

25/2/2012  
1:00 P.M.

Total No. of Printed Pages—7

2 TDC CHM M 4

(iv)  $[\text{Fe}(\text{CN})_6]^{4-}$   
(iii) 12 DQ  
c. (i) 2D  
d. (ii)  $\text{SF}_6$   
e. (iv) Silicon  
f. (iv) Bismuth salt

2012

CHEMISTRY  
( Major )

FOURTH PAPER

( Inorganic Chemistry )

Full Marks : 60  $\rightarrow$  (18) Pass marks

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Select the correct answer : 1x6=6

sem-III

(a) The complex ion which obeys the EAN rule is 36

- (i)  $[\text{Cr}(\text{NH}_3)_6]^{3+} \rightarrow 24 + (2 \times 6) = 3 \Rightarrow 33$
- (ii)  $[\text{Pt}(\text{NH}_3)_4]^{2+} \rightarrow \dots$
- (iii)  $[\text{Fe}(\text{CN})_6]^{3-} \rightarrow 26 + (2 \times 6) + 3 = 35$
- (iv)  $[\text{Fe}(\text{CN})_6]^{4-} \rightarrow 26 + (2 \times 6) + 2 = 36$

ser - (I)

(b) The CFSE for the  $d^3$  ion in strong crystal field is

- (i)  $4 Dq$
- (ii)  $8 Dq$
- (iii)  $12 Dq$
- (iv)  $16 Dq$

ser - (II)

(c) The spectroscopic free ion ground term for  $d^1$  is

- (i)  $^2 D$
- (ii)  $^5 D$
- (iii)  $^3 P$
- (iv)  $^1 S$

ser - (I)

(d) The least labile species is

- (i)  $[AlF_6]^{3-}$
- (ii)  $SF_6$
- (iii)  $[SiF_6]^{2-}$
- (iv)  $[PF_6]^-$

unit - II  
(ser)

X  
CNS  
ser - (II)

(e) The substance which is not used as a moderator in nuclear reactor is

- (i) heavy water
- (ii) graphite
- (iii) cadmium
- (iv) silicon

\* (f) Thiourea form a yellow precipitate with acid solution of

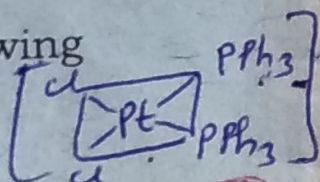
- ~~(i)~~ copper salts
- (ii) cadmium salts
- ~~(iii)~~ bismuth salts
- (iv) aluminium salts

2. Answer the following :

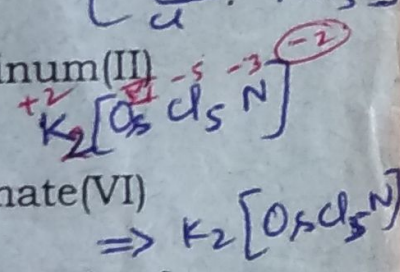
2x6=12

(a) Write the formula of the following complexes :

(i) cis-dichlorobis-(triphenylphosphine)platinum(II)

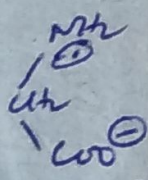


(ii) Potassium-pentachloronitridoosmate(VI)

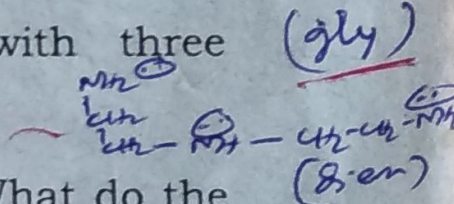


(b) Write the name and formula of each of the following types of ligands :

(i) A bidentate ligand with one acidic and one neutral donor



(ii) A tridentate ligand with three neutral donors



(c) Define macrocyclic ligand. What do the numbers 18 and 6 signify in the complex

18  $\Rightarrow$  ring of 18 atoms  
6  $\Rightarrow$  Total 6-oxygen atom.  
[Rb(dibenzo-18-crown-6) (NCS)]?

~~Chute~~ (d) What do you mean by inert and labile complexes?

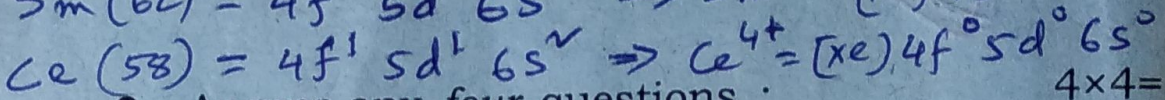
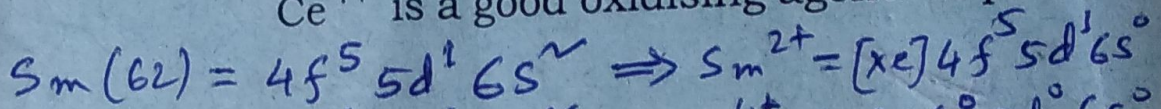
12P-1000/494

Labile  $\Rightarrow$  Outer orbital octahedral complex  
 $sp^3d^2$  (Turn Over) 5  
 $\Rightarrow d^1$  &  $d^2$  & high spin d  
 Inert  $\Rightarrow d^3$  (high spin)

(e) Write a note on radio carbon dating.

Age of the archaeological sample containing carbonaceous material

(f)  $Sm^{2+}$  is a good reducing agent and  $Ce^{4+}$  is a good oxidising agent. Explain.



3. Answer any four questions :

4x4=16

(a) What is the basis of crystal field theory? Draw the splitting patterns for octahedral, tetrahedral and square planar complexes in a crystal field.

4

(b) What is meant by crystal field stabilization energy? Calculate the CFSE for each of the following octahedral systems :

4

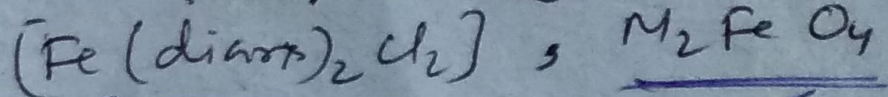
- $3 \times 29 \quad e_g^1 \Rightarrow (i) \quad d^4 \text{ high-spin} \rightarrow 0.6 \Delta_0 = 6$
- $3 \times 29 \quad e_g^2 \Rightarrow (ii) \quad d^5 \text{ high-spin} \rightarrow 0 \Delta_0 = 0 Dq$
- $6 \times 29 \quad e_g^0 \Rightarrow (iii) \quad d^6 \text{ low-spin} \rightarrow 2.4 \Delta_0 = 24 Dq$

(c) Explain what you mean by Russell-Saunders coupling. What are spectroscopic terms? Give example.

4

(d) On the basis of valence bond theory, explain the structures of the following ions :

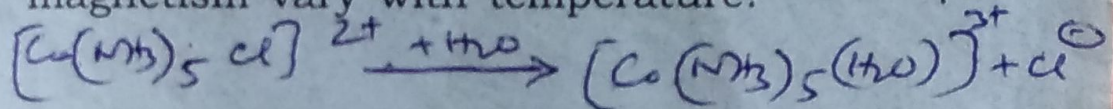
- (i)  $[Cu(NH_3)_4]^{2+} \rightarrow dsp^2 \rightarrow \text{sq. planar}$
- (ii)  $[Co(NO_2)_6]^{3-} \rightarrow d^2 sp^3 \rightarrow \text{no}_2^- (\text{strong})$



(e) (i) How are the following oxidation states stabilized? Give examples : 2 <sup>⊕</sup>  
~~1~~ ✓ Divalent silver  $\rightarrow [Ag(Py)4]^{2+}$   $[Ag(dip)2]$   
~~2~~ ✓ Hexavalent iron  $[Ag(phen)3]^{3+}$

✓ (ii) Describe briefly nephelauxetic effect.  $\rightarrow$  cloud expanding / decrease of  $(e^- - e^-)_{rep}$  / effective 2

(f) What do you mean by diamagnetism and paramagnetism? How does paramagnetism vary with temperature? <sup>increase in the size of the orbitals</sup> 4



4. Answer either (a) or (b) :  ~~$[Co(NH3)5Cl]^{2+}$~~  =  $K [Co(NH3)5Cl]^{2+} \times [H2O]$

Calc

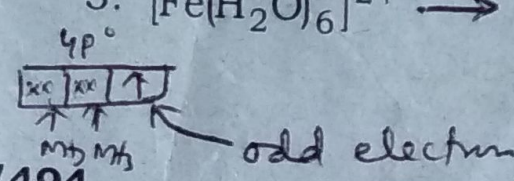
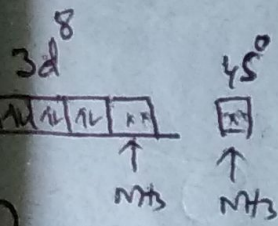
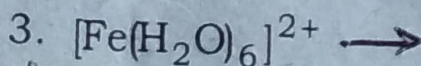
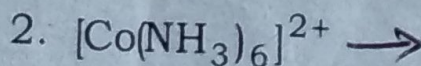
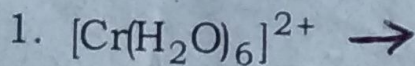
(a) What is acid hydrolysis? Explain the mechanism of acid hydrolysis of  $[CoCl(NH3)5]^{2+}$ . Discuss the effect of the following factors on the rate of aquation of a hexacoordinated complex : 1+2+4=7

- (i) Charge on the complex
- (ii) Chelation

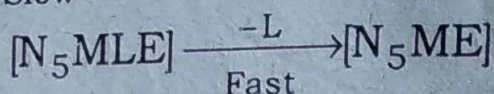
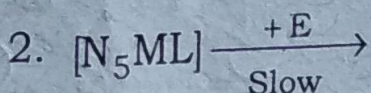
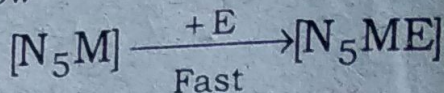
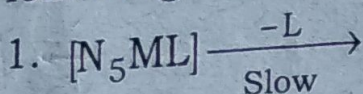
Calc

(b) (i) Predict whether the following complexes are inert or labile. Give reasons :

3



- Q.1111 (ii) Explain the mechanism of the following reactions : 2+2=4



5. Answer any *three* of the following : 3×3=9

(a) Explain the term 'zone of stability' in a plot of neutron (*n*) number vs. proton (*p*) number. 3

(b) What is tracer technique? Describe giving suitable examples the use of this technique in medical science. 3

(c) Explain :

$1\frac{1}{2} \times 2 = 3$

(i) U-238 cannot be commonly used as nuclear fuel.

(ii) The true mass of an atom is always less than the sum of the masses of its constituents.

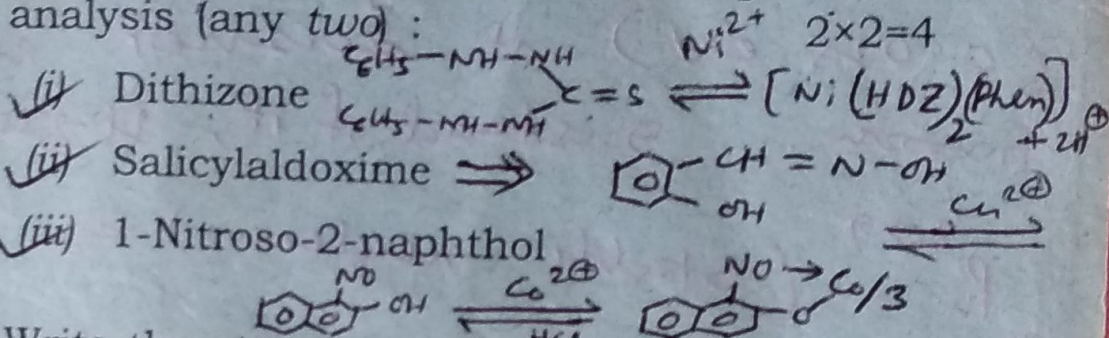
(d) Explain the principle of gaseous diffusion method of separation of isotopes. 3

(e) How will you explain the enormous and inexhaustible energy of the Sun? 3

6. What is lanthanide contraction? What are its important consequences?

1+2=3

7. (a) Discuss giving suitable examples the use of the following reagent in inorganic analysis (any two):

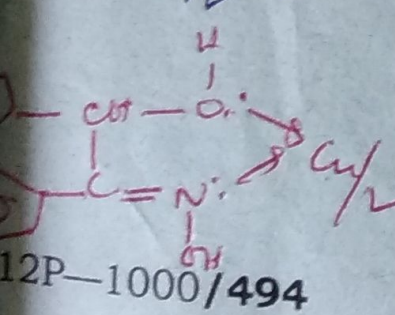
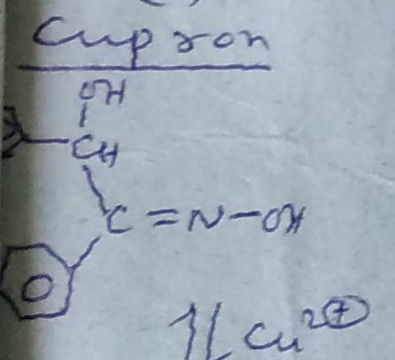


(b) Write the structures of the compounds formed by—

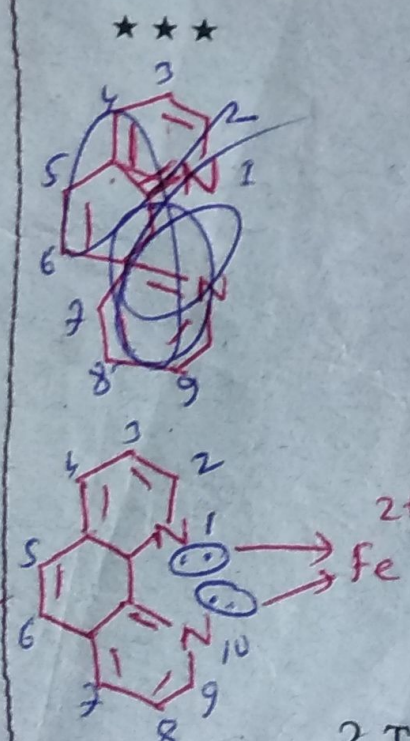
- (i) benzoin- $\alpha$ -oxime with  $Cu^{2+}$ ;
- (ii) 1,10-phenanthroline with  $Fe^{2+}$ ;
- (iii) oxine with  $Mg^{2+}$ .

1  $\times$  3 = 3

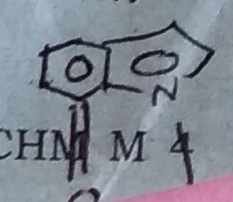
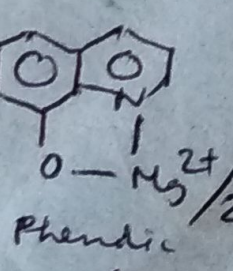
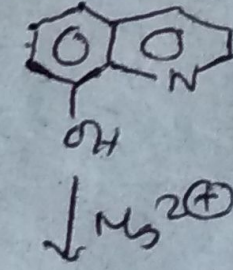
Benzoin- $\alpha$ -oxime  
(or)



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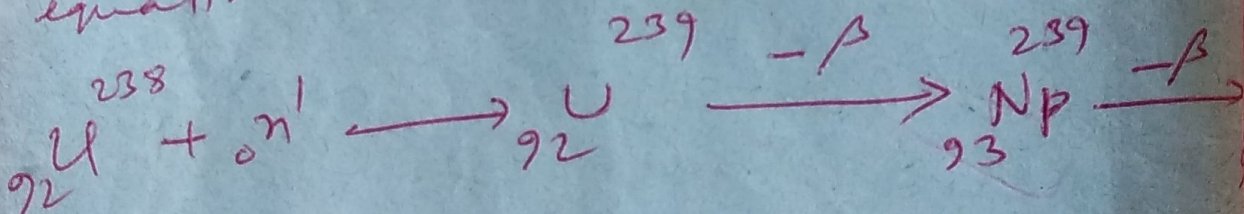
oxine (8-hydroxyquinoline)



5(c)(i)

U-238 is not a suitable nuclear fuel as it is fissionable only with the help of fast neutrons of energy about 1.3 MeV. If U-238 is bombarded by slow neutrons (0.025 eV) it does not undergo fission. Instead of it, U-238 forms

${}_{94}^{239}\text{Pu}$  (stable nucleus) by following equation:-



— x —