B.Sc. 1st Semester (Honours) Examination, 2019 (CBCS)

Subject : Chemistry

Paper : 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 from the following: 2×5=10

(a) Draw the PV—P isotherms for a real gas at temperatures T_1, T_B and T_2 with explanation where $T_2 > T_B > T_1$ and T_B is the Boyle temperature.

(b) Find an expression for the number of molecules per cm^3 of an ideal gas.

(c) Find the value of [⌈(9/2)/⌈(4)].

(d) Explain whether (i) latent heat of melting and (ii) specific gravity are extensive properties.

(e) For a certain mechanical process with an ideal gas, Δu = ΔH. Comment on the nature of the process (The terms have their usual significance).

(f) Why a carnot engine does not exhibit an efficiency of 100%?

(g) Can an elementary reaction be of zero order? Explain.

(h) Comment: Arrhenius factor is independent of temperature.

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

(a) (i) For one-dimensional motion of an ideal gas, Maxwell's speed distribution formula may be explained as $P_u = \left(\frac{m}{2\pi KT}\right)^{1/2} e^{-\frac{mu^2}{2KT}} du$. Arrive at Maxwell's kinetic energy distribution for the ideal gas as per above mentioned speed distribution.

(ii) Find the percentage error in calculating the average kinetic energy of an ideal gas if one uses the average speed for such calculation.

(iii) What is the dimension of frequency of binary collisions? 2+2+1=5

(b) (i) Explain whether (PdV – VdP) is an exact differential.

(ii) Is $\left[\frac{\delta(A/T)}{\delta(1/T)}\right]_V$ a state function? Explain.

(iii) Why it is impossible to produce work by an isolated system during an isothermal process? 2+2+1=5

(c) (i) How can we determine the activation energy of a chemical reaction graphically?

(ii) Consider the following reaction:

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$

Determine the expression of K_2 for the above mentioned reaction. 2+3=5

(d) (i) Derive the thermodynamic equation of states

$$\left(\frac{\partial U}{\partial V}\right)_P = C_P \left(\frac{\partial T}{\partial V}\right)_P - P \;\&$$

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right].$$

(ii) Define Turn Over Number. (2+2)+1=5

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

(a) (i) Calculate the C_V value of gaseous CH_4 at high temperature limit.

(ii) Explain when and how does Dieterici's equation get converted to van der Waals equation.

(iii) Assuming CO_2 to behave ideally, find the value of γ from the principle of equipartition of energy.

(iv) A certain gas has the equation of $P = \frac{RT}{V-BT} - \frac{A}{V^3}$, where "A" and "B" are the characteristic parameters of the gas. Determine the value of "A" and "B". 2+2+2+(2+2)=10

(b) (i) Show that two isothermal P-V plots of a system can never intersect.

(ii) Comment on the change in entropy of a system during an adiabatic irreversible process with reason.

(iii) Correlate "inversion temperature" with "Boyle temperature".

(iv) 5 moles of an ideal monotomic gas at 27°C and 10 atm pressure is expanded adiabatically against a constant pressure of 2 atm till the equilibrium is reached. Calculate the final temperature and the amount of work done. 2+2+2+(3+1)=10

(c) (i) show that the observed rate constant for a reaction catalysed by both acids and bases with respective catalytic rate constant of K_{H+} and K_{OH^-} will pass through a minimum when H^+ Concentration is varied. Calculate the pH at which this minimum is observed at temperature 298K if $K_{H^+}/K_{OH}=100$.

(ii) Show that any property proportional to the concentration of the reactant can be used to study a 1st order reaction without knowing the proportionality constant.

(iii) If a 1st order reaction is 45% complete in 30 minutes, how long will it take for 90% completion?

(iv) Show the graphical variation of the rate of a 2nd order reaction with concentration of the reactant with explanation. 4+2+2+2=10

(d) (i) A reaction is catalysed by a metal ion in solution. Suggest a suitable kinetic method for determination of the concentration of the ion.

(ii) Show that for a van der Waals gas $\left(\frac{\partial C_V}{\partial V}\right)_T$ is estimated to be zero.

(iii) Find the value of ΔU for the photosynthesis process if $\Delta H = -1500$ J mole^{-1} of glucose at 27°C (ΔH and ΔU have their usual significance).

(iv) Compute ΔS for the process H_2O (l, –10°C) → H_2O (s, –10°C), if specific heat of liquid water be 1 cal K^{-1} gm^{-1}, that of ice be 0·5 cal K^{-1} gm^{-1} and latent heat of fusion of ice be 80 cal gm^{-1}. 2+2+2+4=10
