SG - 503

Total No. of Pages : 3

Seat No. 192

M.Sc. (Part - I) (Semester - II) (NEP) Examination, March - 2023

CC-203 : PHYSICAL CHEMISTRY - II

Sub. Code : 90165/90075

Day and Date : Saturday, 17 - 06 - 2023 **Total Marks : 80**

Time : 10.30 a.m. to 1.30 p.m.

Instructions:
1) **Question one is compulsory.**
2) **Solve any two questions from section-I and Section-II.**
3) **All questions carry equal marks.**
4) **Figures to the right indicates marks.**
5) **Use of log-tables non programmable scientific calculator is allowed.**
6) **Neat diagrams and sketches should be drawn wherever necessary.**

Q1) Answer the following. [16]

a) What is electric double layer?

b) What do you mean by streaming current?

c) The plot of surface tension verses applied potential is called as....

d) What is streaming current coefficient?

e) Write the Eigen value of a given wave function e^{-x} with $\frac{d^2}{dx^2}$ operator.

f) Write an expression for angular momentum operator.

g) Write the expression of Hamiltonian operator.

h) Two different wave functions are orthogonal means that the integral over all space of their product $\int \psi_i^* \psi_j \, d\tau = ?$

i) Write the Stern-Volmer equation of quenching.

j) A photophysical process shows deactivation of molecules from singlet excited state to the singlet ground state is _____

k) T^1- S^0 by nonradiation process is called. - (Fluorescence Phosphorescence)

l) Give any two photophysical and photochemical process.

m) Why heterogeneous catalysis is called as contact catalysis?

n) A catalyst does not affect the final position of equilibrium although it shortens the time. True or False.

o) In Haber process for the synthesis of ammonia along with iron, molybdenum is also used what is the role of molybdenum`?

p) Give the SI unit of activation energy.

P.T.O.

SECTION - I

Q2) a) Describe commutator operator. Determine the commutators $\left[x,\frac{\partial}{\partial x}\right],\left[y,\frac{\partial}{\partial x}\right]$ and $\left[\frac{\partial}{\partial x},\frac{\partial}{\partial x^2}\right]$ using wave function (ψ). **[8]**

b) What is Hermitian operator? Prove that the operator $\frac{h}{2\pi i}x\left(-\frac{d}{dx}\right)$ is not Hermitian. **[8]**

Q3) a) In an electrocapillary measurements of surface tension of Hg in contact with 2.0 NHCl gave the following data. **[8]**

γ surface tension (dynes cm^{-1})	414	406	391
V cell potential (V)	−0.20	0.00	+0.20

i) Based on the above data, calculate (a) the charge of the electrode, q_{M1}, for the change in potential from –0.20 to 0.00 V;

ii) The charge of the electrode, q_{M2}, for the change in potential from 0.00 to + 0.02 V;

iii) If q_{M1} is assigned a potential of –0.06 V, and q_{M2} of +0.06V, calculate the differential capacitance of the interface.

b) What is diffuse charge double layer? Derive an expression of capacitance by Gouy-Chapmann model. **[8]**

Q4) a) What is electrokinetic phenomenon'? Derive and expression for electro osmotic coefficient'? **[6]**

b) Describe the Dual nature of a particle in quantum mechanics. **[6]**

c) In an electrocapillary measurement, mercury is in contact with a solution. If the height of the column is 2 cm, the inner diameter of the capillary tube is 0.5 mm, and the density of mercury at 25 °C is 13.5457 g cm^{-3} and at 0 °C is 13.5951g cm^{-3}, what are the surface tension values of mercury at these two temperatures? **[4]**

SECTION - II

Q5) a) What is ionic strength? Explain the effect of ionic solution on the rate of reaction. [6]

b) Explain in brief the any one technique to determine the rate constant of chemical reaction. [6]

c) Explain the kinetics of enzymatic reaction. [4]

Q6) a) Define the quantum yield of fluorescence. The quantum yield and observed fluorescence lifetime of aqueous tryptophan are 0.2 and 2.6 ns, respectively. Calculate fluorescence rate constant (kf). [8]

b) Draw the Joblonski diagram and explain in detail type of activation and deactivation process. [8]

[16]

Q7) Short notes on any three of the following :

a) Operators

b) Steady state approximations in kinetics

c) Quenching phenomenon in fluorescence

d) Reference electrodes

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M.Sc. (Part-I) (Semester - II)
Examination, March/April, 2024
CHEMISTRY (PCH201) (NEP 2.0)
Physical Chemistry - II
Subject Code : 94701 / 90165 / 90075

Day and Date : Tuesday, 16-04-2024 **Total Marks : 80**

Time : 10.30 a.m. to 1.30 p.m.

Instructions :

1) Attempt in all five questions
2) Question one from Section **IA is compulsory**
3) Attempt any two questions from **Section-IB and any two questions from Section-II.**
4) All questions carry **equal** marks
5) Answers to the Sections I and II should be written in the same answer book
6) Figure to the **right** indicates **marks**
7) Use of **log-table/nonprogrammable scientific calculator** is **allowed** for all sections (i.e. **IA, IB** and **II**).
8) Any device capable of **Photocopying, Scanning, Data Storage, Browsing etc. (e.g. Mobile, iPad, etc.) is Strictly Prohibited.**
9) Neat diagrams and **sketches** should be drawn wherever necessary

SECTION - IA

Q.1 Answer the Following (one mark each) **(16)**

a) The existence of zero-point energy is consequence of ..... in case of particle confined in one dimensional box.

b) Show that $\psi = Ae^{ikx}$ is an ‹ eigenfunction of the operator $\frac{h}{2\pi i}\frac{\partial}{\partial x}$. What is the eigenvalue?

c) Explain the meaning of $|\psi|^2 d\tau$.

d) The orthonormal set of wave functions for a given system can be represented by the expression $\int \psi_i^* \psi_j d\tau = \delta_{ij}$; the symbol δ_{ij} is called as .....

e) Define 'micro-canonical' ensemble.

f) State equipartition principle.

g) Write the values of σ (symmetry factor) for a rotational motion of CO and N_2 gases.

h) Give relationship between partition function and internal energy.

i) Calculate the ionic strength of 0.3 molar aqueous $CaCl_2$ solution.

j) Write Debye-Hückel limiting law for osmotic coefficient.

k) State the type of electrode for Ag|AgCl(s), Cl^-(aq)

l) Give relationship between molal and mole fraction scale activity coefficient.

m) Rate of reaction between cation and neutral reactant will ..... (increase/ decrease/not change) on increasing the ionic strength of the reaction medium.

n) What is the overall order of reaction between acetone and iodine catalysed by acid.

o) Under steady state approximation, the concentration of reactive intermediate will ..... (increase/decrease/remain constant) with time.

p) State secondary salt effect.

SECTION-IB

Q.2 a) Solve the Schrödinger wave equation for a particle confined in a box and obtain an equation for energy. Sketch it for first few energy levels and comment on the concept quantization. **(08)**

b) Evaluate the transition dipole moment integral for an electron in one dimensional box and state the selection rule for electronic transitions. **(08)**

Q.3 a) What is thermodynamic probability? Show how this definition can be used to derive a general equation for the distribution of particles over different energy levels if the particles are assumed to be independent and indistinguishable. **(08)**

b) In statistical mechanics, the entropy S of a system is set equal to k ln W, where k is the Boltzmann constant, and W is the total number of microstates accessible to the system. Can you justify this equality? **(08)**

Q4. a) State assumptions of interionic interaction theory. Based on this and balancing of retarding forces with forces on ions due to applied electric field, show that the molar conductivity decreases with concentration in the limit of very low concentrations. What this resultant equation is called as? **(08)**

b) Write an equation for Debye-Hückel limiting law in terms of osmotic and activity coefficients. State its validity for different types of electrolytes in aqueous medium. Write the forms of activity coefficients and their interrelationships. **(08)**

SECTION-II

Q.5 a) Discus in brief Michaelis-Menten mechanism of enzyme catalysis. With help of Lineweaver-Burk Plot, explain how the maximum rate and K_M in can be evaluated? **(08)**

b) State steady state approximation and explain its utility in obtaining the rate laws for catalysed gaseous chemical reactions with suitable examples. **(08)**

Q.6 a) Operators for the components of angular momentum are given by **(06)**

$$\hat{L}_x = \frac{h}{2\pi i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \hat{L}_y = \frac{h}{2\pi i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right), \hat{L}_z = \frac{h}{2\pi i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

Prove that: $[\hat{L}_x.\hat{L}_y - \hat{L}_y.\hat{L}_x] = \frac{ih}{2\pi}\hat{L}_z$

b) Discuss the utility of osmotic coefficient in evaluation of ion-association in electrolytic solutions through Bjerrum model. **(06)**

c) Calculate the vibrational partition function for molecular chlorine at 300 K. Given: Vibrational frequency is 565 cm^{-1}. **(06)**

Q7. Write notes on any four of the following: (16)

a) Step-up and step-down operators

b) Debye-Falkenhagen effect

c) Primary salt effect

d) Sackur-Tetrode equation

e) Hermitian operators

f) Autocatalytic reaction with examples

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