SECTION - IV

Assertion Reason Type

Assertion Reason type MCQs having only one option correct. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.
- 14. Assertion : Ethyl xanthate is used as a collector in froth floatation process.

Reason : Collectors depress the floatation property of one of the components of the ore and thus help in the separation of different minerals present in the same ore.

15. Assertion : Pb, Sn and Bi are purified by liquation method.

Reason : Pb, Sn and Bi have low melting point as compared to impurities.

SOLUTIONS

In MgO,
$$\frac{r_c}{r_a} = 0.5$$
 means NaCl type
 \therefore Ratio is 4 : 4 : 4

- 4. (a): No. of oxygens $=\frac{1}{4} \times 12 = 3$ No. of Re = $\frac{1}{9} \times 8 = 1$ $Formula = ReO_3$
- 5. (d): Number of atoms in $ccp = 4 = O^{2-1}$ Number of tetrahedral voids = $2 \times N = 2 \times 4$

Number of A^{2+} ions $= 8 \times \frac{1}{4} = 2$

Number of octahedral voids

= Number of B^+ ions = N = 4Ratio, $O^{2-}: A^{2+}: B^+ = 4: 2: 4 = 2: 1: 2$

- Formula of oxide = AB_2O_2
- **6.** (c, d): $MgCl_2$ Ionic crystal I_2 — Molecular crystal
- 7. (b, c): Na⁺ occupy all the tetrahedral voids in Na₂O and Zn²⁺ occupy half of the tetrahedral voids.
- 8. (c, d): (c) is not true because impurity defect changes the mass but not the volume. (d) is not true because Frenkel defect neither changes mass nor volume.



- **9.** (**a**,**b**,**d**) : All the four unit cells are found *i.e.*, primitive, body centred, face centred and end centred.
- **10.** (**a**, **b**, **c**) : PbZrO₃ shows antiferroelectricity.
- **11. (b) :** Total no. of atoms in 1 unit cell = $(12 \times 1/6) + 3 + (2 \times 1/2) = 6$



- 12. (a) : Height of unit cell = $4r\sqrt{2/3}$ Base area = $6 \times \sqrt{3}/4(2r)^2$ Volume = height × base area = $4r\sqrt{2/3} \times 6 \times \sqrt{3}/4(2r)^2 = 24\sqrt{2}r^3$
- **13.** (d) : Packing fraction

Volume of the atoms in one unit cell

$$\frac{6 \times 4/3\pi r}{24\sqrt{2}r^3} = \frac{\pi}{3\sqrt{2}} = 0.74 = 74\%$$

Packing fraction = 74%; Empty space = 26%

14. (a)

=

16. (d): Hexagonal close packing and cubic close packing are equally close packed (space occupied = 74%). Both have a coordination number 12.

15. (d)

18. (b): When an atom or an ion is missing from its normal lattice site, a lattice vacancy or defect is created, which is called Schottky defect. Due to missing atoms or ions, density of the crystal will be lowered.

19. (5.234) : Given, structure = fcc, a = 500 pm
For CuCl, M = 63 + 35.5 = 98.5 g mol⁻¹, d = ?
For fcc, Z = 4
Using formula
$$d = \frac{Z \times M}{N_A \times a^3}$$

or $d = \frac{4 \times 98.5 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1} \times (500)^3 \times 10^{-30} \text{ cm}^3}$
= 5.234 g cm⁻³

20. (2):
$$d = \frac{Z \times M}{a^3 \times N_A}$$

For *fcc* lattice, Number of atoms per unit cell, Z = 4Substituting values in equation, we get

$$8 = \frac{4 \times M}{(400 \times 10^{-10})^3 \times 6.023 \times 10^{23}}$$

$$M = \frac{8 \times (400 \times 10^{-10})^3 \times 6.023 \times 10^{23}}{4}$$

∴ $M = 77.0944 \text{ g mol}^{-1}$
77.0944 g of solid has 6.023×10^{23} atoms
∴ 256 g of solid will have

$$= \frac{6.023 \times 10^{23}}{77.0944} \times 256 \text{ atoms}$$

$$= 20 \times 10^{23} = 2 \times 10^{24}$$

Comparing it with $N \times 10^{24}$, we get N = 2



A mmonia (NH₃) has attracted attention in recent years as a carbon-free fuel that does not emit carbon dioxide. For use as a fuel, it should have a lower combustion temperature and produce only nitrogen (N₂) and water. Now, researchers have succeeded in developing a new catalyst that burns NH₃ at a low temperature and produces N₂. The results are expected to contribute to climate change countermeasures and increased renewable energy use.

The novel catalyst ($CuO_x/3A2S$) is a mullite-type crystal structure $3Al_2O_3 \cdot 2SiO_2$ (3A2S) carrying copper oxide (CuO_x). When NH₃ was burned with this catalyst, researchers found that it stayed highly active in the selective production of N₂, meaning that it suppressed NO_x formation, and the catalyst itself did not change even at high temperatures.



64

GENERAL PRINCIPLES OF ISOLATION OF ELEMENTS

- 1. (a): The more stable CO_2 has higher enthalpy of formation than CS₂.
- **2.** (b) : In blast furnace, Fe_2O_3 is reduced to Fe by CO.

 $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2\uparrow$

- 3. (c): The enthalpy of formation of Al_2O_3 is very high and therefore, it cannot be reduced by carbon. It is reduced by electrolytic method.
- 4. (c): Ellingham diagrams simply suggest whether the reduction process is feasible or not based on thermodynamic concepts but it cannot tell anything about kinetics of reaction.
- 5. (c): Froth floatation method is suitable for sulphide ores thus, PbS i.e., galena is best concentrated by this method.
- 6. (b,c,d) : Cassiterite (SnO_2) , Magnetite (Fe₃O₄), Limonite [FeO(OH).*n*H₂O], Haematite $(Fe_{2}O_{3}).$
- 7. (a, b, d) : In a blast furnace $2C + O_2 \xrightarrow{\Delta} 2CO$

- $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$ When ZnO is heated with carbon, Zn is obtained. $ZnO + C \longrightarrow Zn + CO$
- While when MgO is heated at 2000°C in electric furnace we get Mg.
- $MgO + C \longrightarrow Mg + CO$
- 9. (a,b) 8. (c, d)

- 10. (b, c,d): (a) CuFeS₂ + Cu₂S $\xrightarrow{\Delta}$ No reaction
 - (b) $2CuO \xrightarrow{\Delta} Cu_2O + 1/2 O_2$
 - (c) $2Cu_2O + Cu_2S \xrightarrow{\Delta} 6Cu + SO_2$
 - (d) $CuSO_4 \xrightarrow{\Delta} CuO + SO_2 + 1/2 O_2$

Both CuO and CuSO₄ upon heating produces Cu₂O and CuO respectively and further Cu₂O and CuO on heating with Cu₂S gives Cu.

- 13. (a) : Carbonate ores are
 - (1) Siderite : FeCO₃
 - (2) Malachite : $CuCO_3 \cdot Cu(OH)_2$
 - (4) Calamine : $ZnCO_3$
 - Sulphide ore is (5) Argentite : Ag_2S .
 - Hydroxide ion is present in
 - (2) Malachite : $CuCO_3 \cdot Cu(OH)_2$
 - (3) Bauxite : $Al_2O_3 \cdot 2H_2O$ or $AlO_x(OH)_{3-2x}$

where 0 < x < 1

Oxide ore is bauxite (3) only.

- 14. (c): Collectors adsorb themselves on polar groups to grains of ores and thus derive them on the surface to pass on into the froth.
- 15. (a): Liquation method is used to purify metals having lower melting point than that of impurities. The temperature is adjusted just above the melting point of the ore. The ore melts and flows away while infusible impurities left behind.

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CLASS XII

Chapterwise Practice questions for CBSE Exams as per the latest pattern and marking scheme issued by CBSE for the academic session 2018-19.

GENERAL INSTRUCTIONS

- (i) All questions are compulsory.
- (iii) Q. no. 6 to 12 are short answer questions and carry 2 marks each.
- (v) Q. no. 25 to 27 are long answer guestions and carry 5 marks each.
- (ii) Q. no. 1 to 5 are very short answer guestions and carry 1 mark each.
- (iv) Q. no. 13 to 24 are also short answer guestions and carry 3 marks each.
- (vi) Use log tables if necessary, use of calculators is not allowed.

Time Allowed : 3 hours

Maximum Marks: 70

General Principles and Processes of Isolation of Elements The *p*-Block Elements (Group 15 to 18)

- 1. Write an equation for the disproportionation reaction of P₄ in sodium hydroxide.
- 2. There are many minerals in the earth's crust which contain aluminium, but only bauxite is an important ore of this metal. Explain.
- 3. What is the covalency of nitrogen in N_2O_5 ?
- 4. Write any two uses of pyrophoric alloys.
- 5. What is the correct order of the thermal stability of hydrogen halides (H-X)?
- Suggest a condition under which magnesium 6. (i) could reduce alumina.
 - (ii) Predict condition under which Al might be expected to reduce MgO.
- 7. Complete the following reactions :
 - (i) $XeF_2 + PF_5 \longrightarrow$ (ii) $XeF_4 + O_2F_2 \longrightarrow$
- 8. Complete and balance the following reactions :
 - Red phosphorus is reacted with iodine in (i) presence of water.

- (ii) The preparation of ammonium sulphate from gypsum, ammonia and carbon dioxide.
- 9. Describe the properties of an ore which is to be concentrated by (i) leaching with alkali (ii) floatation (iii) panning (iv) electromagnetic separation.

OR

Name one metal that is refined by each of the following processes : (i) Mond process (ii) electrolysis (iii) van Arkel process (iv) zone refining.

- 10. The only binary compounds of the noble gases are fluorides and oxides of Kr, Xe and Rn. Give reasons.
- 11. Why is leaching of gold by metal cyanides carried out in the presence of oxygen? Give the chemical equation. Name the metal used as reducing agent.
- Nirtic oxide becomes brown when released in 12. (i) air. Why?
 - (ii) BiCl₃ is more stable than BiCl₅. Why?
- 13. Write down the reactions which occur in upper, middle and lower zones in the blast furnace during the extraction of iron from iron ore.



- 14. How will you obtain the following from sulphuric acid? (i) SO₂ (ii) SO₃ (iii) SO₂Cl₂
- **15.** What is coupling of reaction? How is it useful in metallurgy?
- **16. (i)** Why does the reactivity of nitrogen different from phosphorus?
 - (ii) Can PCl₅ act as an oxidising as well as reducing agent?
- **17.** Mention the name, composition and uses of any three alloys of copper.
- **18.** Give one example in each case to explain the following properties :
 - (i) Sulphuric acid is a dibasic acid.
 - (ii) Sulphuric acid is a dehydrating agent.
 - (iii) Sulphuric acid is an oxidising agent.
- **19.** State the principles of the following methods of refining crude metals :
 - (i) Zone refining (ii) Liquation method
 - (iii) Chromatographic method
- 20. (i) What do you mean by hydrometallurgy?(ii) What is matte?
- **21.** Explain the following :
 - (i) Zinc, but not copper, is used for the recovery of Ag from the complex [Ag(CN)₂]⁻.
 - (ii) Partial roasting of sulphide ore is done in the metallurgy of copper.
 - (iii) Why is chalcocite roasted and not calcined during recovery of copper?

OR

An inorganic compound (*X*) gives a brick red flame on performing flame test. This compound gives the following tests also :

- (i) Smells of chlorine when placed in moist air.
- (ii) If KI and CH₃COOH are added to the suspension in water, a brown colour is obtained.

Identify (*X*) and write down equations for reactions (i) and (ii).

- **22. (i)** Explain, why a basic flux is used in the extraction of iron but an acidic flux is used in case of copper?
 - (ii) For the extraction of iron in a blast furnace what is used as a reducing agent?
- **23. (i)** Write one chemical method for the preparation of fluorine.
 - (ii) Write one use of helium gas and liquid helium each.
 - (iii) Draw the structure of pyrophosphoric acid.

- **24.** (i) What role is played by CO_2 in getting pure alumina (Al₂O₃) in the extraction of aluminium?
 - (ii) Aluminium metal is frequently used as a reducing agent for the extraction of metals such as chromium, manganese, etc. Explain.
 - (iii) Why does copper obtained in the extraction from copper pyrites have a blistered appearance?
- **25.** Explain the following with proper reason :
 - (i) Nitrogen is a gas while other members of Vth group are solids.
 - (ii) A bottle of liquor ammonia should be cooled before opening.
 - (iii) Ammonia has a higher boiling point than phosphine.
 - (iv) PF_5 is known but NF_5 is not.
 - (v) The experimentally determined N—F bond length in NF₃ is greater than the sum of single bond covalent radii of N and F.

OR

What happens when (Give balanced equations)

- (i) Sodium iodate is treated with sodium bisulphite solution.
- (ii) Chlorine is passed into cold aqueous potassium hydroxide.
- (iii) Sodium chloride is heated with $K_2Cr_2O_7$ and conc. H_2SO_4 .
- (iv) Bromine reacts with Na_2CO_3 solution.
- (v) Ammonia reacts with excess chlorine.
- **26. (i)** Write the principle behind the froth floatation process. What is the role of collectors in this process?
 - (ii) Give reasons for the following :
 - (a) Zinc oxide can be reduced to the metal by heating with carbon but not Cr_2O_3 .
 - (b) Extraction of copper directly from sulphide ores is less favourable than that from its oxide ore through reduction.

OR

- (i) Write the reactions involved during extraction of copper from copper pyrites.
- (ii) During the extraction of copper, explain why inner wall of the Bessemer converter is lined with silica?
- **27.** Account for the following :
 - (i) The boiling points of noble gases increase with the increase in atomic number.



- (ii) Neon is generally used in warning signal illumination.
- (iii) For protecting electrical instruments, neon is generally used in safety devices.
- (iv) Why does NO₂ dimerise?
- (v) SF_6 is known but SH_6 is not known.

OR

Answer the following :

- (i) Describe the Contact process for the manufacture of sulphuric acid with special reference to the reaction conditions, catalysts used and yield in the process.
- (ii) How is XeO₃ obtained? Write the related chemical equations. Draw the structure of XeO₃.

SOLUTIONS

1. $P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3^{f}$ Sodium Phosphine hypophosphite

2. Because extraction of aluminium from bauxite is economically feasible.

3. Covalency depends upon the number of shared pairs of electrons. Since, nitrogen atom has 4 shared electron pairs, hence the covalency of nitrogen in N_2O_5 is 4.

4. Pyrophoric alloys contain rare earth metals and are used in the preparation of ignition devices such as tracer bullets and shells and flints for lighters.

5. Thermal stability decreases as the strength of H-X bond decreases, which in turn, decreases as the size of the halogen atom increases, *i.e.*, HF > HCl > HBr > HI.

6. (i) ΔG° of formation of Al₂O₃ at temperatures below 1623 K is less negative than ΔG° of formation of MgO. Thus, below 1623 K magnesium can reduce Al₂O₃ to Al.

(ii) The temperature of intersection of the Al \rightarrow Al₂O₃ and Mg \rightarrow MgO curves in the Ellingham diagram is 1623 K. Above this temperature, ΔG° of formation of Al₂O₃ is more negative than ΔG° of formation of MgO. Thus, above 1623 K aluminium can reduce MgO into Mg.

7. (i)
$$XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^-$$

(ii) $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$

8. (i) $2P + 3I_2 \longrightarrow 2PI_3$ $2PI_3 + 3H_2O \longrightarrow H_3PO_3 + 3HI$ (ii) $2NH_3 + H_2O + CO_2 \longrightarrow (NH_4)_2CO_3$ $CaSO_4 + (NH_4)_2CO_3 \longrightarrow (NH_4)_2SO_4 + CaCO_3$

9. (i) The metal must be amphoteric (or acidic), so that it can be dissolved in base, leaving behind the gangue and perhaps some other metals.

(ii) The desired mineral must be wet by oil more than by soapy water such as many sulphides.

(iii) The desired mineral must be much more dense than the gangue which will be washed away by running water while the mineral is left behind.

(iv) Either the ore of the metal or the impurities associated with it are magnetic in nature.

(i) Ni (ii) Cu (iii) Zr (iv) Ga

10. The only binary compounds of noble gases are fluorides and oxides of Kr, Xe and Rn because the ionisation energies of He, Ne and Ar are much higher than for Xe to allow the formation of similar compounds. The ionisation enthalphy of Kr is little lower than Xe and it forms KrF_2 .

The ionisation enthalphy for Rn is less than that for Xe and it is expected to form compounds similar to Xe. However, Rn is radioactive and its isotopes have short half-lives. Therefore, only RnF_2 and a few complexes are known.

11. Leaching of gold by metal cyanides is carried out in the presence of oxygen because it is an oxidation reaction where Au is oxidised to Au^+ which combines with CN^- ions to form soluble complex, *i.e.*,

Zinc metal is used as the reducing agent, the pure metal is then displaced from the solution by active metal. $2K[Au(CN)_2] + Zn \rightarrow K_2[Zn(CN)_4] + 2Au$

12. (i) Nitric oxide combines with oxygen when exposed to air to give nitrogen dioxide which is brown in colour.

$$2NO + O_2 \longrightarrow 2NO_2$$

(ii) Bi has little tendency to form pentahalides because +5 oxidation state of Bi is much less stable than +3 oxidation state due to inert pair effect.

13. Reduction of iron oxide in blast furnace : **Lower zone of the blast furnace :**

$$C + O_2 \longrightarrow CO_2 + heat$$

$$C + CO_2 \longrightarrow 2CO$$

Coke is burnt to give temperature upto 2200 K at lower part of the blast furnace.

Middle zone of the blast furnace : CO moves up in the furnace. The temperature range in the middle zone of the blast furnace is 900-1500 K.

$$FeO + CO \longrightarrow Fe + CO_2$$

Limestone is also decomposed to CaO which removes silicate impurity of the ore as slag.



$$\begin{array}{c} \text{CaCO}_{3} \longrightarrow \text{CaO} + \text{CO}_{2} \\ \text{CaO} + \text{SiO}_{2} \longrightarrow \begin{array}{c} \text{CaSiO}_{3} \\ \text{Slag} \end{array}$$

Upper zone of the blast furnace : Temperature range in this zone is 500-800 K. Here, ores are reduced to Fe by CO.

 $3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$ $Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$ $Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$

14. (i) SO_2 is obtained by heating copper with conc. H₂SO₄.

 $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

It can also be obtained by boiling sulphur with conc. H_2SO_4 .

 $S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$

(ii) H_2SO_4 when treated with P_2O_5 loses water and forms SO₃.

 $H_2SO_4 + P_2O_5 \longrightarrow 2HPO_3 + SO_3$

(iii) SO_2Cl_2 is formed when conc. H_2SO_4 is treated with excess of PCl₅.

 $H_2SO_4 + 2PCl_5 \longrightarrow SO_2Cl_2 + 2POCl_3 + 2HCl_3$

15. If the value of ΔG° is positive for any reaction, then to make such reaction spontaneous, it is coupled with another reaction of large negative ΔG° value, so that the sum of the two ΔG° becomes negative. This is known as coupling of reaction.

In the metallurgy, thermodynamically infeasible reaction is coupled with a reaction which has more negative ΔG° , so that net ΔG° becomes negative.

16. (i) Nitrogen exists as a diatomic molecule with a triple bond between two N-atoms. The bond dissociation enthalphy of this triple bond ($N \equiv N$) is very high (941.94 kJ mol⁻¹) due to which nitrogen is inert and unreactive at room temperature.

In contrast, phosphorus exists as a tetraatomic molecule (P_4) . As P—P bond is much weaker than N \equiv N bond, therefore, P-P bond can be broken easily and hence, phosphorus is much more reactive than nitrogen.

(ii) The oxidation state of P in PCl_5 is + 5. Since, P has five electrons in its valence shell, therefore, it cannot increase its oxidation state beyond +5 by donating electrons, therefore, PCl₅ cannot act as a reducing agent. However, it can decrease its oxidation state from +5 to +3 or some lower value, therefore it can act as an oxidising agent. e.g., PCl₅ oxidises Ag to AgCl, Sn to SnCl₄.

$$\begin{array}{c} 0 & +5 & +1 & +3 \\ 2Ag + PCl_5 \longrightarrow 2AgCl + PCl_3 \\ 0 & +4 \\ Sn + 2PCl_5 \longrightarrow SnCl_4 + 2PCl_3 \end{array}$$

17.

Name	Composition	Uses
(i) Brass	Cu (60–80%), Zn (40–20%)	For making scientific instruments and parts of machinery.
(ii) Bronze	Cu (80%), Sn (10%), Zn (10%)	For making cooking utensils and coins.
(iii) German Silver	Cu(25–30%), Zn(25–30%), Ni(40–50%)	For making silver wires, resistance wires, etc.

18. (i) H_2SO_4 forms two series of salts, *i.e.*, both the hydrogen atoms are replaceable.

 $H_2SO_4 \Longrightarrow H^+ + HSO_4^- \Longrightarrow 2H^+ + SO_4^{2-}$ $H_2SO_4 + NaOH \longrightarrow NaHSO_4 + H_2O$ Sodium hydrogen sulphate (acid salt) $H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$ Sodium sulphate

(normal salt)

(ii) H_2SO_4 has great affinity for water molecules and hence, acts as a dehydrating agent e.g.,

$$\text{HCOOH} \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{H}_2\text{O} + \text{CO}$$

(iii) H₂SO₄ oxidises metals, non-metals and other compounds.

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

2HI + H_2SO_4 \loggamma I_2 + SO_2 + 2H_2O

19. (i) Zone refining is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal.

(ii) Liquation method is used for purification of such metals when the impurities are less fusible than the metals themselves, *i.e.*, the melting points of the metals are lower than those of the impurities.

(iii) Chromatographic method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. The adsorbed components are removed (eluted) by using suitable eluent.

20. (i) The process of extraction of a metal by dissolving the ore in a suitable reagent followed by precipitation or displacement by a more reactive or more electropositive metal is called hydrometallurgy. This process is based on the principle of electrochemical series, that a more electropositive metal displaces a less electropositive metal from its salt solution e.g.,

 $Ag_2S + 4NaCN \longrightarrow 2Na[Ag(CN)_2] + Na_2S$ $2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag \downarrow$



(ii) During the smelting of roasted copper pyrites ore, a molten mass is obtained at the hearth of the blast furnace. This molten mass contains mostly cuprous sulphide and a little ferrous sulphide, which is called as matte.

21. (i) Zinc is more powerful reducing agent in comparison to copper. Zinc is also cheaper than copper.(ii) Partial roasting of sulphide ore forms some oxide. This oxide then reduces the remaining sulphide ore into metal.

 $2CuS + 3O_2 \longrightarrow 2CuO + 2SO_2$

 $2CuO + CuS \longrightarrow 3Cu + SO_2$ (Auto reduction) (iii) Chalcocite is a sulphide ore. It is to be converted into oxide and thus roasting and not calcination is done.

Compound (X) gives a brick red flame in flame test. Thus, it is a calcium compound. It smells of chlorine on exposure, which suggests that it is bleaching powder. It is confirmed by reaction (ii).

(i)
$$CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$$

(ii) $CaOCl_2 + 2CH_3COOH \longrightarrow$
 $(CH_3COO)_2Ca + H_2O + Cl_2$
 $2KI + Cl_2 \longrightarrow 2KCl + I_2^{\uparrow}$
(brown vapours)

22. (i) Iron ore contains silica as the impurity, so for extraction of iron from its ore a basic flux (limestone) is required.

 $\begin{array}{c} \text{CaCO}_{3} \longrightarrow \text{CaO} + \text{CO}_{2} \\ \text{SiO}_{2} + \text{CaO} \longrightarrow \text{CaSiO}_{3} \\ \text{Acidic-} & \text{Basic-} & \text{Slag} \\ \text{impurity flux} \end{array}$

On the other hand copper ore contains ferrous sulphide as the impurity. After roasting the ore ferrous sulphide is converted to ferrous oxide, which is basic in nature. Therefore acidic flux (SiO_2) is required for extraction of copper.

 $\begin{array}{l} 2FeS+3O_{2} \longrightarrow 2FeO+2SO_{2} \uparrow \\ FeO+SiO_{2} \longrightarrow FeSiO_{3} \\ Basic- Acidic- Slag \\ impurity flux \end{array}$

(ii) For the extraction of iron, coke or charcoal is used as reducing agent. But the actual reducing agent is carbon monoxide, formed from coke.

23. (i)
$$2K_2MnF_6 + 4SbF_5 \longrightarrow 4 KSbF_6 + 2MnF_4$$

 $2MnF_4 \longrightarrow 2MnF_3 + F_2$
 $2K_2MnF_6 + 4SbF_5 \longrightarrow 4KSbF_6 + 2MnF_3 + F_2$

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In this reaction, weak Lewis acid MnF_4 is displaced by stronger one, SbF_5 from K_2MnF_6 . Being unstable in nature MnF_4 decomposes to MnF_3 and F_2 .

(ii) Helium gas is used in gas cooled nuclear reactors and liquid helium is used as cryogenic agent for carrying out various reactions at low temperatures.



24. (i) The aluminate in solution is neutralised by passing CO₂ gas and hydrated Al₂O₃ is precipitated. 2Na[Al(OH)₄]_(aq) + CO_{2(g)} \rightarrow Al₂O₃.*x*H₂O_(s)

+ 2NaHCO_{3(aq)}

(ii) Aluminium has great affinity for oxygen. It acts as a reducing agent when the metal having high melting point is to be extracted from its oxide.

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$$

(iii)

(iii) Copper obtained in the extraction from copper pyrites has a blistered appearance due to the evolution of SO₂, which get trapped in cooler parts of surface of copper. $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

25. (i) The nitrogen atom is small in size. It can undergo lateral overlapping forming multiple bonds, *i.e.*, nitrogen molecule consists one sigma and two π -bonds (N \equiv N). The discrete molecules are held together by weak van der Waals' forces. Thus, nitrogen is a gas. As the size increases, the lateral overlap is not strong and multiple bonds are not formed. Hence, the rest of the members of Vth group are solids.

(ii) Liquor ammonia has high vapour pressure at room temperature. It is cooled before opening as to reduce the vapour pressure inside the bottle in order to prevent bumping.

(iii) Nitrogen being more electronegative, hydrogen bonding is observed in ammonia, *i.e.*, association of molecules occurs through hydrogen bonding. This property is absent in phosphine.

(iv) Nitrogen cannot extend its valency from 3 to 5 due to absence of *d*-orbitals while phosphorus shows pentacovalency as *d*-orbitals are present in it.

(v) The bond length is high due to repulsion of the bonded pair by both nitrogen and fluorine atoms. This is due to their smaller size and high electron density.

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OR

(i)
$$2NaIO_3 + 5NaHSO_3 \longrightarrow$$

 $3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2$
(ii) $Cl_2 + 2KOH_{(aq)} \longrightarrow KCl + KClO + H_2O$
(iii) $4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \longrightarrow$

$$2CrO_2Cl_2 + 4NaHSO_4 + 2KHSO_4 + 3H_2O$$
(iv) $3Br_2 + 3Na_2CO_3 \longrightarrow 5NaBr + NaBrO_3 + 3CO_2$
(Conc. and hot)

(v)
$$NH_3 + 3Cl_3 \longrightarrow NCl_3 + 3HCl_3$$

26. (a) Froth floatation method : The method is used for removing gangue from sulphide ores and it is based upon the fact that the surface of sulphide ore is preferentially wetted by oils while that of gangue is preferentially wetted by water. In this process, a suspension of the powdered ore is made with water and collectors and froth stabilisers are added to it.

Collectors (e.g., pine oil, fatty acids, xanthates, etc.) enhance non-wettability of the mineral particles and froth stabilisers (e.g., cresols, aniline) stabilise the froth. The mineral particles become wet by oils while the gangue particles wet by water. A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed which carries the mineral particles. The froth is light and skimmed off.

(ii) (a) Carbon is suitable reducing agent for reduction of zinc oxide. Reduction of Cr₂O₃ by carbon is not thermodynamically favourable.

(b) Free energy change for the reduction of copper sulphide to copper by carbon is positive, whereas, $\Delta_r G^\circ$ for the reduction of copper oxide to copper by carbon is negative and hence feasible.

OR

(i) The following reactions take place during extraction of copper from copper pyrites.

$$\begin{array}{c} 2\text{CuFeS}_2 + \text{O}_2 \longrightarrow \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2^{\uparrow} \\ 2\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2^{\uparrow} \\ 2\text{FeS} + 3\text{O}_2 \longrightarrow 2\text{FeO} + 2\text{SO}_2 \\ \text{FeS} + \text{Cu}_2\text{O} \longrightarrow \text{FeO} + \text{Cu}_2\text{S} \\ \text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3 \\ (\text{Sand}) \qquad (\text{Slag}) \\ \text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \longrightarrow 6\text{Cu} + \text{SO}_2^{\uparrow} \end{array}$$

(ii) The molten matte in the converter contains small amounts of ferrous sulphide. In presence of blast of hot air, ferrous sulphide is converted to ferrous oxide, which is basic in nature. To remove this basic impurity, the inner wall of the Bessemer converter is lined with an acidic flux, *i.e.*, silica (SiO₂).

This silica reacts with ferrous oxide giving the fusible product ferrous silicate, which floats on the surface of molten mass and can be removed.

$$\begin{array}{c} 2\text{FeS} + 3\text{O}_2 \longrightarrow 2\text{FeO} + 2\text{SO}_2 \\ \text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3 \\ \text{(Impurity)} \quad (\text{Flux}) \quad (\text{Slag}) \end{array}$$

27. (i) With the increase in the molecular mass, the size of the noble gas is increased, consequently the extent of van der Waals' forces is also increased among the molecules. Due to the increase in the forces with the increase in molar mass, the boiling point will also increase.

(ii) It is because neon light is visible through mist and fog and that too from long distance.

(iii) It is because of the property of neon to carry extremely high current under high pressure even low voltage, it is used in safety devices for protecting electrical instruments.

(iv) Because NO_2 contains odd number of valence electrons and on dimerisation, it is converted to stable N_2O_4 molecule with even number of electrons.

$$N \not\subseteq_{O}^{O} \xrightarrow{\text{Dimerisation}} {}_{O}^{O} \not\geq N - N \not\subseteq_{O}^{O}$$

(v) Flourine is most electronegative atom, hence it brings out the maximum covalency of sulphur, but hydrogen, being less electronegative is not able to do so, hence, formation of SH_6 is not possible.

OR

(i) Contact process : It involves three steps :

(a) Burning of sulphur or sulphide ore in air to generate SO₂.

 $S + O_2 \rightarrow SO_2$; $4FeS_2 + 11O_2 \rightarrow 8SO_2 + 2Fe_2O_3$ (b) Conversion of SO_2 to SO_3 by reaction with oxygen in the presence of $\rm V_2O_5$ catalyst.

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$
; $\Delta_r H^\circ = -196 \text{ kJ mol}^{-1}$

(c) The SO_3 gas from the catalytic converter is absorbed in conc. H₂SO₄ to form oleum (H₂S₂O₇). Dilution of oleum with water gives H₂SO₄ of desired concentration.

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$

(Oleum)
 $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$
 VaO_4 and has obtained by 1

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(ii) XeO_3 can be obtained by hydrolysis of XeF_4 and XeF_6 .

 $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24 \text{ HF} + 3O_2$ $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

Structure :
$$V_{0} = V_{0}$$

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Class XII MONTHLY TUNE UP! PRACTICE PROBLEMS



These practice problems enable you to self analyse your extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Performance analysis table given at the end will help you to check your readiness.

- Electrochemistry
- Chemical Kinetics

Total Marks : 120

(a) X

NEET / AIIMS

Only One Option Correct Type

- 1. According to Kohlrausch's law the limiting value of equivalent conductivity of an electrolyte A_2B is given by
 - (a) $\lambda_{A^{+}}^{\infty} + \lambda_{B^{2-}}^{\infty}$ (b) $\frac{1}{2}\lambda_{A^{+}}^{\infty} + \lambda_{B^{2-}}^{\infty}$ (c) $\lambda_{A^{+}}^{\infty} + \frac{1}{2}\lambda_{B^{2-}}^{\infty}$ (d) $2\lambda_{A^{+}}^{\infty} + \lambda_{B^{2-}}^{\infty}$
- Using electrolytic method, if cost of production of 1 L of oxygen at STP is ₹ x, the cost of production of 10 L of hydrogen at STP will be
 - (a) 10x (b) x/16 (c) 10x/32 (d) 10x/2
- 3. For the reaction, $A + B \rightarrow C + D$. The variation of the concentration of the products is given by the curve



4. Consider the reaction, 2A + B → products. When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is

Time Taken : 60 Min.

(a)	s^{-1}	(b) $L \mod^{-1} s^{-1}$
(c)	$mol L^{-1} s^{-1}$	(d) none of these.

- 5. The solution of $CuSO_4$ in which copper rod is immersed is diluted to 10 times, then the reduction electrode potential
 - (a) increases by 0.030 V
 - (b) decreases by 0.030 V
 - (c) increases by 0.059 V $\,$
 - (d) decreases by 0.059 V

6. In acidic medium, MnO₂ is an oxidant as : MnO_{2(s)} + 4H⁺ + 2e⁻ → Mn²⁺ + 2H₂O If the pH of the solution is decreased by one unit, the electrode potential of the cell will be changed by

(a) -0.118 V (b) 0.118 V (c) 0.236 V (d) -0.236 V

7. *k* for a zero order reaction is 2×10^{-2} mol L⁻¹ sec⁻¹. If the concentration of the reactant after 25 sec is 0.5 M then the initial concentration must have been (a) 0.5 M (b) 1.25 M

(u)	0.0 101	(U)	1.20 101
(c)	12.5 M	(d)	1.0 M

8. In the upper atmosphere, H₂O and oxygen react bimolecularly to form two OH⁻. ΔH for this reaction is 72 kJ/mol at 500 K and $E_a = 77$ kJ/mol, then E_a for two bimolecular recombinations of 2OH⁻ radicals to form H₂O and O is

73

(a)	3 kJ mol^{-1}	(b) 4 kJ mol^{-1}
(c)	5 kJ mol ⁻¹	(d) none of these.

9. Calculate the standard free energy change for the reaction, $2Ag + 2H^+ \rightarrow H_2 + 2Ag^+$.

(Given :
$$E_{Ag}^{+}/Ag = 0.80 \text{ V}$$
)

(a) + 154.4 kJ (b) + 308.8 kJ

(c)
$$-154.4$$
 kJ (d) -308.8 kJ

10. EMF of an $H_2 - O_2$ fuel cell

- (a) is independent of partial pressures of $\rm H_2$ and $\rm O_2$
- (b) decreases on increasing $p_{\rm H_2}$ and $p_{\rm O_2}$
- (c) increases on increasing p_{H_2} and p_{O_2}
- (d) varies with the concentration of OH⁻ ions in the cathodic and anodic compartments.
- 11. The energy of activation for forward and backward change for an endothermic reaction; $X \rightarrow Y$ are E_f and E_b respectively. Which of these is correct?
 - (a) $E_b < E_f$
 - (b) $E_b > E_f$
 - (c) $E_b = E_f$
 - (d) No relation between them
- 12. For three reactions of 1, 2 and 3 order respectively, the rate constants k_1 , k_2 and k_3 are equal if concentration is expressed in terms of mol L⁻¹. If concentration is expressed in terms of mol mL⁻¹,

their relation is $\frac{k_1}{x_1} = \frac{k_2}{x_2} = \frac{k_3}{x_3}$. The values of x_1, x_2 and x_3 are (a) $10^3 \ 10^6 \ 10^9$ (b) $10^9 \ 10^6 \ 10^3$

(a) 10^3 , 10^6 , 10^9 (b) 10^9 , 10^6 , 10^3 (c) 10^{-3} , 10^{-6} , 10^{-9} (d) 10^{-9} , 10^{-6} , 10^{-3}

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.
- **13. Assertion :** The cell potential of mercury cell is 1.35 V which remains constant.

Reason : In mercury cell, the electrolyte is a paste of KOH and HgO.

CHEMISTRY TODAY | AUGUST '18

14. Assertion : During electrolysis of $CuSO_{4(aq)}$ using copper electrodes, copper is dissolved at anode and deposited at cathode.

Reason : Oxidation takes place at anode and reduction at cathode.

15. Assertion : If the activation energy of a reaction is zero, the rate constant becomes independent of the temperature.

Reason : Lower the activation energy, faster is the reaction.

JEE MAIN / ADVANCED

Only One Option Correct Type

- 16. The inactivation of a viral preparation in a chemical bath is found to be first order reaction. If in the beginning 2.5% of the virus is inactivated per minute, the rate constant of the viral inactivation is (a) $4.16 \times 10^{-2} \text{ s}^{-1}$ (b) $4.16 \times 10^{-3} \text{ s}^{-1}$
 - (c) $4.16 \times 10^{-4} \text{ s}^{-1}$ (d) $4.16 \times 10^{-5} \text{ s}^{-1}$
- **17.** Value of E_3° may by calculated from

Fe
$$\xrightarrow{E_1^\circ}$$
 Fe^{2+ $\xrightarrow{E_2^\circ}$} Fe³⁺
 $\xrightarrow{E_3^\circ}$ fe³⁺
(a) $\frac{E_1^\circ}{E_2^\circ} + 1$ (b) $\frac{E_2^\circ + 2E_1^\circ}{3}$
(c) $\frac{E_1^\circ + E_2^\circ}{2}$ (d) $\frac{E_1^\circ + 2E_2^\circ}{2}$

18. A 1.0 M of each metal halides AX_3 , BX_2 , CX_3 and DX_2 is electrolysed using platinum electrodes. If

 $E_A^{o_{3^+/A}} = 1.50 \text{ V}, E_{B^{2^+/B}}^{o_{2^+/B}} = 0.34 \text{ V},$ $E_C^{o_{3^+/C}} = -0.74 \text{ V}, E_{D^{2^+/D}}^{o_{2^+/D}} = -2.37 \text{ V}, \text{ the correct}$ sequence in which the various metals are deposited at the cathode, is

(a)
$$A, B, C, D$$
 (b) D, C, B, A
(c) A, B, C (d) C, B, A

19. The value of concentration of *C* after 5 h of reaction (parallel) if initial concentration of *A* is 0.25 M, is



(a)
$$7.56 \times 10^{-2}$$
 M (b) 7.56×10^{-3} M
(c) 0.756 M (d) 7.56×10^{-4} M

More than One Options Correct Type

20. The rate constant of a reaction is given by : $k = 2.1 \times 10^{10} e^{-2700/RT}$

It suggests that

- (a) log k vs. $\frac{1}{T}$ will be straight line with slope = $\frac{-2700}{2.303 R}$
- (b) $\log k vs. \frac{1}{T}$ will be a straight line with intercept on $\log k$ axis = $\log 2.1 \times 10^{10}$
- (c) the number of effective collisions are $2.1 \times 10^{10} \text{ cm}^{-3} \text{s}^{-1}$
- (d) half-life of the reaction increases with increase of temperature

- **21.** If $\vec{E}_{Ni^{2+}|Ni} = 0.25V$, $\vec{E}_{Cu^{2+}|Cu} = 0.34V$, $\vec{E}_{Ag^{+}|Ag} = 0.8V$ and $\vec{E}_{Zn^{2+}|Zn} = -0.76V$, then which of the following reactions under standard condition will not take place in the specified direction spontaneously?
 - (a) $\operatorname{Cu}_{(s)} + \operatorname{Ni}_{(aq)}^{2+} \rightarrow \operatorname{Cu}_{(aq)}^{2+} + \operatorname{Ni}_{(s)}$
 - (b) $\operatorname{Cu}_{(s)} + 2\operatorname{Ag}_{(aq)}^+ \rightarrow \operatorname{Cu}_{(aq)}^{2+} + 2\operatorname{Ag}_{(s)}$
 - (c) $\operatorname{Cu}_{(s)} + 2\operatorname{H}^+_{(aq)} \rightarrow \operatorname{Cu}^{2+}_{(aq)} + \operatorname{H}_{2(g)}$
 - (d) $\operatorname{Zn}_{(s)} + 2\operatorname{H}_{(aq)}^{+} \rightarrow \operatorname{Zn}_{(aq)}^{2+} + 3\operatorname{H}_{2(g)}$
- **22.** If 90 g of water is electrolysed completely with 50% current efficiency
 - (a) 10 Faraday of electricity will be consumed
 - (b) 20 Faraday of electricity will be consumed
 - (c) 168 L (STP) of gases will be produced
 - (d) 84 L (STP) of gases will be produced.

3 AMAZING FACTS YOU MUST KNOW

1. DNA is flame retardant

Coating cotton cloth with DNA, researchers found the genetic material reduced the fabric's flammability. When it's heated, the phosphate from DNA produces phosphoric acid, which replaces the water in cotton fibers as a flame-retarded residue. The bases, which contain nitrogen, react to produce ammonia which inhibits combustion.



${f 2.}$ Super fluid Helium defies gravity and climbs on walls

A remarkable transition occurs in the properties of liquid helium at the temperature 2.17 K (very close to absolute zero), called the "lambda point" for helium. Part of the liquid becomes a "superfluid", a zero viscosity fluid which will move rapidly through any pore in the apparatus.



${\mathfrak S}.$ Peanuts Are One of the Ingredients in Dynamite

Peanut oil can be processed to produce glycerol, which can be used to make nitroglycerine, an explosive liquid used in dynamite. However, there are other processes that can be used to make dynamite without using peanuts at all. So, this little fact isn't completely false and it isn't completely true. 23. For the reaction $A \to B$, the rate law expression is $-\frac{d[A]}{dt} = k[A]^{1/2}$. If initial concentration of A

is A_0 . Which of the following statements are true regarding this reaction?

- (a) The plot of \sqrt{A} against 't' will be linear.
- (b) The half life period is $t_{1/2} = \frac{\sqrt{2}(\sqrt{2}-1)}{k}\sqrt{A_0}$.
- (c) There is a linear decrease of rate of reaction with time.
- (d) The integrated form of rate expression is $\sqrt{k} = k \sqrt{k}$

$$\sqrt{A} = -\frac{\pi}{2}t + \sqrt{A_0}.$$

Numerical Value Type

- 24. For the decomposition of dimethyl ether the value of A in the Arrhenious equation $k = Ae^{-E_a/RT}$ is 1.26×10^{13} and value of E_a is 58.5 kcal. Calculate half life period for first order decomposition at 527 °C.
- **25.** A current of 1.70 A is passed through 300 mL of 0.160 M solution of $ZnSO_4$ for 230 sec with a current efficiency of 90%. Find the molarity of Zn^{2+} after the deposition of Zn. Assume the volume of the solution remains constant during electrolysis.
- 26. Calculate the *emf* at 298 K of the cell : $Zn|ZnSO_4(aq0.01M)||KCl(aq satd.), Hg_2Cl_{2(s)}|Hg$ Given, the potential of calomel electrode is 0.242 V and the standard potential of the zinc electrode is -0.763 V.

Comprehension Type

Suppose 50 bacteria are placed in a flask containing nutrients, so that they can multiply. A study at 35 $^{\circ}$ C gave the following results :

Time (minutes):015304560Number of bacteria:1002004008001600

27. The rate constant for the reaction is

- (a) 0.0462 min^{-1} (b) 0.462 min^{-1}
- (c) 4.62 min^{-1} (d) 46.2 min^{-1}

 The expression used for calculating the rate constant value in this experiment is

(a)
$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$
 (b) $k = -\frac{2.303}{t} \log \frac{a}{a+x}$
(c) $k = \frac{0.693}{t}$ (d) $k = \frac{x}{t}$

Matrix Match Type

29. Match the Column-I with Column-II and choose the correct answer using the codes given below :

		Colu	mn-I			Column-II
		(Ter	rm)			(Unit)
(A)	Spe	ecific co	onduct	(p)	$ohm^{-1} cm^2 eq^{-1}$	
(B)	Ce	ll const	ant	(q)	cm ⁻¹	
(C)	Eq	uivalen	t		(r)	ohm ⁻¹ cm ² /mol
	cor	nductar	nce			
(D)	Мс	olar cor	ductar	nce	(s)	$\mathrm{ohm}^{-1}\mathrm{cm}^{-1}$
Co	des	:				
	Α	В	С	D		
(a)	q	р	r	s		
(b)	r	р	q	s		
(c)	s	q	p	r		
(d)	q	s	p	r		

30. Match the Column-I with Column-II and choose the correct answer using the codes given below :

e	0	
Column-I		Column-II
(Graph)		(Slope)
(A) <i>C</i> vs t for zero order	(p)	Unity
(B) log <i>C</i> vs t for first order	(q)	Zero
(C) $\left(-\frac{dC}{dt}\right) vs C$ for zero order	(r)	- <i>k</i>
(D) in $(-dC/dt)$ vs lnC for	(s)	-k/2.303
first order		
(where, $k =$ rate constant, $C =$	conc	centration of
reaction at any time <i>t</i>).		

Codes	:			
Α	В	С	D	
(a) r	S	q	р	
(b) s	р	q	r	
(c) p	q	S	r	
(d) q	r	S	р	

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CHEMISTRY MUSING

PROBLEM SET 61

Chemistry Musing was started from August '13 issue of Chemistry Today. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / JIPMER with additional study material. In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today. The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct

solutions will be published in the next issue. We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

JEE MAIN/NEET

- 1. Which of the following statements is incorrect?
 - (a) When pH > 10.5 xenon trioxide in solution forms hydrogen xenate ion.
 - (b) Partial hydrolysis of XeF₆ gives oxyfluorides.
 - (c) Xenon trioxide on treatment with xenon oxytetrafluoride gives xenon trioxydifluoride.
 - (d) $XeOF_4$ can be stored in Ni containers for long period.
- 2. The van der Waals' constant 'b' for oxygen is 0.0318 L mol⁻¹. Calculate the diameter of the oxygen molecule.

(a)	1.466 Å	(b)	2.932 Å
(c)	2.113 Å	(d)	3.819 Å

3. The product of the given reaction is



4. The amount of energy released when 10^{12} atoms of Cl are converted to Cl⁻ ions, is 58×10^{-10} J

$$\begin{aligned} \text{Cl}_{(g)} + e^- &\rightarrow \text{Cl}_{(g)}^-\\ \text{Calculate the } \Delta_{eg}H \text{ of Cl atom in eV atom}^{-1}.\\ (a) & -0.036 \text{ eV atom}^{-1} \quad (b) & -3.48 \text{ eV atom}^{-1}\\ (c) & -0.038 \text{ eV atom}^{-1} \quad (d) & -0.361 \text{ eV atom}^{-1} \end{aligned}$$

5. *Ortho*-isomers have dipole moments. In which cases dipole moments are maximum and minimum?

	X	Y	X	Y
	(Max	imum)	(Minin	num)
(a)	Cl	Cl	CH ₃	CH_3
(b)	OH	CH ₃	Cl	Cl
(c)	OH	NO_2	CH ₃	CH_3
(d)	OH	NO ₂	Cl	Cl
		JEE ADV	ANCED	

6. Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell, $Ag|Ag^+$ (satd. Ag_2CrO_4 soln.) || Ag^+ (0.1 M)|Ag is 0.164 V at 298 K.

					100			
(C)	4.75	x 10	•••••	(a)	2.29	× 10		
(a)	4 75	$\times 10^{-4}$		(\mathbf{J})	2 20	~ 10	-4	
(a)	4.75	$\times 10^{-1}$	-	(b)	2.29 :	$\times 10$		



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COMPREHENSION H₃PO₄ 150°C 0 $CH_{3} - CH_{2} - CH_{2} - Br \xrightarrow{Mg}_{dry \text{ ether}} A \xrightarrow{(i) \text{ Et } -C - H \\ (ii) \text{ H}_{2}O \xrightarrow{} B} A \xrightarrow{Me - C \equiv C - H \\ -(C_{3}H_{8}) \xrightarrow{} F}$ $J \xleftarrow{\text{Br}_2}_{\text{CCl}_4} H \xleftarrow{(i) \text{Pd/BaSO}_4}_{(ii) \text{H}_2} G \xleftarrow{\text{Me} - I}_{\text{dry ether}}$

- 7. Identify "Z" compound, $X \xrightarrow{Mg Hg} Y \xrightarrow{H^+} Z$ where X is a functional isomer of "W" which is next higher homologue of "I"
 - Me Me (a) Me - C - C - Et (b) Me - C - C - MeОН ОН



- 9. If an element (at.wt. = 40) crystallises in *fcc* lattice, with a = 0.50 nm. If it contains 0.25% Schottky defects, the density of unit cell approximately is (use $N_A = 6 \times 10^{23}$)
- 10. Calculate total number of alkene products when 2-chloro-2-cyclobutyl hexane react with alcoholic KOH and heat. ک ک





PHYSIC

78 CHEMISTRY TODAY | AUGUST '18

YQUASK

Do you have a question that you just can't get answered? Use the vast expertise of our MTG team to get to the bottom of the question. From the serious to the silly, the controversial to the trivial, the team will tackle the questions, easy and tough. The best questions and their solutions will be printed in this column each month.

1. How to distinguish between phenol and benzyl alcohol? (Poulami Das)

Ans. Phenol is a benzene hydroxide in which -OH group is directly attached to benzene, but benzyl alcohol is a 1-phenylmethanol in which -CH₂OH group is directly attached to benzene, not -OH group. The test which can distinguish between alcohol and phenol can be used to distinguish between benzyl alcohol and phenol. e.g.,

Ferric chloride test : Phenol gives violet colour with neutral FeCl₃ solution.

$$6 \underbrace{\bigcirc}_{\text{Phenol}} + \text{FeCl}_3 \longrightarrow 3\text{H}^+ + [\text{Fe}(\text{OC}_6\text{H}_5)_6]^{3-} + 3\text{HCl}}_{(\text{Violet complex})}$$

Benzyl alcohol \Rightarrow No reaction

Bromine water test : Phenol gives white ppt. with Br₂-water due to the formation of 2, 4, 6-tribromophenol.



2. Which has more calories, table sugar or aspartame? (Lakshay Sareen, Amritsar)

Ans. Calories are the measure of the energy made available when we digest and metabolize food. A substance that we do not metabolize, releases no energy, it "has no calories" and is not a food.

However, aspartame is metabolized. Aspartame produces 4 kilocalories of energy per gram when metabolized, sucrose (table sugar) produces 3.9 kilocalories. However, aspartame is approximately 200 times sweeter than sucrose, so it is consumed in much smaller doses.

Thus, metabolism of aspartame does yield calories, but far fewer than those obtained from the amount of sucrose required to produce the same sweetening effect.

3. Why doesn't the planet Uranus explode if it contains so much hydrogen and methane?

(Swapnil Sharma, Karnataka)

Ans. The planet Uranus indeed contains a significant amount of hydrogen and methane, both are highly flammable gases. However, the burning of methane or hydrogen requires oxygen. There is no free oxygen on the planet Uranus. Methane is only explosive and flammable as long as there is oxygen or some other oxidizing agent present.

 $CH_4 + 2O_2 \rightarrow CO_2 + 2 H_2O + energy$

In the presence of oxygen, hydrogen is highly flammable, combusting to form water molecules according to the reaction : $2H_2 + O_2 \rightarrow 2H_2O + energy$

The atmosphere of the planet Uranus contains mostly hydrogen, helium, and methane. Interestingly, the methane in the atmosphere is what gives Uranus its distinctive blue color. Since, Uranus contains effectively zero free oxygen, the hydrogen and methane in the atmosphere does not burn or explode.



CHEMISTRY TODAY | AUGUST '18 79





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2. (c) : Read alc. KOH in the question as aq. KOH.



3. (d):



-OH is at para position so, it will be electron releasing. Me Me Me



4. (b, c) : As a shortcut, we can use Maxwell thermodynamic square. H



A = Helmholtz function

Thermodynamic potential :

82

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G = Gibbs free energy, U = Internal energy The Maxwell relationship is

$$-\left(\frac{\partial T}{\partial P}\right)_{S} = -\left(\frac{\partial V}{\partial S}\right)_{P} \text{ or } \left(\frac{\partial T}{\partial P}\right)_{S} = \left(\frac{\partial V}{\partial S}\right)_{P}$$

$$S \xrightarrow{H} \qquad P \qquad G \qquad \left(\frac{\partial S}{\partial V}\right)_{T} = \left(\frac{\partial P}{\partial T}\right)_{V}$$

5. (a, b) : In collision theory, apart from activation energy criteria, orientation factor also plays a big role. So, (c) is NOT correct. In collision theory, molecules are assumed to be hard spheres. So, (d) is NOT correct. At higher temperature, reactivity increases.

 $Mn^{+7} \rightarrow Mn^{+2}$ can take place at a faster rate.

Catalysts make temporary bonds with the reactants to give an intermediate complex.

6. (a,c,d) : (a) Baeyer-Villiger oxidation. Migration of electron donor takes place.

(b) Carbon number is increasing without any external reagent addition.



(b): Maximum buffer capacity, $\eta = 2.303 \frac{ab}{a+b}$ = $2.303 \times \frac{0.5 \times 0.5}{(0.5+0.5)} \approx 0.57$ 7.

8. (a, b, c, d)

9. (b): Ti metal has great affinity to oxygen atom and it is coordinated with carbonyl oxygen and makes carbonyl carbon more electrophilic. Intramolecular nucleophilic attack takes place on more electrophilic site.



 t_1 is half-life when initial amount is a_1 and t_2 is halflife when initial amount is a_2 .

According to the problem, $a_1 = 55.5$ kPa; $t_1 = 340$ sec ; $a_2 = 28.9$ KPa; $t_2 = 178$ sec

$$\therefore \quad \eta = \frac{\log \frac{340}{178} + \log \frac{28.9}{55.5}}{\log \frac{28.9}{55.5}} = 8.24 \times 10^{-3} \approx 0$$

11. (40) 12. (225): $\frac{P_2}{P_1} = \frac{V_2}{V_1} \implies P_2V_1 = P_1V_2$

CHEMISTRY MUSING

SOLUTION SET 60

- 1. (c) : Compound (X) is bleaching powder, CaOCl₂. (i) CaOCl₂+2KI+2CH₃COOH \longrightarrow Ca(CH₃COO)₂ +2KCl + H₂O + I₂ (ii) CaOCl₂ + CO₂ \longrightarrow CaCO₃ + Cl₂ White ppt. (iii) CaOCl₂ + H₂O \longrightarrow Ca(OH)₂ + Cl₂ C₂H₅OH + Cl₂ \longrightarrow CH₃CHO + HCl CH₃CHO + 3Cl₂ \longrightarrow CCl₃CHO + 3HCl 2CCl₃CHO + Ca(OH)₂ \longrightarrow 2CHCl₃ + (HCOO)₂Ca 6. 2. (c) : Al₂O₃ <u>conc. NaOH</u> NaAlO₂ + H₂O
- $NaAlO_{2} + HCl_{(dil.)} \longrightarrow NaCl + Al(OH)_{3}$ $2Al(OH)_{3} \xrightarrow{\Delta} Al_{2}O_{3} + 3H_{2}O$
- **3.** (c) : Anti-elimination via E2 mechanism takes place in presence of strong bases as follows :



4. (c) : In $[Cr(H_2O)_6]^{2+}$ ion, Cr is present as Cr^{2+} ion. Electronic configuration of Cr^{2+} ion is $3d^4$. Cr^{2+} ion in high spin states : $t_{2g}^3 e_g^{-1}$ $CFSE = -3 \times 0.4 \Delta_o + 1 \times 0.6 \Delta_o$ $= -1.2 \Delta_o + 0.6 \Delta_o = -0.6 \Delta_o = -0.6 \times 13900 \text{ cm}^{-1}$ $= -8340 \text{ cm}^{-1}$ Cr^{2+} ion in low spin states : $t_{2g}^4 e_g^0$ $CFSE = -4 \times 0.4 \Delta_o + P$

$$= -1.6 \times 13900 + 23500 \text{ cm}^{-1}$$
$$= (-22240 + 23500) \text{ cm}^{-1} = +1260 \text{ cm}^{-1}$$

CFSE value with a negative sign indicates net lowering of energy *i.e.*, gain in stability, hence high spin state is more stable.

5. (c) : Maximum temperature attained by gas in between *B* to *C*. According to equation of straight line,

$$\frac{P-4}{1-4} = \frac{V-1}{2-1}$$

84

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$$\Rightarrow P-4=-3V+3$$

$$\Rightarrow P=7-3V$$
For 1 mole gas, $PV = RT$

$$\therefore \frac{RT}{V} = 7-3V; RT = 7V-3V^2 \qquad ...(i)$$

$$R\frac{dT}{dV} = 7-6V = 0$$

$$V = \frac{7}{6} \quad [\text{put in Eq. (i)}]$$

$$RT = \left(7-3\times\frac{7}{6}\right)\times\frac{7}{6}$$

$$\Rightarrow T = \frac{49}{12R}$$
(b): $PV = \frac{W}{RT}$

(b):
$$PV = \frac{1}{M}RT$$

 $\Rightarrow \rho = \frac{w}{V} = \frac{PM}{RT}$...(i)

Therefore, we need to find the molecular weight of moist air. To find the molecular weight of a mixture of gas, we need the molar composition or mole fraction of the gas mixture.

Partial pressure of water (vapour) = $\frac{60}{100} \times \frac{23.78}{760}$ = 0.0187 atm \therefore Mole fraction of water vapour = $\frac{0.0187}{1}$ = 0.0187 Pressure of (N₂ + O₂) = (1 - 0.0187) atm = 0.9813 atm Let the pressure of N₂ be 79 x, then pressure of O₂ is 21x \therefore 79 x + 21 x = 0.9813 atm $x = \frac{0.9813}{100}$ x = 0.009813 atm

:. $p_{N_2} = 79 \ x = 0.7752 \ \text{atm}$:. $p_{O_2} = 21 \ x = 0.2061 \ \text{atm}$ Mole fraction of $N_2 = \frac{0.7752}{1} = 0.7752$

Mole fraction of $O_2 = \frac{0.2061}{1} = 0.2061$

Effective molecular weight of moist air = $(0.0187 \times 18) + (0.7752 \times 28) + (0.2061 \times 32)$ = 28.63 g/mol

Now, from eq (i), we get

$$\therefore \rho = \frac{1 \times 28.63}{0.082 \times 298} = 1.1716 \text{ g/L}$$



10. (2): Ether will not react in basic medium.



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