

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) 1/4
- 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 $nA \rightarrow \text{product}$, rate constant (k) is $10^{-2} \text{M}^{-2} \text{s}^{-1}$ (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:

2×4=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 $k = k_1 k_3 / k_2$, show that overall activation energy $E = E_1 - E_2 + E_3$.

(e) A Carnot engine whose low temperature reservoir is at 7°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°C but for the same extent of reaction, it takes 5 minutes at 37°C . What is the activation energy of the reaction?

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

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

(h) The rms speed of a gas at 27°C 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

$$\frac{1}{N} \frac{dN_c}{dC} = A C^2 \exp[-mC^2/2kT]$$

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.

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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 $(\partial U/\partial V)_T$ 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,

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