HPAS (Main)—2017

CHEMISTRY

Paper I

Time : 3 Hours

Maximum Marks : 100

Note :— Attempt five questions in all. Question No. 1 is compulsory. All parts of a question must be answered in continuation at one place.

1. (a) Define the molecular partition function. What is physical significance of these properties? Discuss the effect of temperature on the molecular partition function. 7

(b) Explain effective atomic number rule (EAN) with appropriate example. Some 7

(c) Co(CO)₄ and Mn (CO)₅ dimerize but V (CO)₆ does not. Explain. 6

P.T.O.
(a) Explain de Broglie equation showing the relation between wavelength of a particle and its momentum. The kinetic energy of a moving electron is $4.55 \times 10^{-25}$ Joule. Calculate the wavelength of the electron (mass of electron $= 9.1 \times 10^{-31}$ kg and Plank's constant $= 6.6 \times 10^{-34}$ Js). 7

(b) Actinides have the greater tendency to form complexes than lanthanides. Explain. 7

(c) Lanthanides are generally trivalent but Ce$^{+4}$ and Eu$^{+2}$ are more stable. Explain. 6

For the gaseous carbon monoxide, $^{12}_{\text{C}}^{16}_{\text{O}}$, the IR absorption spectrum consists of a single peak that occurs at wave number of $2143$ cm$^{-1}$. The energy of vibrational level is given by:

$$E_{vib} = (v + 1/2)\hbar\omega, \quad v = 0, 1, 2, 3, \ldots \ldots$$

(a) Calculate the energy difference (in Joule) of successive vibrational energy levels of CO (g), assuming it vibrates as simple harmonic oscillator. 7
(b) Calculate the force constant of the C-O bond in carbon monoxide. 7

(c) Sketch the form of Morse Potential energy curve for the vibrational energy of diatomic molecule including the vibrational energy levels, illustrating with their relative spacing. 6

4. (a) Silver crystallizes in an f.c.c. structure with a unit cell length of 408.6 pm. Using Bragg equation, calculate the first-order diffraction angle for the (111) plane using X-ray of wavelength 154.433 pm. 7

(b) In the rotational spectrum of a diatomic molecule the first three transitions are observed at 17.68 cm\(^{-1}\), 35.36 cm\(^{-1}\) and 53.04 cm\(^{-1}\). (i) Calculate the rotational constant, B, of the molecule. (ii) Predict the wave number of the transition from \(J = 4\) to \(J = 5\). 7

P.T.O.
(c) 18.0 g of liquid water vaporizes at 1 bar and 373 K. Calculate q, w, ΔU, ΔS, and ΔU (in SI units) for this process. Given, latent heat of vaporization of liquid water at 1 bar and 373 K is 540 cal g⁻¹).

5. (a) Write IUPAC names of the following:

(i) [CoCl(H₂O)₂(NH₃)₄]Cl₂

(ii) [PtCl(NH₂CH₃)₂(NH₃)]Cl

(iii) [Cr(en)₃]Cl₃

(iv) [Fe(CN)₆]⁴⁻

(v) [Pt(py)₄][PtCl₄]

(vi) [Pt(en)₂Cl₂]Cl₂

(b) Define and differentiate between the following:

(i) Normalized and Orthogonal wave functions

(ii) Eigen value and Eigen function.

(c) Calculate the pH of 0.01 M NH₄Cl in water at 25°C. pKb for NH₄OH is 4.74 Ion product of water is 10⁻¹⁴.
6. (a) Draw the all possible geometrical and optical stereoisomers of \([\text{Pt(en)}_2\text{Cl}_2]\text{Cl}_2\) and \([\text{Co(ox)}_3]^{3-}\) structure.

(b) Derive the Langmuir adsorption isotherm.

(c) Explain the following briefly:

(i) Quantum yield

(ii) Beer-Lambert law

(iii) BET isotherm

7. (a) Heme acts as carrier of \(\text{O}_2\) in the system whereas toxic effect of \(\text{CO}\) can be explained by replacement reaction. Explain.

(b) Giving reason, classify the following molecules into different categories exhibiting pure rotational, pure vibrational, rotational Raman and vibrational Raman spectra.

\[\text{H}_2, \text{HCl, CO}_2, \text{NO}_2, \text{N}_2\text{O}, \text{N}_2, \text{CH}_4\]
(c) Draw the molecular orbital diagrams of O₂ and CO, and give the number of unpaired electrons and bond order in each case.

8. (a) The following chemical reaction is occurring in an electrochemical cell.

\[ \text{Mg(s)} + 2 \text{Ag}^+ (0.0001 \text{ M}) \rightarrow \text{Mg}^{2+} (0.10 \text{ M}) + 2\text{Ag(s)} \]

The \( E^\circ \) electrode values are:

\[ \text{Mg}^{2+}/\text{Mg} = -2.36 \text{ V}; \text{Ag}^+/\text{Ag} = 0.81 \text{ V} \]

For this cell calculate/write

(i) \( E^\circ \) value for the electrode \( 2 \text{Ag}^+/2\text{Ag} \).

(ii) Standard cell potential \( E^\circ_{\text{cell}} \)

(iii) Cell potential \( E \) cell

(iv) Symbolic representation of the above cell

(v) Will the above cell reaction be spontaneous

(b) Infra red spectral analysis of the following three complexes showed a set of two IR bands for the
"CO stretching frequencies. Match the correct set of IR bands to the given compounds and justify your reason for the assignment.

(i) \((\eta^5 - \text{C}_5\text{H}_5)_2\text{Ti(CO)}_2\)

(ii) \((\eta^5 - \text{C}_5\text{Me}_5)(\eta^5 - \text{C}_5\text{H}_5)\text{Ti(CO)}_2\)

(iii) \((\eta^5 - \text{C}_5\text{Me}_5)_2\text{Ti(CO)}_2\)

[1956 and 1875 cm\(^{-1}\); 1930 and 1850 cm\(^{-1}\); 1979 and 1897 cm\(^{-1}\)]

(c) A first order reaction has a rate constant \(1.15 \times 10^{-3}\) s\(^{-1}\). How long will 5 g of this reactant take to reduce to 3 g?