UG 1st Semester Examination 2021

CHEMISTRY (Honours)

Paper : DC-2 (Physical-I) (CBCS)

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

Full Marks: 25

Time : Two Hours

1. Answer any five questions:

1×5=5

- a) If temperature is doubled and the mass of the gaseous molecule is halved, the rms speed of the molecule will change by a factor of
 - (i) 1
 - (ii) 2
 - (iii) 1/2

(iv) ¼

b) If $T \to \infty$, the shape of Maxwell's velocity distribution will become (i) a gaussian.

- (ii) a delta function placed at the origin.
- (iii) a Lorentzian.
- (iv) a straight line parallel to y axis.
- c) Vibrational degree of freedom of CO is
 - (i) 1
 - (ii) 2
 - (iii) 3
 - (iv) 4
- d) The equation of state for one mole of a gas is given by P(V-b)=RT, where b and R are constants. The value of $[\delta H/\delta P]_T$ is
 - (i) V-b
 - (ii) b
 - (iii) 0
 - (iv) RT/(P+b)
- e) Which of the following is not a criterion of spontaneity?
 - (i) $dU_{S,V} < 0$
 - (ii) $dH_{S,P} < 0$
 - (iii) $dS_{U,V} < 0$
 - (iv) $dG_{P,T} < o$
- f) For a reaction $nA \rightarrow product$, rate constant (k) is $10^{-3}M^{-2}s^{-1}$ (where M=molarity), then (i) [A] vs t graph will give straight line
 - (ii) $1/[A]^2$ vs t graph will give straight line
 - (iii) $1/[A]^3$ vs t graph will give straight line
 - (iv) 1/[A] vs t graph will give straight line
- g) If the amount of change of temperature (ΔT) of any one reservoir of a Carnot engine is same in magnitude, the increase in efficiency will be maximum when we

- (i) Decrease the temperature of the cold reservoir.
- (ii) Increase the temperature of the hot reservoir.
- (iii) Decrease the temperature of the hot reservoir.
- (iv) Increase the temperature of the cold reservoir.
- h) A reaction goes to a completion at a finite time. The order of the reaction is
 - (i) fractional-order
 - (ii) first-order
 - (iii) second-order
 - (iv) zero-order
- 2. Answer any four questions:

 $2 \times 4 = 8$

(a) At high temperature the observed $\frac{C_P}{C_V}$ ratio for a non-linear polyatomic ideal gas is $\frac{7}{6}$. Determine the atomicity of the gas.

(b) It is impossible for two reversible adiabatic curves on a P-V diagram to intersect. Justify.

(c) Show that adiabatic P-V curve of an ideal gas is steeper than the corresponding isothermal curve.

(d) A certain reaction takes place in three steps with rate constants k_1 , k_2 and k_3 and activation energies E_1 , E_2 , E_3 . If overall rate constant k= k_1k_3/k_2 , show that overall activation energy $E=E_1 - E_2 + E_3$.

(e) A Carnot engine whose low temperature reservoir is at 7 0 C has an efficiency of 40%. It is desired to increase the efficiency to 50%. By how many degrees should the temperature of the source be increased?

(f) A certain first order reaction is 20% complete in 15 minutes at 27 0 C but for the same extent of reaction, it takes 5 minutes at 37 0 C. What is the activation energy of the reaction?

(g) Calculate Boyle temperature for a gas obeying Van-der-Waals equation,

a=2.44 L² atm mol⁻², b=29.4 ml mol⁻¹

(h) The rms speed of a gas at $27^{\circ}C$ is 400 m s⁻¹. At what temperature the speed will be 1600 m s⁻¹.

3. Answer any two questions:

(a) (i) Find the dimension of 'A' that appears in Maxwell's speed distribution equation

$$\frac{1}{N}\frac{dNc}{dc} = AC^2 \exp[-mC^2/2kT]$$

where terms have their usual significance. What is its SI unit?

Draw the one-dimensional velocity distribution curve of the molecules of an ideal gas and comment on the area under the curve. 2+2+1

(ii) Define mean free path.

(2×6=12)

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(b) (i) Find the numerical value of the compressibility factor of a gas that obeys the equation of state P(V-nb) = nRT. The P and T are such that V/n=10b. 3

(ii) Using suitable thermodynamic equation of state, evaluate $(\delta U/\delta V)_T$ for ideal gas and for the van der Waals gas. What is the physical significance of the difference between two expressions?

(c) (i) If a reversible Carnot cycle working between two temperatures T_1 and T_2 ($T_2 > T_1$) is plotted on a T-S diagram, show that the area enclosed is equal to the work done in the reversible cycle. Indicate the efficiency of the process as a ratio of two areas in the properly drawn diagram.

(ii) Show that the work done in a reversible process is numerically greater than that in an

irreversible process.

(d) (i) Show that for a parallel reaction $A \rightarrow B$ and $A \rightarrow C$, the activation energy of the overall reaction is given by,

 $E = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$; where E_1 and E_2 are the activation energies of two reactions having rate constants k_1 and k_2 respectively.

(ii) For a reaction $A \rightarrow B + C$, it is found that the rate increased by a factor 2.25 when the concentration is increased by a factor 1.5 at the same temperature. What is the order of the reaction with respect to A?

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