SH/1C EMH/CC-II/21

B.Sc. 1st Semester (Honours) Examination, 2022 (CBCS)

Subject : Chemistry

Course : CC-II

Time: 2 Hours **Full Marks: 40**

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: 2×5=10

(a) For the reaction $\propto A \rightarrow$ Products, the plot of $\frac{1}{[A]}$ vs t gives a straight line. What is the order of the reaction?

(b) A spontaneous polymerization reaction is exothermic — Explain.

(c) Calculate the number of binary collisions per cc of N_2 gas at 1 atm. and 25°C.

[The diameter of N_2 – molecule = 3·74Å]

(d) Find out the value of $\lceil \frac{9}{2} / \lceil \frac{5}{2}$.

(e) What is the compressibility factor of the gas? Draw a curve of compressibility factor vs pressure of an ideal gas.

(f) Find the dimension of van der Waals' constant '*a*'.

(g) The efficiency of a Carnot engine can not be 100% — Comment.

(h) Derive Gibbs' – Helmholtz equation.

2. Answer *any two* questions: 5×2=10

(a) (i) How does the Arrhenius equation $K = Ae^{-Ea/RT}$ look at $T \rightarrow \infty$. Mention its significance.

(ii) Find an expression for the half-life period of simple *n*th order reaction.

(iii) What is meant by 'steady-state' of a reaction? 2+2+1

(b) (i) Explain the effect of temperature rise on the mean free path of an ideal gas held at constant pressure.

(ii) Show that the fraction of molecules of an ideal gas moving with speeds between C_{mp} and 1.0001 C_{mp} is constant for any gas at any temperature. 2+3

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(c) (i) Show that the work involved in a reversible, adiabatic pressure change of one mole ideal gas is given by $W = C_V T_1 \left[\left(\frac{P_1}{P_2}\right)^{R/C_P} - 1\right]$, where T_1 is the initial temperature and P_1 and P_2 are the initial and final pressures, respectively.

(ii) Derive the following relationship:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

(4)

(d) (i) Derive an expression for Joule – Thomson co-efficient (μ_{JT}) of a gas obeying the equation $P(V - b) = RT$. Comment on the result you obtain.

(ii) What is meant by 'Clausius Inequality'?

(3+1)+1

3. Answer *any two* questions: 10×2=20

(a) (i) What is homogeneous catalysis? Give one example.

(ii) Prove that for an enzyme catalysis reaction the Michaelis constant is the substrate concentration at which the rate is one-half of the limiting rate.

(iii) Demonstrate graphically the primary salt effect of the following reaction:

$CO(NH_5)Br^{2+} + Hg^{2+} \rightarrow$ Products

Mention the slope value.

(iv) What do you mean by negative order reaction? Give an example.

2+4+2+2

(b) (i) For every process in an isolated system, $\Delta U = 0$. — Justify or criticise the statement.

(ii) Classify each of the following processes as reversible or irreversible:

(I) Freezing of water at 0°C and 1 atm. pressure.

(II) Freezing of super-cooled water at –10°C and 1 atm.

(iii) Draw and explain the T–S diagram for an ideal gas which undergoes Carnot Cycle. What does the enclosed area signify?

(iv) The heats of formation of CO_2 from diamond and graphite are – 94500 cals and – 94050 cals respectively. What is the enthalpy-change in the transformation of diamond to graphite?

2+(1+1)+(3+1)+2

(c) (i) From one-dimensional velocity distribution, find out the average kinetic energy of a molecule moving along one dimension.

(ii) For a van der Waals' gas $P_C = 112{\cdot}2$ atm. and $b = 0{\cdot}03707$ lit mol^{-1}. Find the reduced temperature of a gas at 27°C.

(iii) Higher the critical temperature of a gas easier it is to liquify. — Comment.

(iv) Using equipartition principle, calculate the total energy of methane at room temperature.

4+2+2+2

(d) (i) Obtain an expression for rate constant for a reaction in which a first order is opposed by a first order in terms of equilibrium concentration.

(ii) Prove that $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$.

(iii) The Helmholtz energy of one mole of a certain gas is given by

$$A = -\left(\frac{a}{V}\right) - RTln(V - b) + f(T).$$

set up the expression for pressure of the gas.

(iv) Find the time required for the decomposition of $\frac{n-1}{n}$ th fraction of the initial amount of A undergoing a first order reaction 2A $\rightarrow$ Products.

(v) What is inversion temperature? 3+2+2+2+1
