2016

(6th Semester)

CHEMISTRY

ELEVENTH PAPER

Course No. : 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 Stark-Einstein law of photochemical equivalence. 1+2=3

(b) Calculate the transmittance, absorbance and absorption coefficient of a solution which absorbs 90% of a certain wavelength of light beam passed through a 1 cm cell containing 0·25 *M* solution. 2

(c) Write a short note on 'quenching'. 2

OR

2. *(a)* Discuss the photochemical reaction involving the decomposition of acetaldehyde. 3

(b) Explain the terms 'photosensitization' and 'chemiluminescence'. 2

(c) A certain system absorbs $3{\cdot}25\times10^{18}$ quanta of light per second. On irradiation for 20 minutes, 0·0025 mole of the reactants was found to have reacted. Calculate the quantum yield for the process.
(Avogadro's number $= 6{\cdot}02\times10^{23}$) 2

3. *(a)* Discuss Einstein theory of heat capacity of monatomic crystal and also comment on the results obtained on a plot. 4

(b) Light of wavelength 5500 Å falls on a sensitive plate with work function 1·7 eV. Find *(i)* energy of photon, *(ii)* energy of photoelectron and *(iii)* stopping potential. 3

OR

4. *(a)* Derive Schrödinger wave equation. 4

(b) An electron is confined to a molecule of length 1 nm (about 5 atoms long).

(i) What is its minimum energy?

(ii) What is the first (minimum) excitation from this state?

(Planck's constant = $6{\cdot}26\times10^{-34}$ J-s,

Mass of electron = $9{\cdot}109\times10^{-31}$ kg) 3

5. *(a)* Derive an expression for the molecular translational partition function of an ideal diatomic gas. 5

(b) The first excited state of chlorine atom $^2P_{1/2}$, lies at 0·11 eV above the ground state, $^2P_{3/2}$. Calculate the electronic partition function of chlorine atom at 1000 K. 2

OR

6. *(a)* Derive an expression for the molecular vibrational partition function of an ideal diatomic gas. 4

(b) Calculate the characteristic rotational temperature and the rotational partition function for H_2 gas at 2727 °C, given that the moment of inertia of hydrogen gas molecule at this temperature is $4{\cdot}6033\times10^{-48}$ kg-m^2. 3

7. *(a)* How many normal modes of vibrations are there in CO_2 and H_2O? 2

(b) Describe briefly the types of molecules exhibiting rotational spectra. 2

(c) The pure rotational spectrum of gaseous HCl consists of a series of equally spaced lines separated by 20·80 cm^{-1}. Calculate the *(i)* moment of inertia and *(ii)* internuclear distance. The atomic masses are $^1H = 1{\cdot}673\times10^{-27}$ kg, $^{35}Cl = 58{\cdot}06\times10^{-27}$ kg. 3

OR

8. *(a)* State mutual exclusion rule for vibrational translations. 1

(b) Discuss the basis of Raman spectroscopy. What are Rayleigh, Stokes and anti-Stokes lines? Explain with diagram. 3

(c) State and explain Franck-Condon principle. 3

9. *(a)* Differentiate between electrolytic and electrochemical (galvanic) cells. 4

(b) Write Nernst equation. 1

(c) What are concentration cells? 2

OR

10. *(a)* Differentiate between reversible and irreversible electrochemical cells with examples. 4

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

$$Cr|Cr^{3+}(0{\cdot}1\ M)||Fe^{2+}\ (0{\cdot}01\ M)|Fe$$

Given, $E^{\theta}_{(Cr^{3+}|\,Cr)} = -0{\cdot}75\ V$

$E^{\theta}_{(Fe^{2+}|\,Fe)} = -0{\cdot}45\ V$ 3

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Subject Code : CHEM/VI/11

Booklet No. A

Date Stamp .....

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To be filled in by the Candidate

DEGREE 6th Semester
(Arts / Science / Commerce / .....) Exam., **2016**

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.**

To be filled in by the Candidate

DEGREE 6th Semester
(Arts / Science / Commerce / .....) Exam., **2016**

Roll No. .....
Regn. No. .....

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

Descriptive Type
Booklet No. B .....

Signature of Scrutiniser(s) *Signature of Examiner(s)* *Signature of Invigilator(s)*

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2016

(6th Semester)

CHEMISTRY

ELEVENTH PAPER

Course No. : 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 for it : 1×5=5

1. The free energy change (ΔG) of a photochemical reaction

(a) is always positive ( )

(b) is always negative ( )

(c) can be both positive and negative ( )

(d) is neither positive nor negative ( )

2. The system for which energy (E) increases quadratically with the quantum number (n) is

(a) particles in a one-dimensional box ( )

(b) hydrogen atom ( )

(c) one-dimensional harmonic oscillator ( )

(d) rigid rotor ( )

3. The unit of the molecular partition function is

(a) cm^{-1} ( )

(b) s^{-1} ( )

(c) $JK^{-1}\ mol^{-1}$ ( )

(d) dimensionless ( )

4. Selection rules for vibrator transitions are

(a) $\Delta J = 0,\ \Delta V = \pm 1, \pm 2, \pm 3 \ldots$ ( )

(b) $\Delta J = \pm 1,\ \Delta V = \pm 1, \pm 2, \pm 3 \ldots$ ( )

(c) $\Delta J = \pm 1, \pm 2, \pm 3, \ldots,\ \Delta V = \pm 1$ ( )

(d) $\Delta J = 0, \pm 1$ ( )

5. If the transference number of cation is greater than that of anion, i.e., $t_+ > t_-$, then liquid junction potential will be

(a) zero ( )

(b) negative ( )

(c) positive ( )

(d) negligibly small ( )

SECTION—B

(*Marks* : 15)

Answer the following questions : 3×5=15

1. State and explain Grotthus-Draper law.

2. Describe Planck's quantum theory of radiation.

3. Write a short note on reference electrode (SHE).

4. What are radiative and non-radiative transitions?

5. Discuss the salient features of the Einstein theory of the heat capacity of monatomic crystals.

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