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SARDAR PATEL UNIVERSITY

M. Sc. (CHEMISTRY) FIRST SEMESTER Examination 2019

Friday, 22nd November 2019

10.00 a.m. to 1.00 p.m.

PS01CCHE23, Topics in Physical Chemistry – I

N.B.: i. Figures to the right of each of the question indicate marks
ii. Unless otherwise mentioned, symbols and notations have their usual standard meanings, please see the required character tables at the end
iii. Neat sketches are to be drawn to illustrate answers, wherever required
1atm = 760 mm, R = 8.314 $JK^{-1}mole^{-1}$, γ_{H2O} = 72.8 mN/m, g =9.8 ms^{-2}

1 **Choose an appropriate answer:** **[08]**

i) The relation between enthalpy and energy is:
(a) $\Delta H = \Delta E - \Delta nRT$ (b) $\Delta H = \Delta E - nRT$
(c) $\Delta H = \Delta q - \Delta nRT$ (d) $\Delta H = \Delta q - nRT$

ii) Gibbs – Duhem equation is mostly applied at:
(a) $dT = dP \neq 0$ (b) $dT = 0$ (c) $dP = 0$ (d) $dT = dP = 0$

iii) The micellar equilibria is represented by, $n \, . \, S \Leftrightarrow M_n$, where n is equal to:
(a) 1 (b) 0 (c) α (d) < M

iv) Which of the following is **NOT CORRECT** ?
(a) The shape of meniscus depends upon the balance between cohesion of a liquid to its adhesion
(b) The meniscus is concave when both the cohesion and adhesion are equal
(c) The meniscus is concave when cohesion dominates the adhesion
(d) The meniscus is concave when the adhesion dominates the cohesion

v) Two substances are in equilibrium in a reversible chemical reaction. If the concentration of each substance is doubled, then the value of the equilibrium constant will be

(a) Doubled (b) Halved (c) Same (d) One fourth of its original value

vi) In the reaction, represented by, $2SO_2 + O_2 \leftrightharpoons 2SO_3$; ΔH = - 42 Kcal; the forward reaction will be favored by:

(a) Low temperature (b) High pressure c) Neither a nor b (d) Both a and b

vii) Solid $CuSO_4$ dissolves in water, one of the reasons is
(a) instantaneous dipole-induced dipole forces (dispersion or London forces) between the Cu^{2+} and the SO_4^{2-} ions

(b) instantaneous dipole-induced dipole forces (dispersion or London forces) between the water molecules

(c) the ion-dipole forces between the ions and the water molecules
(d) the electrostatic force of attraction between the Cu^{2+} and the SO_4^{2-} ions

viii) A solute is most likely to be highly soluble in a solvent if the solute is _____ and the solvent is _____.

(a) ionic or polar, polar (b) non-polar, ionic
(c) ionic or polar, non-polar (d) non-polar, polar

2 Answer the following questions as directed **(ANY SEVEN).** **[14]**

i) Define briefly the driving force for a spontaneous process in terms of appropriate laws of thermodynamics.

ii) How absolute entropy of a substance is measured experimentally ?

iii) Define volume of mixing for a solution and what is inferred if it is negative ?

iv) What are surface active agents ? Give one example each for ionic and nonionic type surfactants.

v) Define: Overpotential and its importance in electrochemistry.

vi) Give brief account on rate of reaction.

vii) What does a reaction coordinate diagram indicates?

viii) How particle collisions and physical states of the reactants influence the reaction rates?

ix) Give the standard relation for thermodynamic properties of micellization.

3 a) What are activity coefficients, γ ? Derive the relation for determining γ using Gibbs – Duhem equation. **[06]**

b) (i) Define the terms: $(\gamma_\pm)^{\nu+\,\nu-} \cong (\gamma_+)^{\nu+}\ (\gamma_-)^{\nu-}$ and give the relations for $\gamma_\pm$ and γ_+ **or** γ_- for dilute aqueous solutions of $BaCl_2$. **[03]**

(ii) Calculate the change in chemical potential for one mole of an ideal gas at 25 °C and 500 mm pressure. **[03]**

OR

b (i) Derive the Raoults law: $x_1' = P_i / P_i^*$ for an ideal solution under equilibrium conditions taking chemical potentials as base. [03]

(ii) State Debye – Huckel limiting law and calculate the activity coefficients of Cu^{2+} and NO_3^{1-} ions in 2×10^{-3} M aq. solution of $Cu(NO_3)_2$. [03]

4 a) Derive the expression, $r = k[A] = k[A_0]e^{-k_A t}$ where k_A is the rate constant wrt concentration of A, for the integrated rate law for the aA→Products reaction. [06]

b) Explain rate laws and equilibrium constants for elementary reactions. [06]

OR

b) (i) For the reactions: [03]

$$A+B \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} C \quad ; \quad C+B \xrightarrow{k_2} D$$

find $-dC_A/dt$, $-dC_B/dt$, dC_C/dt and dC_D/dt

(ii) Write at least three examples of reactions where catalyst being used at industrial scale. [03]

5 a) Discuss Guoy-Chapman model of electrical double layer around an ion with its success and limitations. [06]

OR

a) Derive Butler-Volmer equation for cathodic current density (η is negative). [06]

[03]

b) (i) Write Lippmann equation with terms involved in it along with significance of this equation. [03]

(ii) Describe briefly ion-solvent interactions. [03]

6 a) Derive Young – Laplace equation and explain how it is useful in describing the shape of a given surface ? [06]

b) (i) Calculate the radius of spherical water droplet given the pressure difference of inside and outside is 291.2 kPa [03]

(ii) Explain the driving force for the micellization of an ionic surfactant. [03]

OR

b) (i) What is capillary rise and how it can be used to measure the surface tension? [03]

(ii) Estimate the height of the water inside a capillary tube of 0.25 mm radius considering that $\theta = 0$, $\rho_{H2O} = 0.9956$ g.cm^{-3}. (work out the units) [03]

—X—