M. Sc. Chemistry Examination, 2018

(4th Semester)

Inorganic Chemistry Special

Paper - XIV - I

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - I - 4141

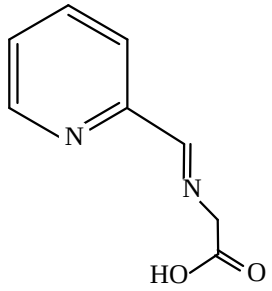
Answer ***any five*** of the following questions :

1. a) Given are the Pascal's constant and constitutive corrections for :

Atom	λ
C	–6.0
H	–2.93
O_2(carboxylate)	–7.95
O(alcohol)	–4.61

Constitutive corrections for atoms	$\lambda \times 10^6$ (cgs)
C (ring)	–0.24
C=N	+0.80

Calculate the diamagnetic correction for



b) With suitable example, explain how the magnetic behaviour of a species may change on coordination of solvent molecule(s). 3+2

2. Derive the relation :

$\chi_M(\text{dia}) = -[Ne^2/(6mc^2)]\Sigma\bar{r}^2$; What are the significances of $\chi_M(\text{dia})$? 5

3. What are first-order and second-order Zeeman effects ? Derive an expression for Van Vleck equation. 5

4. a) State and explain Lande Interval Rule.

b) What is spin-orbit coupling constant (ξ) ? For d^3 system show that $\lambda = \pm\xi/2S = \pm\xi/n$.

What are the factors that affect λ values ? 2+3

5. a) A Ni(II) complex gives $\mu_{exp} = 2\cdot65$ BM. Assuming spin

c) "Upon excitation at 450 nm, $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) exhibits a strong luminescence band at ~610 nm in ethanol-methanol (4 : 1, v/v) at room temperature while at 77K the luminescence maximum is blue-shifted to ~580 nm with significant enhancement of luminescence quantum yield and lifetime". Predict the nature of the emitting excited state(s) in the complex and also provide a reasonable explanation for the blue-shift of emission maximum as well as enhanement of quantam yield and lifetime. 3

d) What do you mean by zero-zero spectroscopic energy ($E_{0\text{-}0}$) ? Howcan the $E_{0\text{-}0}$ value of chemical species be estimated ? 2

e) What do you mean by photosensitizer ? Discuss the role of $[Ru(bpy)_3]^{2+}$ as sensitizer in photodecomposition of water. 2+2

state equilibrium and using $\mu_{Oh} = 3 \cdot 20$ BM and $\mu_{sp} = 0$, calculate the spin-state equilibrium (K).

b) What do you understand by super exchange interactions in magnetic materials ? Explain different modes of orbital overlaps involved in such interactions. How would you explain the preference of super-exchange interactions over direct metal-metal bonding in $[Cu_2(HCOO)_4(SCN)_2]^{2-}$? 2+3

6. Derive Bleany-Bower's equation for an isotropic dimeric Cu(II) complex. Get the energies of different levels. 5

UNIT - I - 4142

Answer ***all*** the questions.

7. Someone predicts the reaction : $A + B \rightarrow A^+ + B^-$ occurs through outer sphere mechanism. The observed rate constant of this reaction is -0.5 V . It is known that $E^0_{OX}(A/A^+) = -0.5$ V, $E^0_{red}(B/B^+) = 0 \cdot 9$ V, self-exchange rate constant for $A/A^+ = 2 \cdot 0 \times 10^{-3}\ M^{-1}\ s^{-1}$ and self-exchange rate constant for $B/B^- = 2 \cdot 0 \times 10^{-4}\ M^{-1}\ s^{-1}$. Is the prediction correct ? Comment. 4

8. Explain with reasoning why $[Co(H_2O)_6]^{2+/3+}$ system has unusually high exchange rate. $4\frac{1}{2}$

9. Cite one example of inner sphere electron transfer reaction where bridging ligand is retained with the oxidizing centre. Explain why the bridging ligand is retained. 4

10. a) "Chemiluminescence processes can be considered as the reverse of a photochemical processes." Evaluate the correctness of the statement. 2

b) Explain the different radiative and non-radiative processes in the light of Jablonski diagram when a molecule is excited by a photon. $1\frac{1}{2}$