

B.Sc 1st Semester (Honours) Examination, 2021 (CBCS)

Subject: Chemistry

(Physical Chemistry-I Theory)

Paper: CC-2

Time: 2 Hours

Full Marks: 40

Candidates must give their answer legibly, in their own words as far as practicable.

Answer any *eight* questions from the following:

8 x 5 = 40

1. Write down the equation of state proposed by Dieterici. Arrive at the expression of critical constants T_c and V_c obtained from this equation. Convert Dieterici equation of state into its reduced form.
2. Plot the reversible Carnot cycle for ideal gas system in (a) S vs. T diagram and (b) U vs. S diagram, labelling clearly all the steps involved. Write down the thermodynamic criteria of a gas to be ideal.
3. (a) State the differences between Joule-Thomson cooling and adiabatic cooling.
(b) Write down the condition of spontaneity of a process in terms of entropy and Gibbs free energy. Change in G is more convenient index for ascertaining spontaneity of a process than change in entropy. Why?
4. Considering the internal energy (U) as a function of entropy (S) and volume (V), derive the corresponding Maxwell relation. Calculate the entropy change when an ideal gas expands into vacuum from a volume of 10 lit to 20 lit at 300 K. Also show the variation of entropy as a function of pressure (graphically) for an ideal gas.
5. (a) Explain how the internal energy of C_2H_2 is partitioned according to the equipartition of energy principle. Calculate its C_v value at high temperature limit.
(b) The molecules of an ideal gas are confined to move in a plane. Derive the expression for the M-B distribution of kinetic energy.
6. The first order rate constant (k) of a reaction $A \rightarrow$ products follow the equation $\log k = 53.22 - \frac{36000}{T}$. Calculate the energy of activation at 27°C. Draw the rate versus time profile for i) a zero-order reaction ii) a first order reaction.
7. What is meant by turn-over number? Write down two most prominent features of an enzyme. The rate ' r ' of a reaction of a substrate (S), catalysed by an enzyme (E) is given

by the equation: $r = \frac{k_1[E][S]}{(k_2 + [S])}$, Draw, giving justification, r vs. $[S]$ graph. Suggest one linear plot for determination of k_1 and k_2 .

8. A gas obeys the equation of state $P(V-b) = RT$
- (a) Is it possible to liquefy the gas? Justify.
 - (b) Show that the gas does not have the Boyle temperature.
9. (a) The rate constant of a zero-order reaction is $0.2 \text{ mol dm}^{-3}\text{h}^{-1}$. If the concentration of the reactant after 30 mins is 0.05 mol dm^{-3} , then what will be its initial concentration?
- (b) If a reaction $A + B \rightarrow P$ is exothermic to the extent of 30 kJ/mole and the forward reaction has an activation energy of 70 kJ/mole , find the activation energy for the reverse reaction.
10. (a) Assuming the expression for Maxwell distribution in 3D, plot $\frac{1}{c^2} \left(\frac{dN_c}{dc} \right)$ vs C for O_2 and CH_4 gases at a given temperature. Also assume both the gases are ideal. Give explanation in favour of your answer.
- (b) Two van der Waals gases have the same b but different a . Which one would occupy greater volume under identical conditions of temperature and pressure?

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