TYBSc Sem-VI
Physical Chemistry 2016-2017

QP Code : 77150

(2½ Hours) [Total Marks :75

N.B. : (1) All questions are compulsory.
(2) Figures to the right indicate full marks.
(3) Use of logarithmic table/non programmable calculator is allowed.

Physical constants:

$N = 6.022 \times 10^{-23}$
$k = 1.38 \times 10^{-23}\ JK^{-1}$
$F = 96500$ Coulombs
$R = 8.314\ JK^{-1}mol^{-1}$
$h = 6.626 \times 10^{-34}\ Js$
$c = 3.0 \times 10^{8}\ ms^{-1}$
$\frac{2.303RT}{F} = 0.0592$ at 298K
Mass of electron $= 9.109 \times 10^{-31}$ kg
1 amu $= 931$ MeV $= 1.66 \times 10^{-27}$ kg
$\pi = 3.142$
C = 12 amu
H = 1 amu
O = 16 amu
Br = 80 amu

1. Attempt any **three** of the following:-

(A) Derive an expression for wave number of P-branch and R-branch lines in a vibrational rotational spectrum of a diatomic molecule. 5

(B) The equilibrium internuclear distance in the molecule of HBr is 142.0 pm. Calculate the frequency separation between successive lines in pure rotational spectrum in m^{-1}. 5

(C) Calculate the number of modes of vibration in the molecule of CO_2 using appropriate expression, draw them. Giving reason, predict which modes are IR active and which one/s are Raman active. 5

(D) The vibrational frequency of CO molecule is $2.51 \times 10^{13}\ s^{-1}$. Assuming vibrations to be harmonic, Calculate (i) vibrational frequency for the molecule in m^{-1}, (ii) the force constant of the bond. 5

(E) Derive the expression for moment of inertia of a diatomic molecule with masses m_1 and m_2 separated by internuclear distance 'r'. 5

(F) Answer the following:-

(a) Define dipole moment. 1

(b) Why some molecules have zero dipole moment where as others possess dipole moment? 2

(c) Explain the geometry of BF_3 and NH_3 on basis of dipole moment. 2

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2. Answer any **three** of the following:- 5

(A) Describe the Tafel's theory for hydrogen overvoltage. 5

(B) The overvoltage of hydrogen on a certain cathode is 0.34 V. Calculate the minimum voltage that must be applied to evolve hydrogen on this cathode from a solution of pH 3.6

(C) $\psi(x) = A\sin\left(\frac{2\pi x}{\lambda}\right) + B\cos\left(\frac{2\pi x}{\lambda}\right)$ 5

From the above equation, derive the expression for the wave function ψ in a clamped string using boundary condition. Also draw the wave function ψ_n for $n = 1, 2$ and 3.

(D) Answer the following:-

(p) State Heisenberg's uncertainty Principle. Give its significance. 2

(q) State the characteristics of wave function ψ. 3

(E) Differentiate between matter waves and electromagnetic waves. 2

The velocity of an electron in motion is 5.93×10^5 ms^{-1}. Calculate 3

(i) The kinetic energy of electron

(ii) The wavelength of the matter wave associated with the electron in nm.

(F) State the expression for time independent schrodinger wave equation for the particle of mass 'm' moving in three dimension and explain the terms involved. 5

3. Answer any **three** of the following:-

(A) Describe with the help of neat labelled diagram, the stop flow method used to study fast reactions. Give two examples of fast reactions. 5

(B) Explain the method of electrolysis of water to produce hydrogen. 5

(C) Explain the low resolution NMR spectrum of methanol and ethanol. 5

(D) (a) State the expression for collision frequency of a bimolecular reaction and identify the terms involved. 2

(b) Give any three drawbacks of collision theory of reaction rates. 3

(E) Explain the principle, construction and working of silicon solar cell. 5

(F) Answer the following with respect to NMR spectroscopy.

(a) State the reasons for using tetramethylsilane as internal standard. 3

(b) What is meant by spin-lattice relaxation? 2

4. Answer any **three** of the following:-

(A) What are tracers? Explain the use of tracer in studying reaction mechanism with the help of a suitable example. 5

(B) What is meant by nuclear transmutation and artificial radioactivity? Differentiate between the two. 5

(C) Explain the use of moderator, coolant, reflector, fuel and control rods in a nuclear power reactor. 5

(D) Explain the use of phosphors and the working of photomultiplier tube in scintillation counter used to detect and measure radioactivity. 5

(E) The half-life of ^{235}U is 7.1×10^8 years and its daughter element is ^{231}Th with half-life 24.75 hour. Find the weight of ^{231}Th in equilibrium with one gram of ^{235}U. 5

(F) Find the Q Value and threshold energy of the following reaction 5

$$^{232}Th + {}^{4}He \rightarrow {}^{235}U + {}^{1}n$$

Given

^{232}Th = 232.1103 amu
^{4}He = 4.0038 amu
^{235}U = 235.1170 amu
^{1}n = 1.0086 amu

(A) State **True / False** for the following statements. 4

(a) Rule of mutual exclusion is applicable to linear molecule with centre of symmetry.
(b) The energy difference between any two successive vibrational energy levels is constant.
(c) Dipole moment is a scalar quantity.
(d) In-plane bending vibrations are classified as rocking and wagging.

OR

(A) Choose the correct answer:- 4

(p) For stokes line in Raman spectra (i) $\lambda_s > \lambda_i$ (ii) $\lambda_s = \lambda_i$ (iii) $\lambda_s < \lambda_i$

(q) For pure rotational spectra

(i) $I = \frac{\mu}{r^2}$ (ii) $B = \frac{h}{8\pi^2 Ic}$ (iii) $\overline{\Delta v} = B$

(r) The vibrational degree of freedom for non-linear molecule of H_2O is

(i) 2 (ii) 3 (iii) 4

(s) Rotational spectra is observed for

(i) CH_4 (ii) CH_3Cl (iii) C_6H_6

(B) State **true** or **false** for the following statements. 4

(a) The phenomenon like Black body radiation is explained by taking into account the wave nature of light.
(b) The mathematical expression of Tafel's equation is $\eta = a - b \log I$
(c) The de Broglie relation shows that the wavelength is directly proportional to the momentum of a particle.
(d) Electroplating reduces corrosion of metal.

OR

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(B) Choose the correct answer.

(p) Hamiltonian operator is

(i) kinetic energy operator (ii) potential energy operator

(iii) total energy operator

(q) If the operator $\frac{d^2}{dx^2}$ operates on the function sin 3x, the eigen value is

(i) 9 (ii) -9 (iii) 3

(r) The deposition potential is given by

(i) (Reversible potential) + (overvoltage)

(ii) (Reversible potential) - (overvoltage)

(iii) (Overvoltage) -(Reversible potential)

(s) Hydrogen overvoltage is also called as _____

(i) acid overvoltage (ii) alkali overvoltage

(iii) bubble overvoltage

4

(C) State **true** of **false** for the following statements.

(a) According to collision theory of reaction rates, the rate of reaction is proportional to the total number of collisions per cm^3 per second.

(b) A fuel cell is a device that combines hydrogen and carbon-di-oxide to produce electricity and water.

(c) In NMR spectroscopy, resonance refers to equal magnitude of absorbed and precessional frequency.

(d) FeS_2 is used as a cathode in lithium - ion cell.

OR

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(C) Choose the correct answer.

(p) The most likely alternative to fossil fuel for clean energy in future is

(i) butane (ii) hydrogen (iii) propane

(q) The nuclear spin of $^{13}_{6}C$ ____

(i) zero (ii) integral (iii) half integral

(r) At low pressure many gaseous reactions are

(i) first order (ii) second order (iii) third order

(s) A semiconductor with excess holes is called

(i) p-type (ii) n-type (iii) p-n junction

3

(D) State true or false for the following statements.

(a) Threshold energy for nuclear reactions is calculated for exoergic reactions.

(b) Energised projectiles are used to induce artificial radioactivity.

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(c) ^{238}U is a fertile material .

OR

(D) Choose the correct answer:- 3

(p) The examples of fissile material is given by

(i) ^{232}Th (ii) ^{233}U (iii) ^{238}U

(q) One curie activity is defined as

(i) $3.7x10^{10}$ dps (ii) $8.7x10^{13}$ dps (iii) $3.7x10^{4}$ dps.

(r) Radioactive equilibrium is

(i) irreversible

(ii) affected by temperature and pressure

(iii) reached in very short time as compared to chemical equilibrium.

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