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 $T \rightarrow \infty$, 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 $[\partial H/\partial P]_T$ 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) $dG_{p,T}<0$

f) For a reaction nA → product, rate constant (k) is $10^{-2}M^{-2}s^{-1}$(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) $1/[A]^2$ 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: 2×4=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,

$a=2.44\ L^2\ atm\ mol^{-2}$, $b=29.4\ ml\ mol^{-1}$

(h) The rms speed of a gas at 27^0C is 400 m s^{-1}. At what temperature the speed will be 1600 m s^{-1}.

3. Answer any two questions: (2×6=12)

(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. 1

(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? 3

(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. 4

(ii) Show that the work done in a reversible process is numerically greater than that in an irreversible process. 2

(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,

$E = \frac{k_1E_1 + k_2E_2}{k_1 + k_2}$; where E_1 and E_2 are the activation energies of two reactions having rate constants k_1 and k_2 respectively. 3

(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? 3