WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 1st Semester Examination, 2020, held in 2021

CEMACOR02T-CHEMISTRY (CC2)

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) Starting from the Maxwell speed distribution formula find an expression for the most probable speed of gas molecules properly mentioning the justifications involved therein. — 3

(b) According to the energy equipartition principle the γ value of a non-linear molecule M_xN is found to be 1.167. Find x assuming ideal behaviour (here $\gamma = \overline{C}_p / \overline{C}_V$). — 2

(c) The binary collision frequency for collision between identical molecules is given as $Z_{AA} = \frac{1}{\sqrt{2}} \sigma \rho^2 \left(\frac{8k_{\mathrm{B}}T}{\pi m} \right)^{1/2}$ where σ is effective collision cross-section, ρ is number density of gas molecules and m is mass of each molecule. Find the unit of Z_{AA}. — 2

(d) The van der Waals constants a and b may be determined from any of the two pairs of critical parameters $(T_c \text{ and } p_c)$ or $(T_c \text{ and } \overline{V}_c)$. Which one is more suitable for experimental determination of the constants? — Justify. — 2

(e) How is the van der Waals equation of state modified in the limit of very high pressure? Determine the Boyle temperature of the gas in this limit. — 1+3

2. (a) Maxwell speed distribution formula of gas at temperature T is given as — 1+2

$$f(c) = 4\pi \left(\frac{m}{2\pi k_{\mathrm{B}} T} \right)^{3/2} c^x e^{-mc^2/2k_{\mathrm{B}}T}$$

(k_{B} is Boltzmann constant, m is mass of each molecule)

(i) State the physical significance of $f(c)$

(ii) Find x using only dimensional argument.

(b) Explicitly differentiate between Maxwell speed distribution and Maxwell velocity distribution. — 2

(c) Show that the fraction of molecules of an ideal gas with speeds in the range c_{mp} to $1.0001c_{mp}$ is constant for a given gas at a given temperature (c_{mp} denotes the most probable speed). — 3

(d) State the Law of corresponding states. — 1

(e) For a van der Waals gas the critical temperature is 32.1°C and the critical pressure is 50.0 atm. Calculate the van der Waals constants and the molecular diameter. Clearly mention the assumption(s), if any, in your calculation. 3+1

UNIT-II

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

(b) Show that the work-done in a reversible adiabatic expansion of an ideal gas can be given as $w = \dfrac{p_i V_i - p_f V_f}{\gamma - 1}$ $(\gamma = C_p / C_V)$. 2

(c) For which of the following systems is the system's energy conserved in every process: 2

(i) a closed system; (ii) an open system;

(iii) an isolated system; (iv) a system enclosed in adiabatic walls?

(d) A mole of water vapour initially at 200°C and 1 bar undergoes a cyclic process for which $\mathbf{w = 338\ J}$. Find $\mathbf{q}$ for this process. 2

(e) For a cyclic process one can write $\oint dq = \oint dw$. Does it indicate that heat is completely converted to work? — Justify. 2

(f) (i) Represent the Carnot cycle on a *T* versus *S* diagram with proper explanation. Express the efficiency of the cycle in terms of the ratio of the areas under the curves with proper explanation. 2

(ii) Express the Carnot cycle on a *H* versus *S* diagram citing proper reasons. 2

(g) State Hess's law of constant heat summation and justify the same from thermodynamic viewpoint. 2

4. (a) Prove that $\left(\frac{\partial \alpha}{\partial p}\right)_T + \left(\frac{\partial \kappa_T}{\partial T}\right)_p = 0$ where α is the coefficient of thermal expansion and κ_T is the isothermal compressibility. 2

(b) Is it always correct to write $dU = C_V\, dT$? — Justify. 2

(c) Show that $C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$. 3

(d) Explicitly justify that entropy is related to unavailable work. $2\frac{1}{2}$

(e) (i) The efficiency of a Carnot cycle can be enhanced by lowering the temperature of the cold heat bath or increasing the temperature of the hot heat bath. Clearly justify which choice you would prefer. $2\frac{1}{2}$

(ii) 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 temperature limit for the Carnot engine. 2

(f) At 25°C at constant volume the following data are given: 2

$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O\ (l)$ $\Delta U = -1550$ kcal

$2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O\ (l)$ $\Delta U = -650$ kcal

Calculate the heat of formation of benzene from acetylene.

UNIT-III

5. (a) For a zero-order reaction plot the variation of concentration of reactants and products with time. 2

(b) On doubling the initial concentration of the reactant the half-life period of the reaction is doubled. What is the order of the reaction? 2

(c) For the mechanism 3

$$A \longrightarrow B \text{ (rate constant } k_1)$$

$$A \longrightarrow C \text{ (rate constant } k_2)$$

Find an expression for the overall activation energy if the overall rate constant is given as $k = k_1 + 3k_2$. Mention the assumption(s) in your answer, if any.

(d) State whether the following statements are True or False: 4

(i) Since the concentrations of reactants decrease with time, the rate ***r*** of a reaction always decreases as time increases.

(ii) The rate of any chemical reaction should always increase with rise of temperature.

(iii) Activation energies are never negative.

(iv) In homogeneous catalysis, a catalyst does not appear in the overall reaction but does appear in the rate law.

6. (a) For a gas phase reaction 2HI ⟶ H_2 + I_2, the rate constants are 1.8×10^{-3} and $7.4\times10^{-4}\,\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ at 700 K and 500 K, respectively. Find the activation energy and the pre-exponential factor. Can you predict the order of the reaction (with justification)? 3

(b) Explain how you would distinguish between the following two reactions: $2\frac{1}{2}$

(i) A ⟶ B and A ⟶ C with rate constants k_1 and k_2, respectively $(k_1 \neq k_2)$

(ii) A ⟶ B + C with rate constant k_3.

(c) For the following mechanism write the overall reaction and identify with reasons each species as reactant, intermediate, product or catalyst. 3

$$A + B \longrightarrow C + D$$

$$2C \longrightarrow F$$

$$F + B \longrightarrow 2A + G$$

(d) Write down the Arrhenius equation in the context of dependence of rate constant of a reaction on temperature and justify the physical significance of the terms involved. $2\frac{1}{2}$

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.*

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