2018

CHEMISTRY

(Major)

Paper : 6.4

(Inorganic Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Choose the correct answer : 1×7=7

(a) Silica gel contains $[CoCl_4]^{2-}$ as an indicator. When activated, silica gel becomes dark blue while upon absorption of moisture, its colour changes to pale pink. This is because

(i) Co(II) forms kinetically labile while Co(III) forms kinetically inert complexes

(ii) Co(II) changes its coordination from tetrahedral to octahedral

(iii) Co(II) changes its oxidation state to Co(III)

(iv) tetrahedral crystal field splitting is not equal to octahedral crystal field splitting

(b) In carbon dating application of radio-isotopes, ^{14}C emits

(i) β-particle

(ii) α-particle

(iii) γ-radiation

(iv) positron

(c) The correct *d*-electron configuration showing spin-orbit coupling is

(i) $t_{2g}^3 e_g^2$

(ii) $t_{2g}^6 e_g^0$

(iii) $t_{2g}^4 e_g^0$

(iv) None of the above

(d) In photosynthetic systems, the redox metalloproteins involved in electron transfer are cytochrome (cyt *b*),

(Continued)

cytochrome *bf* complex (cyt *bf*) and plastocyanin (PC). The pathway of electron flow is

(i) PC → cyt *b* → cyt *bf*

(ii) cyt *bf* → cyt *b* → PC

(iii) cyt *b* → cyt *bf* → PC

(iv) PC → cyt *bf* → cyt *b*

(e) Which one of the following statements is true for half-life of radioactive matters?

(i) It depends on amount of the matter

(ii) It depends on types of the matter

(iii) It depends on phase of the matter

(iv) It depends on temperature of the matter

(f) The lanthanide(III) ion having the highest partition coefficient between tri-*n*-butylphosphate and concentrated HNO_3 is

(i) La(III)

(ii) Eu(III)

(iii) Nd(III)

(iv) Lu(III)

(Turn Over)

(g) The activity of a radioactive source is measured in

(i) sievert

(ii) gray

(iii) becquerel

(iv) watt

2. Answer the following : 2×4=8

(a) Explain why, in terms of electronic transitions, substituting two of the NH_3 in $[Cr(NH_3)_6]^{2+}$ by bipy to form $[Cr(NH_3)_4(bipy)]^{2+}$ leads to more intensely coloured ($\varepsilon > 45000\ L\ mol^{-1}\ cm^{-1}$) complex.

(b) Potassium thiocyanate solution is used as a very sensitive test for the presence of iron(III) ions in solution. Discuss the chemistry behind the test.

(c) Metal ions are often used for diagnostic medical imaging. Explain the fact giving suitable examples.

(d) If the decrease in mass of a radioactive material between 18 and 24 years is 4 g, find the initial mass of the material (half-life of the material is 6 years).

3. Answer any *three* of the following : 5×3=15

(a) What are spectroscopic term symbols? Discuss how Hund's rule determine the term symbols of ground electronic states. 2+3=5

(b) What is meant by lanthanide contraction? Discuss how this phenomenon influences the properties of the transition elements immediately following the lanthanides. 1+4=5

(c) What is a radioactive disintegration series? Specify the different steps involved in the disintegration series of thorium. Why does the thorium series also known as $4n$ series? 1+3+1=5

(d) Name the metal ion present in the metalloenzyme carbonic anhydrase. Discuss the structure and functions of carbonic anhydrase. 1+4=5

(e) (i) What do you mean by labile and inert complexes? How does the *d*-electron configuration affect the labile/inert nature of complexes? 1+2=3

(ii) How will you prepare $K_3[Rh(ox)_3]$ from kinetically inert $K_3[RhCl_6]$? 2

4. Answer any *three* of the following : 10×3=30

(a) (i) Write the basic principle of conductometric titrations. Discuss the conductometric titration curve of sulphuric acid versus dilute ammonia. 2+3=5

(ii) What are the major roles of metal ions in biological systems? 3

(iii) Match the following metal salts with their prospective medicinal uses : 2

Metal salts	*Medicinal uses*
(1) Li_2CO_3	(I) Disinfectant
(2) *cis*-$[Pt(amine)_2X_2]$	(II) Antiulcer; antacid
(3) $AgNO_3$	(III) Manic depression
(4) Bi(sugar) polymers	(IV) Anticancer agent

(b) (i) When does induced radioactivity occur? Write a nuclear equation for the creation of ^{56}Mn through the bombardment of ^{59}Co with neutrons. 2+3=5

(Continued)

(ii) Discuss the ligand substitution mechanism in octahedral complexes. Sketch the reaction profile for the reaction

$$[Co(NEt_3)_5Cl]^{2+} + H_2O \rightarrow [Co(NEt_3)_5(H_2O)]^{3+} + Cl^-$$

Clearly indicate intermediates and transition states. 2+3=5

(c) (i) The fusion reaction given below is one of the final stages in the fusion process that occurs in the Sun :

$$^2_1H + ^3_1H \rightarrow ^4_2He + ?$$

(1) Complete the reaction identifying the missing particle. 1

(2) Calculate the energy released in the fusion reaction using the following information (the mass number of the other particle is also required) : 2

$^2_1H = 3{\cdot}345 \times 10^{-27}$ kg

$^3_1H = 5{\cdot}008 \times 10^{-27}$ kg

$^4_2He = 6{\cdot}647 \times 10^{-27}$ kg

(ii) What do you mean by BOD and COD? What is their significance? 2+2=4

(iii) Carbon monoxide is more dangerous than carbon dioxide. Why? 3

(Turn Over)

(d) (i) The electronic spectrum of $[VCl_4(bipy)]$ shows a single asymmetric band at 21300 cm^{-1} of moderate intensity ($\varepsilon < 800\ L\,mol^{-1}$) with a shoulder at lower energy (17400 cm^{-1}). How many absorption bands are expected if this complex is regarded as a perfect O_h? 2

(ii) Explain why MnO_4^- is intensely purple coloured while ReO_4^- is not highly coloured. 3

(iii) Discuss the separation of the lanthanides via ion-exchange chromatography. 5

(e) (i) How does neutron activation analysis (NAA) work? What types of archaeological samples can be analyzed by NAA? 2+3=5

(ii) Write notes on the following (any *two*) : 2½×2=5

(1) Vibronic-coupling

(2) Orgel diagram

(3) Nuclear belt of stability

★ ★ ★