

VIDYASAGAR UNIVERSITY

B.Sc. Honours Examination 2021

(CBCS)

1st Semester

CHEMISTRY

PAPER-C2T & C2P

PHYSICAL CHEMISTRY - I

Full Marks : 60

Time : 3 Hours

The figures in the right-hand margin indicate full marks.

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

THEORY : C2T

Group – A

Answer any *three* questions. 3×12

 (a) Deduce the expression of Boyle's temperature in terms of a, b, and R where a, b are Van der Waal constant and R is universal gas constant.

- (b) The value of compressibility factor $z \left(z = \frac{PV}{nRT}\right)$ for N₂ at 223 K at 800 atm. pressure is 1.95 and the value of z changes to 1.10 when the temperature and pressure value changes to 373 K and 200 atm. A fixed mass of N₂ occupied a volume of 1 lit. at 223 K and 800 atm. Calculate the volume occupied by the same quantity of N₂ at 373 K and 200 atm. pressure.
- (c) A gas follow the equation of state P(V b) = RT. Can the gas be liquefied explain.
- (d) The value of Van der Waal constant 'a' for the two real gases are 1.333 lit^2 atm mol⁻² and 1.521 lit^2 atm mol⁻² respectively. Explain which of these gas can be liquefied easily. 4+3+3+2
- 2. (a) Calculate the heat of formation of HCl at 348 K from the following data-

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) = HCl(g); \quad \Delta H^\circ = -92300J \text{ at } 298K$$

The mean heat capacity over this temperature range are -

$$H_2$$
 (g); $C_n = 28.53 \text{ JK}^{-1} \text{ mol}^{-1}$

 Cl_2 (g); $C_p = 32.26 \text{ JK}^{-1} \text{ mol}^{-1}$

HCl (g); $C_p = 28.49 \text{ JK}^{-1} \text{ mol}^{-1}$

- (b) Show that decrease in Gibbs energy value is equal to the maximum net work obtainable from the system.
- (c) Under what condition an extensive property may become intensive property? Give an example.

- (d) Derive the expression of Joule-Thomson co-efficient for Van der Waal gas and explain the idea of inversion temperature. 3+3+2+4
- 3. (a) Write the differences between molecularity and order.
 - (b) Explain the Lindeman theory of unimolecular reaction with mathematical derivation.
 - (c) How do you determine the order of a chemical reaction using differential method?
 - (d) The rate of the reaction $2A + B \rightarrow C$ becomes doubled when the concentration of B is only doubled and the rate becomes eight fold when the concentration of both A and B are doubled. Find the order of the reaction with respect to A and B. 2+4+3+3
- **4.** (a) What is protolytic and prototropic mechanism of acid catalyzed reaction? Explain.
 - (b) Mathematically explain the mechanism of enzyme catalysis and establish the Michaelis-Menten equation. What is turnover number?
 - (c) The temperature coefficient of a reaction, $\frac{k_{[T+10]}}{K_T}$, at T = 298 K is 2.00. What will be its value at T = 243K?

(d) Prove that $\left(\frac{\delta s}{\delta p}\right)_T = -\left(\frac{\delta V}{\delta T}\right)_P$. 2+4+3+3

5. (a) Explain the Carnot's theorem and find expression of efficiency of Carnot's engine.

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- (b) For two constituent gases entropy of mixing per mole becomes maximum when constituents are present in equal mole ratio. - Explain.
- (c) Describe the Arrhenius concept on the dependence of reaction rate with temperature.
- (d) 'Reaction of 3rd order are uncommon while those of still higher order are unknown' - Correct or Justify. 4+3+3+2
- 6. (a) Derive the Kirchhoffs equation and briefly describe the effect of pressure on enthalpy of reaction.
 - (b) Establish the equation to calculate the number of binary collision among similar molecules.
 - (c) The pressure correction term $\left(\frac{a}{V^2}\right)$ present in the one mole van der Waal equation will be valid if we consider ternary collision among gas molecule' — explain whether the statement is true or false.
 - (d) Calculate the value of $C_{\rm v},\,C_{\rm p}$ and γ using the idea of equipartition of energy principle. 4 + 3 + 2 + 3

Group – B Answer any *two* questions. 2×2

- 7. Calculate ΔU and ΔS when one mole of an ideal gas undergoes isothermal free expansion from volume V_1 to V_2 .
- 8. In order to increase the efficiency of a Carnot engine which one of the following will be the better choice.
 - (a) Increasing the temp of hot reserviour.
 - (b) Decreasing the temp of the cold reserviour.

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- **9.** Write down the expression of frequency of binary collision of two dissimilar molecule. State each terms involved in the expression.
- 10. A first order reaction can never be completed. Justify or Critrcize.

PRACTICAL : C2P

Answer any one question. 1×15

- 1. Describe the principle and brief process of determination of pH of unknown buffer by colour matching method.
- **2.** Describe the principle and brief process of kinetics of acid-catalyzed hydrolysis of methyl acetate.
- **3.** Describe the principle and brief process of kinetics of decomposition of H_2O_2 . Find the $t(\frac{1}{2})$ of a nth order reaction.

Answer any one question. 1×5

- 4. What is buffer capacity? Calculate the pH of 0.01M acetic acid solution.
- 5. What is pseudo order reaction? Describe the idea of Ostwald dilution method. 2.5+2.5
- 6. Briefly describe the order determination process using $t_{\frac{1}{2}}$ value of a reaction. 2.5+2.5