2021

CHEMISTRY — HONOURS

First Paper

(Group - B)

Full Marks : 50

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

CHT-13a

Unit - I

Answer ***any three*** questions.

1. (a) The number of gas molecules of mass 'm' with speed between C and $C + dC$ is given by

$$dN = AC^2 e^{-mC^2/2kT} dC$$

Calculate the value of 'A'.

How does the above distribution vary with temperature? $\left(\text{Given: } \int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4}\sqrt{\frac{\pi}{a^3}}\right)$

(b) Calculate the number of binary collision per cm^3 per second in helium gas at 27ºC and 1 atm. Given that the diameter of He atom = 2×10^{-8} cm. 3+2

2. (a) Write down the Maxwell distribution for molecular speed of gases in three dimensions and describe the features using graphical plot.

(b) Use the Maxwell's distribution of molecular speed to estimate the fraction of N_2 molecules at 500 K that have speeds in the range of 290–300 ms^{-1}. 3+2

3. (a) The virial equation of state in terms of P is given by (neglecting terms of higher order)

$$Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)P + \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right)P^2.$$

Set up an expression for the initial slope of 'Z' versus 'P' curve of a real gas and obtain an expression for the Boyle temperature of the gas.

(b) Apply the equipartition principle to calculate $\gamma = \frac{C_P}{C_V}$ for N_2O assuming it to be ideal. 3+2

4. (a) Derive the reduced equation of state for '*n*' moles of a real gas obeying the van der Waals equation.

(b) Consider the following equation of state for a gas :

$$P\bar{V} = RT\left(1 + {}^{b}\!/_{\bar{V}}\right)$$

Would it be possible to liquefy the gas? Explain. 3+2

5. (a) What is Lennard–Jones 6-12 potential? Draw the Lennard–Jones potential against the internuclear distance plot.

(b) At normal temperature, iodine is a solid but fluorine is a gas. Explain. 3+2

Unit - II

Answer ***any two*** questions.

6. (a) Identify the extensive and intensive properties among the following :

free energy, molar entropy, heat capacity, pressure.

(b) Calculate Q, W, ΔE and ΔH when one mole of ideal gas is reversibly expanded from 10 atm pressure and 2 lit to 5 atm isothermally at 27ºC. 2+3

7. (a) Show that $\left(\frac{\partial E}{\partial V}\right)_T = 0$ for an ideal gas.

(b) Calculate the enthalpy of formation of NH_3, given the enthalpy of combustion of NH_3 and H_2 are – 90.6 kcal mol^{-1} and – 68.3 kcal mol^{-1} respectively. 2+3

8. (a) Derive the integrated form of Kirchhoff's equation to show the variation of ΔH^{o} of a reaction with temperature. Under what condition this variation becomes independent of temperature?

(b) The heat capacity of a substance is often given by :

$$\bar{C}_P = a + bT + {}^{C}\!/_{T^2}$$

Use this expression to estimate the change in molar enthalpy of carbon dioxide when heated from 20ºC to 40ºC

Given : $a = 44{\cdot}22\ JK^{-1}\ mol^{-1}$, $b = 8{\cdot}79 \times 10^{-3}\ JK^{-2}\ mol^{-1}$, $C = -\ 8{\cdot}02 \times 10^{5}\ JK\ mol^{-1}$. 3+2

CHT-13b

Unit - I

Answer ***any three*** questions.

9. (a) State the two important deductions of Carnot's theorem.

(b) Prove both the deductions qualitatively. 2+3

10. (a) State the two famous statements of second law of thermodynamics by naming them properly.

(b) Show that both the statements are equivalent. 2+3

11. (a) What is Clausius Inequality?

(b) A certain mass of ideal gas expands into vacuum to twice its initial volume. Calculate ΔU and ΔS of the process. 2+3

12. (a) Using Maxwell's relations derive the equation of state : $\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$

(b) Define Joule–Thomson effect and Inversion temperature. 2+3

13. (a) Differentiate between Joule–Thomson cooling and adiabatic cooling.

(b) Draw S-T diagram of a Carnot cycle labelling the diagram, mentioning properly all the processes involved. 2+3

Unit - II

Answer ***any two*** questions.

14. (a) The half-life period of a first-order reaction is 15 min. Calculate the rate constant and time taken to complete 80% of the reaction.

(b) What is a pseudo first-order reaction? Explain with an appropriate example. 2+3

15. (a) What is homogeneous catalysis? Explain with a suitable example.

(b) Rate constants of a reaction at 300 K and 310 K are $4{\cdot}5\times10^{-5}$ sec^{-1} and $9{\cdot}0\times10^{-5}$ sec^{-1} respectively. Evaluate the activation energy and pre-exponential factor of the reaction. What should be the order of this reaction? 2+3

16. (a) Calculate the activation energy of a reaction, whose rate constant gets tripled by a rise of temperature from 22ºC to 32ºC.

(b) Derive the Michaelis–Menten equation for enzyme catalysis explaining all the terms involved. 2+3