SEAT No._____ Sc

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[22/A-9]

SARDAR PATEL UNIVERSITY
B.Sc. EXAMINATION (SEM-VI)
APRIL-2018
PHYSICAL CHEMISTRY
US06CCHE06

DATE : 06/04/2018 (Friday)
TIME : 10.00 to 1.00 PM **Marks: 70**

Q-1 Choose one most appropriate option out of four provided to you. **(10)**

(i) Which of the following is used for elucidating the mechanism of complex reaction?
(a) The equilibrium approximation (b) the steady state approximation
(c) Both a and b (d) None of these

(ii) At a given temperature, if activation energy is very high then the rate of reaction will be
(a) Medium (b) Fast (c) Slow (d) Very high

(iii) The reaction coordinate which have maximum potential energy is called
(a) Simple complex (b) Ionic complex
(c) Catalytic complex (d) Activated complex

(iv) The symmetry number for HCl and HCN is
(a) 1 (b) 2 (c) 3 (d) 4

(v) The rotational energy of the molecule depends on _____ of the molecule.
(a) Molar mass (b) Moment of inertia
(c) Stiffness of bond (d) Size of container

(vi) The degeneracy of J^{th} rotational energy level is given by g_j=
(a) 2J+1 (b) 2J-1 (c) J=1 (d) J-1

(vii) Electrochemical detector belongs to
(a) Bulk property (b) universal
(c) Solute property (d) Selective

(viii) Which of the following solvent is expected to have maximum compressibility factor?
(a) n-pentane (b) n-hexane (c) n-heptane (d) n-octane

(ix) When oxalic acid is shaken with ether and water, it _____ in water.
(a) Associates (b) Dissociates
(c) Remains same (d) Remains unaffected

(x) When the solute undergoes association in one of the solvent then the Nernst distribution law is modified as
(a) $C_1=C_2^{1/2} \times K$ (b) $C_2^{1/2} \times C_1 = K$
(c) $C_1 = K \times C_2^2$ (d) $C_1 = K \times C_2^3$

Q-2 Give answers of any ten questions. **(20)**

(i) Explain Franck-Rabinovich effect.
(ii) Suggest a probable mechanism for the reaction: $Hg_2^{+2} + Tl^{+3} \rightarrow 2Hg^{+2} + Tl^{+}$
(iii) Can the activation energy of a reaction be zero or negative? Why?
(iv) State assumptions involved in Boltzmann distribution law.
(v) Define: Thermal energy, Degeneracy of energy levels
(vi) Give the importance and limitations of Boltzmann distribution law.
(vii) What are the most important advantages of UV detector?
(viii) Describe any two types of column packing in HPLC.
(ix) Enlist the different stationary phase used in HPLC.
(x) What are the limitations of distribution law?
(xi) Write the characteristics of liquid which can be proved as good extractant.
(xii) Name the factors that promote rate and selectivity of an extraction process.

[P.T.O.]

Q-3 (a) The mechanism for the reaction $H_2 + Br_2 \rightarrow 2HBr$ is as follows. **(5)**

(i) $Br_2 \xrightarrow{k_1} 2Br$

(ii) $Br + H_2 \xrightarrow{k_2} HBr + H$

(iii) $H + Br_2 \xrightarrow{k_3} HBr + Br$

(iv) $H + HBr \xrightarrow{k_4} H_2 + Br$

(v) $2Br \xrightarrow{k_5} Br_2$

Using the mechanism and steady state approximation for [H] and [Br], derive the rate law expression for the formation of HBr.

(b) Discuss the activated complex theory for bimolecular gaseous reaction. **(5)**

OR

Q-3 (a) Discuss the kinetics of opposing reaction in which the forward as well as backward reactions are both first order. **(5)**

(b) Discuss the Lindemann theory of unimolecular reaction. **(5)**

Q-4 (a) Derive equations for partition function of one dimensional and three dimensional translational motions. **(5)**

(b) Derive equations for partition function and thermal energy of rotational motion. **(5)**

OR

Q-4 (a) Derive equations for partition function and thermal energy of vibrational motion. **(5)**

(b) State and explain different types of energy possessed by a gas molecule at any temperature. Enlist the molecular properties on which these different energies depend. **(5)**

Q-5 Draw the schematic diagram of HPLC. Give principle, apparatus and basic functions of each part of HPLC. **(10)**

OR

Q-5 Discuss the effect of temperature on HPLC. Also give the advantages and applications of HPLC. **(10)**

Q-6 (a) Discuss briefly the various factors that are responsible for affecting the process of extraction. **(5)**

(b) Distribution ratio of $PdCl_2$ in tri-n-butyl-phosphate (TBP) towards 3M HCl is 2.3. How many times the extraction should be carried out using 5 ml TBP each time to extract 99.5% $PdCl_2$ from 15 ml 3M HCl solution? **(5)**

OR

Q-6 (a) Write a note on batch extraction and continuous extraction. Give the advantages of solvent extraction. **(5)**

(b) In presence of dithiozane at $P^H=6$, a metal X gets 95% extracted with v ml of methylenechloride to V ml of aqueous solution. Under the same condition metal Y is 5% extracted. Calculate the efficiency of separation of metal X and Y. If volume of methylenechloride and aqueous solution is same. **(5)**