SH-I/Chemistry-102C-2(T)/19

B.Sc. Semester I (Honours) Examination, 2018-19

CHEMISTRY

Course ID : 11412 **Course Code : SHCHE/102/C-2(T)**

Course Title: Physical Chemistry I

Time: 1 Hour 15 Minutes **Full Marks: 25**

The figures in the margin indicate full marks.
Candidates are required to give their answers in their own words as far as practicable.

1. Answer *any five* questions: 1×5=5

(a) Draw Andrew's isotherms for CO_2 at $T > T_c$ and $T < T_c$.

(b) Write the relation between Boyle temperature and Inversion temperature of a gas.

(c) State the spontaneity criteria for an isolated system in terms of entropy.

(d) At 27 °C for equal volume of N_2, O_2 and CO_2, which one has the maximum average velocity?

(e) For two 1st order reactions with rate constants k_2 and k_1 ($k_2 > k_1$), plot concentration of reactant vs. time in a single graph.

(f) How is the first law of thermodynamics applicable in Hess's law?

(g) 'Arrhenius A factor always have the same unit as the rate constant' — Comment.

(h) Whether Joule–Thomson expansion is a reversible or irreversible process?

2. Answer *any two* of the following: 5×2=10

(a) (i) Establish the relation between mean free path of the gas molecules with T and P. 2

(ii) Calculate the root mean square deviation for O_2 at 27 °C. 3

(b) (i) Deduce the rate law for the following reaction mechanism: 2

$$A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A \text{ (fast)}$$

$$A + B \xrightarrow{k_2} P \text{ (slow)}$$

(ii) Prove that for an ideal gas $\left(\frac{\partial H}{\partial V}\right)_T = 0$. 2

(iii) State the standard state for Iodine. 1

(c) (i) The heat of neutralization of HCN by NaOH is 2900 Cal. Calculate the heat of ionization of 1 mole of HCN; given that heat of reaction of $H^+ + OH^- = H_2O$ is 13800 Cal. 2

(ii) The rate constant of a reaction is given by $\ln k = A - \frac{B}{T} + c \ln T$ where A, B, C are constants. Find the value of Activation energy for the reaction. 2

(iii) Find the dimension of reaction rate. 1

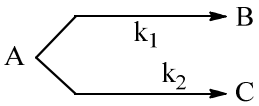
(d) (i) Transform van der Waal's equation of state into cubic form. Plot van der Waal's equation in a P vs. V diagram for a fixed temperature. 2+1=3

(ii) Define turn-over number. 2

3. Answer *any one* question: 10×1=10

(a) (i) Show the equivalence of Clausius and Planck-Kelvin statement. 4

(ii) Consider the parallel reaction 3



Here both the reactions are of 1st order and $k_1 = 3k_2$.

If 60% decomposition of A takes place in 20 minutes find k_1 and k_2.

(iii) Transform 3-dimensional Maxwell's speed distribution into kinetic energy distribution. 3

(b) (i) Write the thermodynamic equation of state involving Helmhlotz free energy. Derive the corresponding Maxwell's relation from that equation. 1+2=3

(ii) Calculate the average energy of N_2O molecule using Equipartition Principle at high temperature. 3

(iii) Convert van der Waal's equation of state into Virial form. 2

(iv) Find the $t_{1/2}$ of a zero order reaction. 2

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