WEST BENGAL STATE UNIVERSITY
B.Sc. Honours 1st Semester Examination, 2022-23

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

1. (a) Plot the Maxwell speed distribution profile of He(g) at, temperature T K. How will the plot change if the temperature is changed to 2T K. Give reasons for your answer.   2

   (b) Find an expression for the most probable speed from the Maxwell speed distribution formula clearly stating the conditions involved.   3

   (c) Show that the fraction of molecules of an ideal gas with speeds in the range c_{mp} to $1.0001\ c_{mp}$ is constant for a given gas at a given temperature (c_{mp} is the most probable speed).   2

   (d) Is it possible to liquefy a gas obeying the equation of state $p\overline{V} = RT(1 + b/\overline{V})$? Justify your answer, where b is van der Waals constant.   2

   (e) (i) Find $\left(\dfrac{\partial U}{\partial V}\right)_{T,n}$ for a van der Waals gas and hence deduce a physical significance of the associated van der Waals constant.   3+1

   (ii) What value do you expect for the quantity $\left(\dfrac{\partial U}{\partial V}\right)_{T,n}$ for an ideal gas (no derivation)? Justify.

2. (a) Molecular speed distribution of gas at a temperature T is given as   1+3

$$f(c) = \frac{1}{n}\frac{dn}{dc} = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} c^x e^{-mc^2/2k_B T}.$$

   (i) What does the quantity $f(c)$ signify?

   (ii) Find x using only dimensional argument.

   (b) Distinguish between Maxwell speed and velocity distributions of a gas at a given temperature.   2

(c) Calculate the ratio of number of molecules having speed in the range $2c_a$ and $(2c_a + dc)$ to the number of molecules having speed in the range c_a and $(c_a + dc)$ (c_a is the average speed).   3

(d) Two gases have compressibility factor values as 1.02 and 0.98. Which one is easier to liquefy? Justify your answer.   2

(e) Van der Waals equation in the virial form at a pressure p is given as   2

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

Deduce the condition when the behavior of the gas approaches ideality.

Find an expression for the initial slope of Z vs. p curve and comment on the relative magnitudes of the slope when, the gas behaves nearly ideal.

UNIT-II

3. (a) An ideal gas is isothermally expanded from an initial volume V_i to a final volume V_f in the following two cases: 2+2

Case-I: expansion from V_i to V_f in one step

Case-II: expansion from V_i to V_1 to V_2 to V_f where $V_i < V_1 < V_2 < V_f$.

(i) Indicate the process on separate p vs. V diagrams, and compare the net work done in the two cases.

(ii) What change in the 'net work done' do you expect if the total number of steps of the expansion process is very largely increased?

(b) Show that $C_p - C_V = \left[\left(\dfrac{\partial U}{\partial V}\right)_{T,n} + p\right]\left(\dfrac{\partial V}{\partial T}\right)_{p,n}$ and hence show that $C_p - C_V = nR$ 4+1

for an ideal gas.

(c) Represent the Carnot cycle on a T-S diagram with appropriate justification, and express the efficiency of the cycle in terms of the ratio of the areas under the curves.   3

(d) A Carnot engine converts $1/6^{th}$ of the supplied heat to work. The efficiency of the engine gets doubled when the temperature of the sink is reduced by 10 °C. Find the temperatures of the source and sink.   2

(e) Consider the following two cases for the formation of $SO_3(g)$ from sulfur: 2

Case-I: $S + O_2 \rightarrow SO_2$ enthalpy change $= \Delta H_I$

$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$ enthalpy change $= \Delta H_{II}$

Case-II: $S + \frac{3}{2}O_2 \rightarrow SO_3$ enthalpy change $= \Delta H_{III}$

How do you expect ΔH_{III} to be connected with ΔH_I and ΔH_{II}? Explain the underlying reason.

4. (a) Two reversible adiabats can never intersect. Justify or criticize. 2

(b) Show that $\alpha = -\dfrac{1}{\rho}\left(\dfrac{\partial \rho}{\partial T}\right)_p$ where ρ is the mass density and α is the thermal expansion coefficient. 2

(c) $\Delta H = q_p$ is valid for a process in which the pressure is not constant throughout but only the initial and final pressures are same. Justify or criticize. 2

(d) Comment on the physical significance of the results of Joule's experiment being expressed as $\left(\dfrac{\partial U}{\partial V}\right)_{T,n} = 0$ and $\left(\dfrac{\partial H}{\partial p}\right)_{T,n} = 0$ (no derivation required). 2

(e) The efficiency of a Carnot engine remains unchanged when the temperatures of the hot and cold heat baths are increased by 200 K and 100 K, respectively. If the temperature of the hot bath is increased by 100 K at fixed temperature of the cold bath, the efficiency is increased by 20%. Find the working temperatures of the Carnot engine. 4

(f) At constant volume at 300 K 3+1

$$2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l) \qquad \Delta U = -1600 \text{ kcal mol}^{-1}$$

$$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l) \qquad \Delta U = -650 \text{ kcal mol}^{-1}$$

Calculate the heat of polymerization of acetylene to benzene at constant pressure. State the assumption(s), if any, in your calculation.

UNIT-III

5. (a) In the study of the kinetics of acid-catalyzed hydrolysis of methyl ester the reaction mixture pipetted out at different intervals of time is poured into a large volume of ice-cold water. Justify the reason for this step. 2

(b) Plot the variation of concentrations of reactant and product with time for a zero-order reaction (with appropriate explanation). And derive the expression of its half life period. 2+2

(c) $MX_2 \rightarrow M + X_2$ 3

The rate constant for the above decomposition is found to be $k = 3.02 \times 10^{-4} \text{s}^{-1}$ at 310 °C. Calculate the fraction of MX_2 that would be decomposed after heating for 2 h at 310 °C.

(d) According to the transition state theory the rate constant may be expressed as 2

$$k = \dfrac{RT}{N_A h} e^{\Delta S^{0\#}/R} e^{(1-\Delta n^{\#})} e^{-E_a/RT}$$

Using this expression find the unit of the pre-exponential factor, and comment on its temperature dependence.

6. (a) Both the order and molecularity of a reaction can be fraction. Justify or contradict. 2

(b) (i) Explain the physical significance of the terms present in the Arrhenius equation (showing the variation of rate constant of a reaction with temperature). 2+1

(ii) Based on your answer justify the expected rate of a reaction in the limit $T \to \infty$.

(c) The rate constant of a second-order reaction $(2A \to P)$ is expressed as 4

$$\log(K/L \, \text{mol}^{-1}\text{s}^{-1}) = 10.88 - \frac{3223}{T/K}$$

Find E_a and $t_{1/2}$ at 25 °C if the initial reactant concentration is 4×10^{-3} M (time is monitored in minute).

(d) Distinguish between thermodynamic and kinetic control of product. 2

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