

OPEN STUDENT FOUNDATION

Chapters: 4

STD:12th Chemistry Practice Sheet Day -4

Date : 21/02/24

Section A

- Choose correct answer from the given options. [Each carries 1 Mark] [5]

- State perfect order of ionic radii.
 (A) $\text{Lu}^{3+} < \text{Yb}^{3+} < \text{Eu}^{3+} < \text{La}^{3+}$ (B) $\text{La}^{3+} < \text{Eu}^{3+} < \text{Yb}^{3+} < \text{Lu}^{3+}$
 (C) $\text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+} < \text{Yb}^{3+}$ (D) $\text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+} < \text{Yb}^{3+}$
- Mercury is in liquid form because.....
 (A) as d -orbital is completely filled up so $d-d$ overlapping is not possible.
 (B) as d -orbital is completely filled up so $d-d$ overlapping is possible.
 (C) its s -orbital is completely filled up.
 (D) it's volume is very small.
- Choose the correctly paired gaseous cation and its magnetic (spin only) moment (in BM)
 (A) Cr^{2+} , 4.90 BM (B) Mn^{2+} , 4.90 BM (C) Ti^{2+} , 3.87 BM (D) Co^{3+} , 4.87 BM
- Which of the following arrangements doesnot represent the correct order of the property stated against it ?
 (A) $\text{Sc} < \text{Ti} < \text{Cr} < \text{Mn}$: Number of oxidation states.
 (B) $\text{V}^{2+} < \text{Cr}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+}$: Paramagnetic behaviour
 (C) $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+}$: Ionic size
 (D) $\text{Co}^{3+} < \text{Fe}^{3+} < \text{Cr}^{3+} < \text{Sc}^{3+}$: Stability in aqueous solution
- Match the catalyst to the correct process.

Catalyst	Process
(a) TiCl_4	(i) Wacker process
(b) PdCl_4	(ii) Ziegler Natta polymerisation
(c) CuCl_2	(iii) Contact process
(d) V_2O_5	(iv) Deacon's process

- (A) (a) → (ii), (b) → (iii), (c) → (iv), (d) → (i) (B) (a) → (iii), (b) → (i), (c) → (ii), (d) → (iv)
 (C) (a) → (iii), (b) → (ii), (c) → (iv), (d) → (i) (D) (a) → (ii), (b) → (i), (c) → (iv), (d) → (iii)

Section B

- Write the answer of the following questions. [Each carries 2 Marks] [10]

- What is lanthanoid contraction ? What are the consequences of lanthanoid contraction.
- What are interstitial compounds ? Why are such compounds well known for transition metals ?
- Give method of preparation for $\text{K}_2\text{Cr}_2\text{O}_7$ and its two uses.
- Give Reason : TiCl_3 is paramagnetic while TiCl_4 is diamagnetic.
- Explain structures of manganate and permanganate ions.

Section C

- Write the answer of the following questions. [Each carries 3 Marks] [12]

- Discuss the position of d -block elements in the periodic table.

7. Discuss the magnetic properties of transition elements.
8. Give preparation of potassium dichromate and state its uses.
9. Discuss trends in oxidation states shown by actinoids.

Section D

● Write the answer of the following questions. [Each carries 4 Marks]

[12]

10. How would you account for the following :
 - (i) Of the d^4 species, Cr^{2+} is strongly reducing while manganese(III) is strongly oxidising.
 - (ii) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.
 - (iii) The d^1 configuration is very unstable in ions.
11. Give examples and suggest reasons for the following features of the transition metal chemistry :
 - (i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.
 - (ii) A transition metal exhibits highest oxidation state in oxides and fluorides.
 - (iii) The highest oxidation state is exhibited in oxoanions of a metal.
12. Write down the number of $3d$ electrons in each of the following ions: Ti^{2+} , V^{2+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} and Cu^{2+} . Indicate how would you expect the five $3d$ orbitals to be occupied for these hydrated ions (octahedral).

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OPEN STUDENT FOUNDATION

Chapters: 4

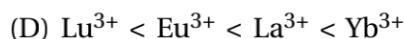
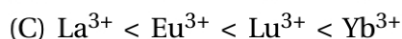
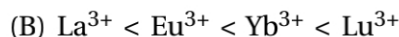
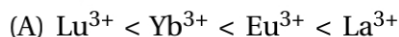
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Section A

- Choose correct answer from the given options. [Each carries 1 Mark] [5]

1. State perfect order of ionic radii.



Ans. (A) $\text{Lu}^{3+} < \text{Yb}^{3+} < \text{Eu}^{3+} < \text{La}^{3+}$

➡ While going from left to right in the periodic table as atomic number increases. Their atomic radii decreases, so ionic radii also decreases.



2. Mercury is in liquid form because.....

(A) as *d*-orbital is completely filled up so *d-d* overlapping is not possible.

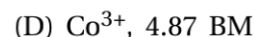
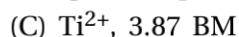
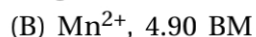
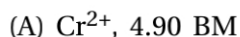
(B) as *d*-orbital is completely filled up so *d-d* overlapping is possible.

(C) its *s*-orbital is completely filled up.

(D) it's volume is very small.

Ans. (A) as *d*-orbital is completely filled up so *d-d* overlapping is not possible.

3. Choose the correctly paired gaseous cation and its magnetic (spin only) moment (in BM)



Ans. (A) Cr^{2+} , 4.90 BM

4. Which of the following arrangements doesnot represent the correct order of the property stated against it ?

(A) $\text{Sc} < \text{Ti} < \text{Cr} < \text{Mn}$: Number of oxidation states.

(B) $\text{V}^{2+} < \text{Cr}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+}$: Paramagnetic behaviour

(C) $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Mn}^{2+}$: Ionic size

(D) $\text{Co}^{3+} < \text{Fe}^{3+} < \text{Cr}^{3+} < \text{Sc}^{3+}$: Stability in aqueous solution

Ans. (B) $\text{V}^{2+} < \text{Cr}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+}$: Paramagnetic behaviour

5. Match the catalyst to the correct process.

Catalyst	Process
(a) TiCl_4	(i) Wacker process
(b) PdCl_4	(ii) Ziegler Natta polymerisation
(c) CuCl_2	(iii) Contact process
(d) V_2O_5	(iv) Deacon's process

(A) (a) → (ii), (b) → (iii), (c) → (iv), (d) → (i) (B) (a) → (iii), (b) → (i), (c) → (ii), (d) → (iv)

(C) (a) → (iii), (b) → (ii), (c) → (iv), (d) → (i) (D) (a) → (ii), (b) → (i), (c) → (iv), (d) → (iii)

Ans. (D) (a) → (ii), (b) → (i), (c) → (iv), (d) → (iii)

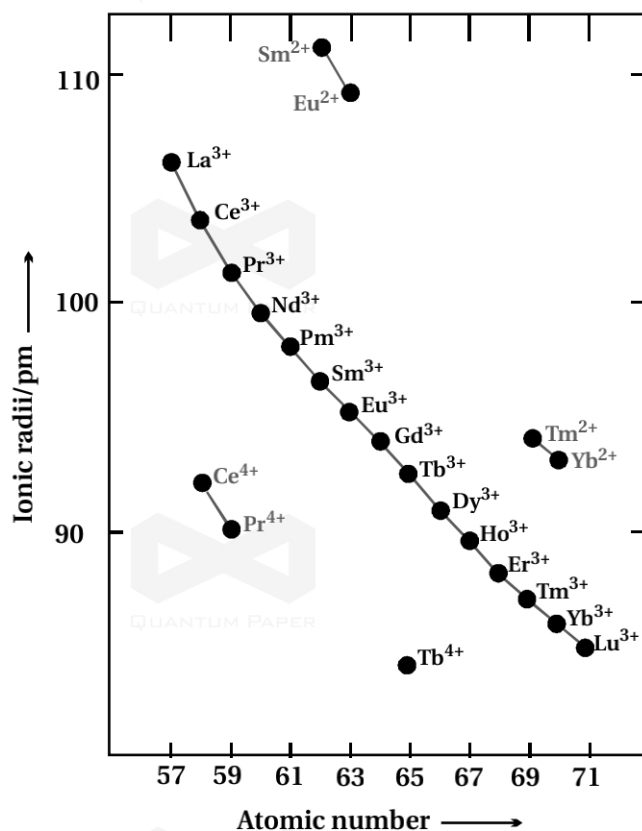
Section B

- Write the answer of the following questions. [Each carries 2 Marks] [10]

1. What is lanthanoid contraction ? What are the consequences of lanthanoid contraction.

➡ In lanthanoid series, there is overall decrease in the atomic and ionic radii cumulatively. This is called lanthanoid contraction and it is the unique feature in the chemistry of lanthanoid.

➡ Reason for lanthanoid contraction :



Trends in ionic radii of lanthanoids

➡ When moved from cerium to lutetium, there is increase in the nuclear charge with the increase in atomic number and the electrons are added in 4f orbital successively at the same time.

➡ The shielding of one 4f-electron by another is very poor because of shape of 4f-orbitals and even poor than d-electrons. As a result, the nuclear charge experienced by 4f-electrons increases which causes reduction in size to an atom or ion. The nuclear charge steadily increase with the atomic number on 4f-electrons and there is constant decrease of size of atom/ion because of poor shielding of 4f-electrons. This is known as lanthanoid contraction.

➡ The decrease in size is more sharp in case of tripositive ions than in atoms.

➡ The atomic radii of elements of second and third transition series are similar because of lanthanoid contraction. Ex. Zr-Hf, Nb-Ta etc. have nearly same size. Because of similar atomic radii, these elements show similar chemical properties and hence are very difficult to separate.

➡ The ionization enthalpies of elements of third transition series are higher than second transition series elements because of lanthanoid contraction though these elements belong to same groups.

➡ The basic strength of hydroxides of lanthanoids decrease from lanthanum to leutetium as a result of lanthanoid contraction the ionic character of hydroxide decreases with the decrease in size of lanthanoids. Hence, Ce(OH)₃ is most basic while Lu(OH)₃ is least basic. These hydroxides are separated on the basis of basic strength.

➡ Elements of third transition series show abnormally high densities because of lanthanoid contraction.

2. What are interstitial compounds ? Why are such compounds well known for transition metals ?

- ➡ Interstitial compounds are those which are formed when small atoms like B, H, C or N are trapped inside the crystal lattice of metals.
 - ➡ The transition elements form interstitial compounds with these elements. The B, H, C and N occupy the vacant spaces in the crystal lattice and as a result, the compounds formed are extremely hard.
 - ➡ They are classified as borides, hydrides, carbides or nitrides depending on nature of atoms trapped in the vacant sites. They are usually non-stoichiometric, neither typically covalent nor ionic. Ex. : TiC, Mn_4N , Fe_3H , $VH_{0.58}$ and $TiH_{1.7}$ etc.
 - ➡ The important physical and chemical characteristics of these compounds are :
 - (i) High melting points and even higher than pure metals.
 - (ii) They are extremely hard. Some borides approach diamond in hardness.
 - (iii) They retain metallic conductivity.
 - (iv) They are chemically inert.
3. Give method of preparation for $K_2Cr_2O_7$ and its two uses.

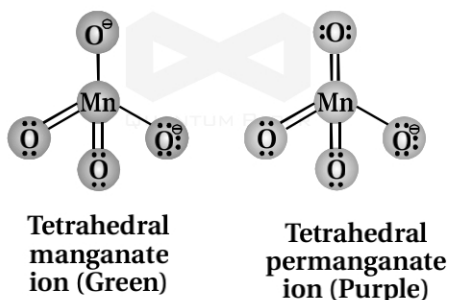
➡ Try Yourself

4. Give Reason : $TiCl_3$ is paramagnetic while $TiCl_4$ is diamagnetic.

➡ Try Yourself

5. Explain structures of manganate and permanganate ions.

➡ Both manganate and permanganate ions are tetrahedral in shape.



- ➡ The π -bonding takes place by overlapping of p -orbitals of oxygen with d -orbitals of manganese in both permanganate and manganate ions. Hence, there is $d\pi$ - $p\pi$ -bonding.
- ➡ The green manganate is permanganatic because of presence of one unpaired electron while purple permanganate is diamagnetic due to absence of unpaired electron.

Section C

- Write the answer of the following questions. [Each carries 3 Marks] [12]
- 6. Discuss the position of d -block elements in the periodic table.
- ➡ In a periodic table, the d -block elements are flanked between s -block elements and p -block elements and these elements occupy the large middle section of periodic table.
- ➡ The elements of d -block are present from group-3 to group-12 in periods 4 to 7. These elements have the d -orbitals of the penultimate energy level of atoms that receive electrons giving rise to four rows of the transition elements i.e., $3d$, $4d$, $5d$ and $6d$ as follows :
 - (i) The first transition series OR $3d$ -series belongs to 4th period.
 - (ii) The second transition series OR $4d$ -series belongs to 5th period.

(iii) The third transition series OR $5d$ -series belong to 6th period.

(iv) The fourth transition series OR $6d$ -series belongs to 7th period.

⇒ Hence, there are in all forty elements with ten elements in each series.

Electronic Configurations of outer orbitals of the Transition Elements (ground state)

1 st Series										
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

2 nd Series										
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

3 rd Series										
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

4 th Series										
	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
Z	89	104	105	106	107	108	109	110	111	112
7s	2	2	2	2	2	2	2	2	1	2
6d	1	2	3	4	5	6	7	8	10	10

7. Discuss the magnetic properties of transition elements.

⇒ In presence of magnetic field, two types of magnetic behaviour is observed for transition elements (i) Paramagnetism (ii) Diamagnetism. Paramagnetic substances are attracted by magnetic field while diamagnetic substances are repelled by the magnetic field.

⇒ Ferromagnetism is extreme form of para-magnetism where substance is very strongly attracted by the magnetic field. The para-magnetism arises from the presence of unpaired electrons in $(n-1)$ d -orbitals each such electron having a magnetic moment associated with its spin as well as orbital motion. For most of the transition elements, the orbital contribution is not of much significance.

⇒ The magnetic moment expresses the para-magnetic behaviour of transition metal ions and is calculated by using "Spin-only" formula

$$\mu = \sqrt{n(n+2)} \text{ BM where,}$$

n = number of unpaired electrons in $(n-1)$ d -orbitals

μ = Magnetic moment in Bohr Magneton (BM)

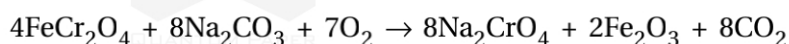
Calculated and Observed Magnetic Moments (BM)

Ion	Configuration	Unpaired electron(s)	Magnetic moment	
			Calculated	Observed
Sc ³⁺	3d ⁰	0	0	0
Ti ³⁺	3d ¹	1	1.73	1.75
Tl ²⁺	3d ²	2	2.84	2.76
V ²⁺	3d ³	3	3.87	3.86
Cr ²⁺	3d ⁴	4	4.90	4.80
Mn ²⁺	3d ⁵	5	5.92	5.96
Fe ²⁺	3d ⁶	4	4.90	5.3 – 5.5
Co ²⁺	3d ⁷	3	3.87	4.4 – 5.2
Ni ²⁺	3d ⁸	2	2.84	2.9 – 3.4
Cu ²⁺	3d ⁹	1	1.73	1.8 – 2.2
Zn ²⁺	3d ¹⁰	0	0	

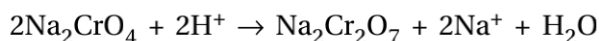
➡ The magnetic moment increases with the increase in number of unpaired electrons. If the magnetic moment is zero, the substance is diamagnetic and is repelled by magnetic field.

8. Give preparation of potassium dichromate and state its uses.

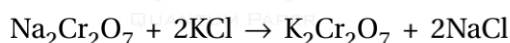
➡ **Preparation :** The yellow coloured sodium chromate is obtained by fusion of chromite ore [FeCr₂O₄] with sodium carbonate in free access of air.



The yellow coloured solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate Na₂Cr₂O₇ · 2H₂O can be crystallized out.



➡ Sodium dichromate is more soluble than potassium dichromate. The latter is therefore prepared by treating the solution of sodium dichromate with potassium chloride.



➡ Thus, orange coloured crystals of potassium dichromate are obtained.

➡ **Uses :** Used as primary standard in volumetric analysis because of its non hygroscopic nature.

➡ It is used in leather industry and formation of azo compounds.

➡ It used as oxidizing agent in organic chemistry.

➡ It is used to measure chemical oxygen demand (COD).

9. Discuss trends in oxidation states shown by actinoids.

➡ As compared to lanthanoids, there is greater range of oxidation states of actinoids because of the fact that 5f, 6d and 7s levels are of comparable energies. Also in actinoids, the 5f orbitals expand beyond 6s and 6p and participate in chemical bonding while in lanthanoids, 4f orbitals are shielded totally by outer electrons. Hence, actinoids show greater range of oxidation states.

Oxidation States of Actinium and Actinoids

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3		3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4	4						
		5	5	5	5	5								
			6	6	6	6								
				7	7									

- ➡ In general, actinoids show (+3) oxidation state. The elements in the first half of the series frequently show higher oxidation states. For example, the maximum oxidation state increases from (+4) in Th to (+5), (+6) and (+7) respectively in Pa, U and Np but decrease in succeeding elements.
- ➡ The actinoids resemble the lanthanoids in having more compounds in (+3) state than in the (+4) state. However, (+3) and (+4) ions tend to hydrolyse.

Section D

- Write the answer of the following questions. [Each carries 4 Marks] [12]

10. How would you account for the following :

- (i) Of the d^4 species, Cr^{2+} is strongly reducing while manganese(III) is strongly oxidising.
 - (ii) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.
 - (iii) The d^1 configuration is very unstable in ions.
- ➡ (i) Since Cr^{2+} is reducing, its configuration changes to d^3 from d^4 . d^3 configuration is half filled t_{2g} which is stable in aqueous solution. Mn^{3+} is oxidizing, its configuration changes to d^5 from d^4 . d^5 is extra stable as it is half-filled.
 - ➡ (ii) Co(II) gets oxidized to Co(III) easily because in presence of strong field ligands, the electrons get paired up forming diamagnetic octahedral complexes. These complexes are highly stable due to high CFSE.
 - ➡ (iii) d^1 configuration is highly unstable because after losing one e^- , the stable configuration (d^0) is attained or such species will undergo disproportionation reaction. For example.



11. Give examples and suggest reasons for the following features of the transition metal chemistry :

- (i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.
 - (ii) A transition metal exhibits highest oxidation state in oxides and fluorides.
 - (iii) The highest oxidation state is exhibited in oxoanions of a metal.
- ➡ (i) The lowest oxide of transition metal is basic because of their ability to get oxidized to higher oxidation states. The highest oxides of transition metal is acidic or amphoteric because of their ability to get reduced to lower oxidation states.
Ex. : MnO is basic, MnO_2 is amphoteric while Mn_2O_7 is acidic.
 - ➡ (ii) This is because of high electronegativities of oxygen and fluorine, the oxides and fluorides of transition metals are stable in highest oxidation states. in highest oxidation states.
Ex. : V_2O_5 , Mn_2O_7 , OsF_6 etc.
 - ➡ (iii) This is because of small size and high electro-negativity of oxygen, in addition it also has ability

to form multiple bonds with a transition elements. As a result, highest oxidation state is exhibited in oxoanions by the metals

Ex. : MnO_4^- , CrO_4^{2-} , VO_2^+ etc.

(+7) (+6) (+5)

12. Write down the number of $3d$ electrons in each of the following ions: Ti^{2+} , V^{2+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} and Cu^{2+} . Indicate how would you expect the five $3d$ orbitals to be occupied for these hydrated ions (octahedral).

	Ions	Electronic configuration	No. of $3d$ -electrons	Octahedral d -orbital Splitting configuration
(i)	Ti^{2+}	$3d^2$	2	$t_{2g}^2 e^0$
(ii)	V^{2+}	$3d^3$	3	$t_{2g}^3 e^0$
(iii)	Cr^{3+}	$3d^3$	3	$t_{2g}^3 e^0$
(iv)	Mn^{2+}	$3d^5$	5	$t_{2g}^3 e^2$
(v)	Fe^{2+}	$3d^6$	6	$t_{2g}^4 e^2$
(vi)	Fe^{3+}	$3d^5$	5	$t_{2g}^3 e^2$
(vii)	Co^{2+}	$3d^7$	7	$t_{2g}^5 e^2$
(viii)	Ni^{2+}	$3d^8$	8	$t_{2g}^6 e^2$
(ix)	Cu^{2+}	$3d^9$	9	$t_{2g}^6 e^2$