WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 1st Semester Supplementary Examination, 2021

CEMACOR02T-CHEMISTRY (CC2)

PHYSICAL CHEMISTRY-I

Time Allotted: 2 Hours Full Marks: 40

The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.

Answer any *three* questions taking *one* from each unit

UNIT-I

Kinetic Theory and Gaseous State

1. (a) At a certain temperature, the speed distribution function depends on the nature of the gas but the energy distribution function is the same for all gases. Justify or criticize. 3

   (b) Define 'mean free path' of a gas molecule. At ordinary temperature and extremely low pressure, the gas molecules collide far more often with the container wall than with one another. — Explain. 4

   (c) For many polyatomic gases, the classical equipartition theorem fails to explain the heat capacity values at low temperatures. — Explain. 3

   (d) Show that the van der Waals equation leads to values of $Z<1$ and $Z>1$, where Z is the compressibility factor, and identify the conditions for which these values are obtained. 3

2. (a) The average speed of a particle in an ideal gas is $\langle v\rangle$. Then show that the number of particles striking a unit area of the wall of the container in unit time is equal to $\frac{1}{4}\frac{N}{V}\langle v\rangle$, where $\frac{N}{V}$ is the number of molecules per unit volume. 4

   Given: $\int_0^\infty xe^{-ax^2}\,dx=\frac{1}{2a}$

   (b) Calculate the average time between collisions for O_2 at 25° C and 1 atm. The diameter of oxygen molecule is 2.4 Å. 3

   (c) The virial equation of state in terms of P is given by 3

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

   At what temperature does the slope of the Z versus P curve (at $P=0$) have a maximum value for the van der Waals gas? What is the value of the maximum slope?

(d) Use the following data to find the value of R: 3

Average speed $< c >$ for an ideal gas at 25° C and 1 bar is 444 ms^{-1}. The molar mass is 32×10^{-3} kg mol^{-1}.

UNIT-II

Chemical Thermodynamics

3. (a) Identify the following systems as open, closed or isolated systems: 3

   (i) A system surrounded by a rigid, impermeable and diathermic wall.

   (ii) A system surrounded by a non rigid, impermeable and adiabatic wall.

(b) **0.1** mole of a perfect gas with C_v independent of temperature is made to undergo a reversible cyclic process consisting of the following steps: 6

Stage 1 (1 lit, 1 atm) ⟶ Stage 2 (1 lit, 3 atm)

Stage 2 ⟶ Stage 3 (2 lit, 3 atm)

Stage 3 ⟶ Stage 4 (2 lit, 1 atm)

Stage 4 ⟶ Stage 1

Calculate q, W, ΔU for each step and for the complete cycle. [Molar $\mathbf{C_v = 1.5\ R}$]

(c) Verify that the results for the cycle satisfy the first law of thermodynamics. 2

(d) Show that the change of entropy is a measure of unavailable work. 2

(e) An ideal refrigerator works between 0° C and T° C. It freezes 2.0 kg of water at 0° C per hour. At the same time, the total heat output to the room is 200 kcal/hr. Calculate T° C. Latent heat of fusion of water at 0° C = 80.0 cal/gm. 3

4. (a) Justify or criticise the following: 2+2

   (i) ΔU is given by the integral $\int C_v\, dT$.

   (ii) $\Delta H = Q$ for a process in which pressure is not constant throughout but for which the final and initial pressures are equal.

(b) Show that the work involved in a reversible, adiabatic volume change from V_1 to V_2 of one mol of an ideal gas is given by 4

$$W = \overline{C_v}\, T_1 \left[\left(\frac{V_1}{V_2} \right)^{R/\overline{C_v}} - 1 \right],$$

where T_1 is the initial temperature.

(c) State Kelvin-Planck and Clausius statements of second law of thermodynamics. 3

(d) Consider the following cycle using 1 mol of an ideal gas, initially at 25° C and 1 atm pressure. 5

Step 1: Isothermal expansion against zero pressure to double the volume.

Step 2: Isothermal reversible compression from $\frac{1}{2}$ to 1 atm.

(i) Calculate the value of $\oint \frac{dQ}{T}$.

(ii) Calculate ΔS for Step 1 and Step 2 respectively.

(iii) Show that ΔS for Step 1 is not equal to the Q for Step 1 divided by T.

UNIT-III

Chemical Kinetics

5. (a) A zero-order reaction can never be elementary. Justify or criticize. 2

(b) For the first-order reactions $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$, show that at any time during the reaction $[B]/[C] = k_1/k_2$. Plot concentration versus time profile of A, B and C when $k_1 = k_2$. 4

(c) The addition of KCl will influence the rate constant of the following reaction at a given temperature. — Justify. 3

$$S_2O_8^{2-} + I^- \longrightarrow \text{Product}$$

(d) Graphically represent the plot of $\log k$ versus pH of a homogeneous acid catalyzed reaction. k is the rate constant. 2

6. (a) 'Unimolecular reactions are not always first-order'. Justify the statement using Lindemann's mechanism. 4

(b) The rate constant of a reaction increases two times when the temperature changes from T K to (T + 10) K, whereas that for another reaction increases three times for the same change in temperature. Find the ratio of their activation energies if they have comparable pre-exponential factors. 3

(c) Show that if A reacts to form either B or C according to $A \xrightarrow{k_1} B$ or $A \xrightarrow{k_2} C$, then E_a, the observed activation energy for the disappearance of A is given by 4

$$E_a = \frac{k_1E_1 + k_2E_2}{k_1 + k_2},$$

where E_1 and E_2 are the activation energies for the first and the second reaction respectively.

N.B. : *Students have to complete submission of their Answer Scripts through E-mail / Whatsapp to their own respective colleges on the same day / date of examination within* 1 *hour after end of exam. University / College authorities will not be held responsible for wrong submission (at in proper address). Students are strongly advised not to submit multiple copies of the same answer script.*

——×——