$[Co(CN)_5I]^{3-}$ is the most stable in the series. Explain giving appropriate reason. 2

(ii) Give chemical equations for the reaction of the following compounds with water and sketch the structures of the products formed : 3+3

P_4O_{10}, N_2O_5, P_4O_6

(iii) Write a brief note on cyanogens. 2

(f) *(i)* Explain the preparation and structures of peroxy acids of sulphur. 4

(ii) Explain the term symbiosis with suitable example. 3

(iii) Write about clathrate compounds with reference to stability, inert gas clathrates and clathrate hydrates. 3

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2013

CHEMISTRY

(Major)

Paper : 4.1

Full Marks : 60

Time : 2½ hours

The figures in the margin indicate full marks for the questions

1. *(a)* Given that π bonding between Si and the lone pairs of N is important, what difference in structure between $(H_3Si)_3N$ and $(CH_3)_3N$ do you expect? 1

(b) Which of the following elements exhibit similar properties and why? 1

$A : 1s^2 2s^2 2p^6 3s^1$

$B : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

$C : 1s^2 2s^1$

(c) Write the increasing order of the thermal stability of the hydrides of Group 16 elements. 1

(d) What is dry ice? Why is it so called? 1

(e) Explain why $PbCl_2$ is white while PbI_2 is yellow. 1

(f) The Latimer diagram for Pu is

$$PuO_2^{2+} \xrightarrow{1{\cdot}02\,V} PuO_2^{+} \xrightarrow{1{\cdot}04\,V} Pu^{4+} \xrightarrow{1{\cdot}01\,V} Pu^{3+}$$

Does Pu(IV) disproportionate to Pu(III) and Pu(V) in aqueous solution? Give reasons. 1

(g) What is laughing gas? How is it prepared? 1

2. *(a)* "Both CO_2 and SiO_2 are covalent compounds but their melting and boiling points differ drastically." Justify the statement giving appropriate reason. 2

(b) What is the trend in the solubilities of the lithium halides (LiF, LiCl, LiBr, LiI) in water? Justify, giving appropriate reason. 2

(c) Using Slater's rules, calculate Z^* for a $3d$ electron in Mn. 2

(d) What are superacids? Explain why is a mixture of SbF_5 and HF called a superacid. 2

3. Answer any *three* : 5×3=15

(a) Successive ionization energies (in kJ mol^{-1}) for three main group elements X, Y and Z are given below :

	I_1	I_2	I_3	I_4	I_5	I_6	I_7
X	800	2427	3660	25033	32824	—	—
Y	1086	2352	4620	6229	37838	47277	—
Z	1012	1903	2912	4957	6274	21269	25397

Comment on the outermost shell electronic configuration and the periodic groups to which the elements belong. 5

(b) *(i)* A common analytical oxidising agent in an acidic solution of dichromate $Cr_2O_7^{2-}$, for which $E^{\ominus}_{Cr_2O_7^{2-}/Cr^{3+}} = +1{\cdot}38$. Is the solution useful for a redox titration of Fe^{2+} to Fe^{3+}? Could there be a side reaction when Cl^- is present with the Fe^{2+} solution? Justify your answer. Given

$$E^{\ominus}_{Fe^{3+}/Fe^{2+}} = +0{\cdot}77\,V$$

$$E^{\ominus}_{Cl_2/Cl^-} = +1{\cdot}36\,V$$

3

(ii) What happens when alkali and alkaline earth metals are dissolved in liquid ammonia? 2

(c) (i) "In contrast to the inertness of carbon halides, the halides of silicon are extremely reactive with water, to the extent that they must be protected from atmospheric moisture." Justify this statement. Give, wherever necessary chemical equation. 3

(ii) Construct a Frost diagram from the following Latimer diagram for Tl : 2

$$Tl^{3+} \xrightarrow{+1{\cdot}25\ V} Tl^{+} \xrightarrow{-0{\cdot}34\ V} Tl$$

(d) Use Wade's rule to calculate the number of framework electron pairs in B_4H_{10}. What structural category does it belong? Sketch its structure. Give a chemical equation to show what happens when $B_{10}H_{14}$ reacts with $(CH_3)_3N$. 2+1+1+1

(e) (i) Discuss the mechanism of formation and depletion of ozone layer in the stratosphere. 4

(ii) Give one clinical use of nitric oxide. 1

4. Answer any *three* : 10×3=30

(a) (i) Why does atomic radius decrease across a period? Explain why the radii of the following ions will be different :

O^{2-}, F^{-}, Na^{+}, Mg^{2+}, Al^{3+}

Arrange these ions in order of increasing radius. 1+1+1

(ii) Knowing the electron gain enthalpy values of $O \rightarrow O^{-}$ and $O^{-} \rightarrow O^{2-}$ as -141 kJ mol^{-1} and 702 kJ mol^{-1} respectively, how can you account for the formation of a large number of oxides having O^{2-} species and not O^{-}? 3

(iii) Arrange BF_3, BBr_3, BCl_3 according to increasing Lewis acid character. Give reasons 2

(iv) Why does sulphur form catenated polysulphides of formulae $[S-S-S]^{2-}$ and $[S-S-S-S-S]^{2-}$ whereas polyoxygen anions beyond O_3^{-} are unknown? 2

(b) (i) Discuss and compare the following melting point (°C) sequences : 3

Cu	1083	Ag	961	Au	1064
Zn	419	Cd	320	Hg	– 39

(ii) Define group electronegativity. How can you explain the following reactions? 3

$$CH_3I + OH^- \rightarrow CH_3OH + I^-$$

$$CF_3I + OH^- \rightarrow CF_3H + IO^-$$

(iii) What do you understand by the term redox potential? How does the redox potential and hence the redox character of elements in aqueous solution change across the period and down the group amongst the representative elements? 4

(c) (i) Discuss liquid ammonia as a solvent in terms of precipitation reaction, acid-base reaction and amphoteric behaviour. 3

(ii) Sketch the structures of two allotropes of carbon namely diamond and graphite. What is the impact of structure on physical properties of two allotropes? 2+2

(iii) What are superoxides? Show with the help of a chemical equation a preparation and a reaction of a superoxide. 1+1+1

(d) (i) The thermal decomposition temperature (°C) of bivalent metal carbonates of group 2 are given below :

$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
300	840	1100	1300

Explain the observed trend. 3

(ii) Explain the preparation, structure and uses of hydrazine. 2+1+1

(iii) What is $p\pi$—$d\pi$ bonding? Give examples to show how this may explain some of the differences in the chemistry of nitrogen and phosphorous. 1+2

(e) (i) Co^{3+} is a moderately hard Lewis acid. It forms both $[Co(NH_3)_5X]^{2-}$ and $[Co(CN)_5X]^{3-}$ type complexes, where X is a halide ligand. The ammine complex is more stable with $X = F^-$ than the complex with $X = I^-$. But the cyanocomplex with $X = F^-$ is not even known while

Or

(i) Why tetrahedral complexes do not show geometrical isomerism? Give a description of geometrical isomerism in square planar complexes of the type Ma_2b_2 and $M(ab)_2$ with examples. 1+2+2=5

(ii) What are π-acceptor ligands? Give examples. Write one method of preparation of $Fe(CO)_5$. Discuss its structure and bonding. Does it satisfy 18-electron rule? Show with calculation. 1+1+2+1=5

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2013

CHEMISTRY

(Major)

Paper : 4.2

Full Marks : 60

Time : 2½ hours

The figures in the margin indicate full marks for the questions

1. Answer the following questions : 1×7=7

(a) I_2 is not soluble in water, but it is soluble in KI solution. Give reasons.

(b) What is the styx number of B_4H_{10} structure?

(c) Other alkali metals form superoxide but lithium does not form. Give reasons.

(d) Which ionic compound of aluminium is used as coagulant and precipitant in treating both drinking water and sewage?

(e) Give one example of a stabilized alkali metal anion.

(f) Among the transition elements, which has the highest density?

(g) Anhydrous $CuSO_4$ is colourless but aqueous solution of $CuSO_4$ is blue. Give reasons.

2. Answer the following questions : 2×4=8

(a) Describe the action of XeF_2 on (i) H_2O and (ii) H_2.

Or

The gaseous XeF_6 molecule does not have a static structure. Explain this statement.

(b) Give the structural representation of $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$.

(c) What is inert pair effect? Why inert pair effect is more prominent for the heaviest element in a group?

(d) Name and draw structure of one hexadentate ligand.

3. (a) How is it possible to form interhalogen compounds? Explain the structure and bonding in ClF_3 and I_3^-. 1+4=5

(b) Give one method of preparation of borazine. In what respect it is similar to benzene? Explain using structural representation. Give one reaction which differentiate it from benzene. 2+2+1=5

Or

For S_4N_4, answer the following : 1+1+1+2=5

(i) One method of preparation of it

(ii) One reaction where the heterocyclic ring is retained

(iii) One reaction where smaller ring is formed

(iv) At least four resonance structures of the molecule

(c) How can $FeCl_3$ be prepared? Why does aqueous solution of ferric chloride become acidic on long standing? Mention one use of ferric chloride each in inorganic analysis and organic preparation. 1+2+2=5

Or

How many oxides of vanadium are known? Give preparation, properties and uses of V_2O_5. 2+3=5

4. *(a)* *(i)* Describe the method of extraction of nickel from its ore. 6

(ii) The hydration energy of group 2 metals are much greater than group 1 metals and among group 2 metals beryllium has the maximum. Give reasons to justify this statement. 2+2=4

Or

(i) What is the principle of precipitation of Na^+ and K^+ ions from aqueous solution? Explain using appropriate reaction, the detection of K^+ and Na^+ ions from their solution in qualitative analysis. 2+3=5

(ii) Describe the method of extraction of gold from its ore. How is lead separated if present with gold? 4+1=5

(b) *(i)* How can you explain the following properties of metals? 5

Brightness, malleability, catalytic activity, semiconductor property and ability to form coordination compound

(ii) Although zinc has no incompletely filled up *d* orbitals, how is it possible for zinc to form complex compounds? Discuss the stereochemistry of coordination compounds of zinc. 2+3=5

Or

(i) Discuss the gradual trend of solubilities of hydroxides and sulphates of alkaline earth metals. 2+3=5

(ii) How are alkali metals generally characterised? What are different oxides formed by alkali metals? Give a brief account of their stability. 2+1+2=5

(c) *(i)* Give IUPAC names of the following : 2

$Na[PtCl_3(NH_3)]$, $[Co(NH_3)_6][Cr(CN)_6]$

(ii) How can the compound $CoCl_3 \cdot 4NH_3$ be represented as told in Werner's theory? How many ions will it produce in aqueous solution? 2+1

(iii) Why are transition metals capable of showing variable oxidation state? Give a brief description of stable and unstable oxidation states of V, Cr, Mn and Fe. 1+4=5