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2016

M.Sc. Part–I Examination

CHEMISTRY

PAPER—III

Full Marks : 75

Time : 3 Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

(Inorganic)

Answer any *five* questions,

taking at least *two* from each group.

Group–A

1. (a) Explain the mechanism of biological nitrogen fixation emphasizing the roles of the metalloenzyme involved in this process.   5

(b) What is essential and beneficial element ?   3

(c) Discuss the toxicity of arsenic & how toxicity can be removed ?   2+3

(d) What is rubridexin ?   2

2. (a) What is the difference between "thermodynamic stability" and "kinetic stability" ?   2

(b) $[Ni(CN)_4]^{2-}$ is a labile complex but $[Fe(CN)_6]^{4-}$ is an inert complex — justify.   3

(c) Discuss 'I'-mechanism with a suitable example.   5

(d) Define a "spectator ligand".   2

(e) How the pair of geometrical isomers of $[Ptcl_2(NO_2)(NH_3)]^-$ can be prepared using the principle of "trans-effect" ?   3

3. (a) What is stepwise and overall stability constant ? Establish the relation between them.   4

(b) The spectra of $[Ti(H_2O)_6]^{3+}$ shows a broad band with a peak arownd $20,100 \text{ cm}^{-1}$ — explain. Calculate D0 in kJ mol^{-1} & ev.   4

(c) MnO_4^- is coloured other than d-d transition — explain.   2

(d) What do you mean by fluxionality ? Discuss the fluxional behaviour of $Fe_2(CO)_4CP_2$ molecule.   5

4. (a) Mo^{2+} is a d^4 system, but $[MoCl_8]^{4-}$ is diamagnetic in nature — explain.   3

(b) How S_4N_4 is prepared ? Give its structure & bonding.   4

(c) The following absorption bonds are formed in the spectrum of $[Cr(CN)_6]^{3-}$: 264 nm (charge transfer), 310 nm and 378 nm. Determine the values of Δ_0 and B.   3

(d) What do you mean by one dimensional solid ? Give examples.   2

(e) The carbonyl dinitrogen complexes are unstable — comment.   3

5. (a) The following character table is given for C_{3v} point group.

C_{3v}	E	$2C_3$	$3\sigma_2$
Γ_1	1	1	1
Γ_2	1	A	B
Γ_3	2	C	D

Find the values for A, B, C & D. Write down the Mullikan symbol for Γ_1, Γ_2 & Γ_3.   3

(b) Show that the elements present in the molecule form a well defined group.   4

(c) State and explain the "Great Orthogonality Theorem".   3

(d) Find the point group of the following in the light of schöenflies notation :

(i) $PCl_5(g)$

(ii) B_2H_6

(iii) Ferrocene

(iv) $VO(acac)_2$

(v) $CH_2 = C = CH_2$ 5

Group–B

6. Write notes on :   5×3

(a) Dioxygen and hydroxide as ligand ;

(b) Creiutz-Taube complex ;

(c) Tungsten blue ;

(d) Clathrate compoounds ;

(e) Silicones.

7. (a) Write down the taso and their symmetry notations for an octaledral complex.   5

(b) Why are low spin complexes usually are not encountered for tetrahedral co-ordination ?   2

(c) Predict the geometry of $Ni_6(CO)_{12}^{2-}$ and $[Rh_6C(CO)_{15}]^{2-}$ using Wade's model.   2+2

(d) (i) How will you synthesize the following :

$\langle\langle - Pd \overset{Cl}{\underset{Cl}{<}} Pd - \rangle\rangle$ from $PdCl_2$

(ii) Osmate from OsO_4.   2+2

8. (a) Suggest the mode of binding in the complex $C_3H_5Mn(CO)_5$ and $C_3H_5Mn(CO)_4$ 2

    (b) Justify the validity of EAN rule for $Os_5C(CO)_{15}$.   2

    (c) (i) Discuss the principle of polarography.

       (ii) Why is oxygen to be expelled from the polaro-graphic cell before the experiment?   3+2

    (d) (i) Discuss the basic principle of atomic absorption spectroscopy.   3

       (ii) Briefly describe the AAS method of estimation of the following elements :

         (a) Arsenic in soil,

         (b) Platinum or gold in rock. $1\frac{1}{2}+1\frac{1}{2}$

9. (a) State the properties of irreducible representation.   3

    (b) What do you mean by the co-set of a sub-group? Show that a sub-group and any of its co-set can not have any element in common.   1+3

    (c) Find the matrix representation of $C_2(x)$ (x-axis is the principle axis of rotation) and σ_h is the cartesian co-ordination system.

    (d) Obtain the hybridisation for the sigma bonds of CH_4 molecule.   5

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2,\ x^2-y^2)$
T_1	3	0	-1	1	-1	$(R_x,\ R_y,\ R_z)$	
T_2	3	0	-1	-1	1	$(x,\ y,\ z)$	$(xy,\ xz,\ yz)$

10. (a) Show that if A is conjugate to B & also to C, then B and C must be conjugate to each other, A, B, C being the elements of a group.   3

    (b) No molecule can have only two orthogonal C_2-axes of symmetry — explain.   3

(c) Find the crystal field splitting of d-orbitals in an octahedral ligand field. 9

0	E	$6C_4$	$3C_2$	$8C_3$	$6C_2'$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	-1	1	1	-1		
E	2	0	2	-1	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	1	-1	0	-1	(R_x, R_y, R_z), (x, y, z)	
T_2	3	-1	-1	0	1		(xy, xz, yz)

10. (a) Show that if A is conjugate to B & also to C, then B and C must be conjugate to each other, A, B, C being the elements of a group. 3

(b) No molecule can have only two orthogonal C_2 axes of symmetry to explain the above point along with any specific example. 3