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UNIVERSITY WITH A PURPOSE

UNIVERSITY OF PETROLEUM AND ENERGY STUDIES
Examination, July 2020

Programme: B.Sc. (H) Chemistry	**Semester : IV**
Course Name: Physical Chemistry IV	**Max. Marks : 100**
Course Code: CHEM2006	**Attempt Duration : 3 hrs.**
No. of page/s:	

Note:

1. Read the instruction carefully before attempting.
2. This question paper has two section, Section A and Section B.
3. There are total of six questions in this question paper. **One** in **Section A** and **five** in **Section B**
4. **Section A** consist of multiple choice based questions and has the total weightage of 60%.
5. **Section B** consist of long answer based questions and has the total weightage of 40%.
6. The maximum time allocated to **Section A** is 180 minutes.
7. **Section B** to be submitted within 24 hrs from the scheduled time i.e. if the examination starts at 10:00 AM, the long answers must be submitted by 09:59:59 AM next day. Similarly, if the examination starts at 2:00 PM it must be submitted by 01:59:59 PM next day. (*Exceptional provision due extraordinary circumstance due to COVID-19 and due to internet connectivity issues in the far-flung areas*)**.**
8. No submission of **Section B** shall be entertained after 24 Hrs.
9. **Section B** should be attempted after **Section A**
10. **The section B** should be attempted in blank white sheets (hand written) with all the details like programme, semester, course name, course code, name of the student, Sapid at the top (as in the format) and signature at the bottom (right hand side bottom corner)
11. Both section A & B should have questions from entire syllabus.
12. The COs mapping, internal choices within a section is same as earlier

Section – A (Attempt all the questions)

(25 × 1 marks)

Q1:

(i) The specific conductance of N/50 KCl solution is 0.002765 $ohm^{-1}cm^{-1}$ at 25 ^{0}C. If the resistance of the solution contained in the cell is 100 ohms, calculate the cell constant. **[3Marks]**

(a) 0.2765 cm^{-1}
(b) 0.02765 cm^{-1}
(c) 0.002765 cm^{-1}
(d) 0.0002765 cm^{-1}

(ii) The role of a catalyst is to change _____. **[2Marks]**

(a) gibbs energy of reaction.
(b) enthalpy of reaction.
(c) activation energy of reaction.
(d) equilibrium constant.

(iii) The resistance of 0.5 M solution of an electrolyte in a cell was fond to be 45 ohm. Calculate the molar conductance of the solution if the electrodes in the cell are 2.2 cm apart and have an area of 3.8 cm^2. **[3Marks]**

(a) 2572 X 10^{-4} Sm^2mol^{-1}
(b) 25.72 X 10^{-4} Sm^2mol^{-1}
(c) 0.45 X 10^{2} Sm^2mol^{-1}
(d) 11.0 X 10^{-1} Sm^2mol^{-1}

(iv) For the strong electrolyte NaOH, NaCl and $BaCl_2$, the molar ionic conductances at infinite dilution are 248.1 X 10^{-4}, 126.5 X 10^{-4}, and 280.0 X 10^{-4} Sm^2mol^{-1}, respectively. Calculate Λ^0m for $Ba(OH)_2$. **[3Marks]**

(a) 5.232 x 10^{-4} Sm^2mol^{-1}
(b) 52.32 x 10^{-4} Sm^2mol^{-1}
(c) 523.2 x 10^{-4} Sm^2mol^{-1}
(d) 5232 x 10^{-4} Sm^2mol^{-1}

(v) Which of the following statements is not correct about order of a reaction. **[2Marks]**

(a) The order of a reaction can be a fractional number.
(b) Order of a reaction is experimentally determined quantity.
(c) The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.
(d) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression.

(vi) Which of the following statements is correct? **[2Marks]**

(a) The rate of a reaction decreases with passage of time as the concentration of reactants decreases.

(b) The rate of a reaction is same at any time during the reaction.

(c) The rate of a reaction is independent of temperature change.

(d) The rate of a reaction decreases with increase in concentration of reactant(s).

(vii) Rate law for the reaction A + 2B → C is found to be

$$\text{Rate} = k[A][B]$$

Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be_____. **[3Marks]**

(a) the same

(b) doubled

(c) quadrupled

(d) halved

(viii) In any unimolecular reaction _____. **[2Marks]**

(a) only one reacting species is involved in the rate determining step.

(b) the order and the molecularity of slowest step are equal to one.

(c) the molecularity of the reaction is one and order is zero.

(d) both molecularity and order of the reaction are one.

(ix) Which of the following statements are in accordance with the Arrhenius equation? **[2Marks]**

(a) Rate of a reaction increases with increase in temperature.

(b) Rate of a reaction increases with decrease in activation energy.

(c) Rate constant decreases exponentially with increase in temperature.

(d) Rate of reaction decreases with decrease in activation energy

(x) During decomposition of an activated complex **[2Marks]**

(a) energy is always released

(b) energy is always absorbed

(c) energy does not change

(d) reactants may be formed

(xi) Ozone is formed by _____ dissociation of molecular oxygen into individual oxygen atoms. **[2Marks].**

(a) Photochemical

(b) Thermochemical

(c) Thermal
(d) Ionic

(xii) Which of the following will result in deviation from Beer's law? **[3Marks]**
(A) Change in a refractive index of medium
(B) Dissociation of analyte on dilution
(C) Polychromatic light
(D) Path length of cuvette

(a) A, B and C
(b) B, C and D
(c) A, C and D
(d) A, B and D

(xiii) The quantum efficiency of a photochemical reaction is defined as _____. **[2Marks]**
a) ratio of molecules decomposed in a given time to the number of quanta absorbed in the same time
b) number of molecules decomposed in a given time
c) number or quanta absorbed percent time
d) ratio of' molecules decomposed in a given time to the number of quanta emitted in the same time

(xiv) In p-type semiconductors, number of holes _____ number of electrons. **[2Marks]**
(a) Equal
(b) Greater than
(c) Less than
(d) Twice

(xv) What are the appropriate reasons for the deviation from the Beer's law among the following? **[2Marks]**
(A) Monochromaticity of light
(B) Very high concentration of analyte
(C) Association of analyte
(D) Dissociation of analyte
a) A, B and D
b) B, C and D
c) A, C and D
d) A, B and C

(xvi) Which of the following is an incorrect statement? **[2Marks]**

(a) First step in photochemistry is excited state (photoexcitation)

(b) Photochemical reactions are caused by absorption of ultraviolet only

(c) When a molecule or atom in the ground state (S0) absorbs light, one electron is excited to a higher orbital level

(d) it is possible for the excited state S_1 to undergo spin inversion

(xvii) Which of the following statements regarding enzymes is false? **[2Marks]**

(a) A given enzyme catalyses just one type of reaction

(b) While most enzymes are proteins, some are composed of RNA

(c) The activity of enzymes is typically impaired at high temperatures

(d) Enzymes act to lower the activation energy of a reaction by stabilising the transition state, but do not participate chemically in the reaction

(xviii) Which one of the following statements regarding V_{max} and K_M is false? **[2Marks]**

(a) V_{max} is the maximum rate at which a particular enzyme-catalysed reaction can proceed.

(b) K_M is the concentration of substrate at which the rate of the reaction reaches V_{max}

(c) A small value of K_M tells us that an enzyme binds strongly to its substrate

(d) A large value of K_M tells us that an enzyme shows little specificity for a given substrate

(xix) Flow of electrons is affected by the following **[2Marks]**

(a) Thermal vibrations

(b) Impurity atoms

(c) Crystal defects

(d) All

(xx) Activation energy of a chemical reaction can be determined by _____**[2Marks]**

(i) determining the rate constant at standard temperature.

(ii) determining the rate constants at two temperatures.

(iii) determining probability of collision.

(iv) using catalyst.

(xxi) The molar extinction coefficient of phenanthroline complex of iron (II) is 12,00 dm^3 mol^{-1} cm^{-1} and the minimum detectable absorbance is 0.01. Calculate the minimum concentration of the complex that can be detected in a Lambert-Beer law cell of path length 1.00 cm. **[3Marks]**

(a) 8.33×10^{-6} M
(b) 83.3×10^{-6} M
(c) 1.2×10^{-6} M
(d) 12.00×10^{-6} M

(xxii) A substance when dissolved in water at 10^{-3} M concentration absorbs 10 per cent of an incident radiation in a path of 1 cm length. What should be the concentration of the solution in order to absorb 90 per cent of the same radiation? **[3Marks]**

(a) 0.218 mol dm^{-3}
(b) 0.0218 mol dm^{-3}
(c) 0.9 mol dm^{-3}
(d) 0.09 mol dm^{-3}

(xxiii) In a first order reaction, it takes the reaction 40.5 minutes to be 25% decomposed. Calculate the rate constant of the reaction. **[3Marks]**

(a) 10.12×10^{-3} min^{-1}
(b) 7.11×10^{-3} min^{-1}
(c) 6.25×10^{-3} min^{-1}
(d) 25×10^{-3} min^{-1}

(xxiv) The rate constant of a second order reaction is 5.70×10^{-5} dm^3 $mol^{-1}s^{-1}$ at 25 ^{0}C and 1.64×10^{-4} dm^3 mol^{-1} s^{-1} at 40 ^{0}C. Calculate the activation energy. **[3Marks]**

(a) 54.48 kJ mol^{-1}
(b) 57.00 kJ mol^{-1}
(c) 1.64 kJ mol^{-1}
(d) 9.38 kJ mol^{-1}

(xxv) The $t_{1/2}$ of a reaction is doubled as the initial concentration of the reactant is doubled. What is the order of reaction? **[3Marks]**

(a) Zero order
(b) First order
(c) Second order
(d) Third order

Section – B (Attempt all the questions)
(5 × 8 marks)

Q2: Discuss the activated complex theory (ACT) of bimolecular reactions. Explain how this theory helps in evaluating standard enthalpy of activation and standard entropy of activation.

Q3: Write a brief note on Norrish Type-I and Norrish Type-II reactions.

Q4: Discuss femtosecond transition state spectroscopy

Q5: Write short notes on the following:
Promoters and inhibitors
Effect of pH on enzyme catalysis

Q6: The E.M.F. of the standard cell written as
$Cd(Hg), CdSO_4.\ 8/3H_2O(s)$ **I** $CdSO_4$ (sat.), $Hg_2SO_4(s)$,Hg
in which the cell reaction is
$Cd(Hg) + Hg_2SO_4(s) + 8/3\ H_2O(l) \rightleftarrows CdSO_4.\ 8/3H_2O(s) + 2Hg(l)$
is 1.0185 V at 25 ^{0}C. Calculate ΔG^0, ΔS^0, and ΔH^0 for the cell reaction if $(\partial E^0/\partial T)p$ for the cell is 5.00×10^{-5} VK^{-1}.

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