2017

(6th Semester)

CHEMISTRY

ELEVENTH PAPER

(CHEM–363)

(Physical Chemistry—III)

Full Marks : 55

Time : 2½ hours

(PART : B—DESCRIPTIVE)

(*Marks* : 35)

The figures in the margin indicate full marks for the questions

1. *(a)* State and explain Beer-Lambert law for light absorption by solutions. Also establish the relationship between absorbance and transmittance through this law. 3+1=4

(b) A 0·003 *M* solution of a coloured substance transmits 75% of the incident light of 500 mm, when placed in a cell of 1·0 cm length. Calculate the molar extinction coefficient and hence the optical density of a 0·001 *M* solution in the same cell at the same wavelength. 3

OR

2. *(a)* Discuss the photochemical reaction involving the dissociation of hydrogen iodide. 3

(b) Discuss the mechanism of photo-sensitization and quenching by taking suitable examples. 2

(c) For the photochemical reaction $B \rightarrow C$, $1{\cdot}0\times10^{-5}$ mole of B was formed on absorption of $6{\cdot}62\times10^{7}$ ergs at 3600 Å. Calculate the quantum yield for the reaction. ($h = 6{\cdot}62\times10^{-27}$ erg-sec) 2

3. *(a)* Discuss in detail the Debye theory of heat capacity of monoatomic solids. Compare and comment on the results obtained by Einstein and Debye on a plot. 3+1=4

(b) Discuss, in detail, the Planck's theory of blackbody radiation. 3

OR

4. *(a)* Set up and solve Schrödinger wave equation for a particle in an infinite one-dimensional (1-D) box. Also normalize the wave function. 4

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(b) A ball of mass 1 g, confined in a 1-D box of length 0·1 m, moves with a velocity of $0{\cdot}01\ ms^{-1}$. Calculate the quantum number, n. Is it possible to observe the quantization of energy levels of the ball? 3

5. (a) Derive multiplication theorem of partition function. 2

(b) Derive an expression for rotational partition function of an ideal diatomic gas. 3½

(c) Calculate the translational partition function for H atom at 3000 K confined to move in a box of volume $2{\cdot}49\times10^{5}\ cm^{3}$. 1½

OR

6. (a) Show that the internal energy of a system of N independent particles is given by

$$U = nRT^2\left[\frac{\partial \ln q}{\partial T}\right]_V$$

Hence show that $U = \frac{3}{2}nRT$ for an ideal gas. 4+1=5

(b) Calculate the entropy change of 1 mole of He when it is heated from 300 K to 600 K at constant pressure.
($R = 1{\cdot}98\ cal\ deg^{-1}\ mol^{-1}$) 2

7. (a) How is microwave spectroscopy utilized in determining the bond distances in polyatomic molecules? Explain. 2½

(b) The pure rotational spectrum of CN gaseous molecule consists of a series of equally spaced lines separated by $3{\cdot}7978\ cm^{-1}$. Calculate the inter-nuclear distance of the said molecule.
(Given : $^{12}C = 12{\cdot}011\ g\ mol^{-1}$ and $^{14}N = 14{\cdot}007\ g\ mol^{-1}$) 3

(c) Explain anharmonicity with the help of Morse potential curve. 1½

OR

8. (a) Discuss electronic spectra of conjugated molecules. 2½

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(b) By taking a suitable example, describe the condition under which a molecule shows vibrational IR spectrum. 2

(c) The fundamental vibrational frequency of HCl is 2890 cm^{-1}. Calculate the force constant of this molecule.

(Given, $^{1}H = 1{\cdot}673 \times 10^{-27}$ kg and $^{35}Cl = 58{\cdot}06 \times 10^{-27}$ kg) 2½

9. *(a)* What is meant by electrode potential? Derive Nernst equation showing the effect of electrolytic concentration on electrode potential. 1+3=4

(b) Write the cell reaction and calculate standard e.m.f. ($E°$) for the cell Zn, $Zn^{2+}(1\ M)|Fe^{2+}(1\ M)$, $Fe^{3+}(1\ M)$; Pt, $E°(Fe^{3+}|Fe^{2+}) = +0{\cdot}77$ V, and $E°(Zn^{2+}|Zn) = -0{\cdot}76$ V. 3

OR

10. *(a)* Derive expression for e.m.f. of concentration cells without transference. 4

(b) The e.m.f. of the cell

$Cd,\ CdCl_2 \cdot 2{\cdot}5\,H_2O$ (satd.) $||AgCl$ (s), Ag

in which the cell reaction is

$$Cd(s) + 2\,AgCl(s) + aq \rightleftharpoons CdCl_2 \cdot \frac{5}{2}H_2O\ (satd.) + 2Ag(s)$$

is 0·6753 volt at 25 °C and 0·6915 volt at 0 °C. Calculate the free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) for the cell reaction at 25 °C.

Physical constants :

$h = 6{\cdot}626 \times 10^{-34}$ J-s

$N_A = 6{\cdot}023 \times 10^{23}\ mol^{-1}$ 3

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Subject Code : CHEM/VI/11

Booklet No. A

Date Stamp .....

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DEGREE 6th Semester
(Arts / Science / Commerce / .....) Exam., **2017**

Subject .....
Paper .....

INSTRUCTIONS TO CANDIDATES

1. **The Booklet No. of this script should be quoted in the answer script meant for descriptive type questions and vice versa.**
2. **This paper should be ANSWERED FIRST and submitted within** *45 minutes* **of the commencement of the Examination.**
3. **While answering the questions of this booklet, any cutting, erasing, over-writing or furnishing more than one answer is prohibited. Any rough work, if required, should be done only on the main Answer Book. Instructions given in each question should be followed for answering that question only.**

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Roll No. .....
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Subject .....
Paper .....

Descriptive Type
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2017

(6th Semester)

CHEMISTRY

ELEVENTH PAPER

(CHEM–363)

(Physical Chemistry—III)

(PART : A—OBJECTIVE)

(*Marks* : 20)

The figures in the margin indicate full marks for the questions

SECTION—A

(*Marks* : 5)

Put a Tick (✓) mark against the correct answer in the brackets provided : 1×5=5

1. One einstein is the energy associated with

(a) 1 photon ( )

(b) 1×10^{21} photons ( )

(c) 1×10^{23} photons ( )

(d) 1 mole of photons ( )

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2. The emissive power (E) of a blackbody at any temperature is equal to

(a) σT^3 ( )

(b) σT^{-3} ( )

(c) σT^4 ( )

(d) σT^{-4} ( )

3. The relationship between molar partition function and work function is given by

(a) $A = -kT \ln Q$ ( )

(b) $A = kT \ln Q$ ( )

(c) $A = (kT)^{-1} \ln Q$ ( )

(d) $A = kT(\ln Q)^{-1}$ ( )

4. The rotational spectrum of a rigid diatomic rotor consists of equally spaced lines with spacing equal to

(a) 1B ( )

(b) 2B ( )

(c) 3B ( )

(d) 4B ( )

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5. The relationship between equilibrium constant and standard e.m.f. of a cell is given by

(a) $\ln k = RT / nFE^{\circ}$ ( )

(b) $\ln k = nFE^{\circ}/RT$ ( )

(c) $\ln E^{\circ} = nk / RT$ ( )

(d) $\ln E^{\circ} = RT / nk$ ( )

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SECTION—B

(*Marks* : 15)

Answer the following questions : 3×5=15

1. Discuss the mechanism of chemiluminescence involving aromatic anions (Ar^-) and aromatic cations (Ar^+).

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2. State and explain photoelectric effect.

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3. Derive the expression for work function and molar partition function.

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4. A sample was excited by the 4358 Å line of sodium. A Raman line was observed at 4447 Å. Calculate the Raman shift in cm^{-1}.

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5. Write a short note on quinhydrone electrode.

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