WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 1st Semester Examination, 2021-22

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) The Maxwell speed distribution of molecules at temperature T kelvin is given as $dn = Ac^2 e^{-mc^2/2k_BT} dc$ in the range of speed c to $c+dc$. Find the expression for A. Deduce the unit of A (k_B is the Boltzmann constant). 2+1

Given: $\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4}\left(\frac{\pi}{a^3}\right)^{1/2}$; $(\alpha > 0)$

(b) Calculate $\gamma (= C_{P,m}/C_{V,m})$ for a non-linear triatomic molecule of an ideal gas. Is your result equally applicable to a non-ideal gas? Justify. 2

(c) Does a gas obeying an equation of state $P(V_m - b) = RT$ have a critical temperature? Justify. 2

(d) How does the mean free path and collision frequency of a gas molecule change on increasing the pressure by two times at constant temperature? 2

(e) At what temperature will oxygen molecules have same average momentum as helium molecules at 27°C? 2

(f) Why the experimental value of molar heat capacities for polyatomic molecules differs from the theoretical values at room temperature? 2

2. (a) Two gases (molar masses M_1 and M_2) exhibit identical Maxwell speed distribution at temperatures T_1 and T_2 respectively. When is such an observation possible? $1\frac{1}{2}$

(b) The exponential term in the Maxwell speed distribution law is negative. Does positive sign in it make any sense? Discuss qualitatively (no derivation). $1\frac{1}{2}$

(c) Derive the formula for root mean square velocity (C_{rms}) of gas molecules using Maxwell's distribution formula. 3

(d) For linear molecules the degree of freedom corresponding to rotation about the molecular axis does not contribute to the total average energy. Justify or criticize. 2

(e) Two flasks A and B have equal volume. Flask-A contains hydrogen gas at 500 K and flask-B contains an equal mass of nitrogen gas at 1000 K. Assume ideal behavior of the gases and compare the mean free paths of the two gases (assume that the collision diameter of nitrogen is twice that of hydrogen). 3

(f) Show that for a gas obeying the equation of state $P(V_m - b) = RT$ the compressibility factor cannot be equal to or less than unity. Justify the significance of the result. 2

UNIT-II

3\. (a) In the context of chemical thermodynamics justify the physical significance of the following statement: 'work or heat is always manifested at the boundary of a thermodynamic system'. 2

(b) Derive the relationship $\left(\frac{\partial H}{\partial p}\right)_T = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial p}\right)_T + V$ and justify that $\left(\frac{\partial H}{\partial p}\right)_T = V$ for solids or liquids. 3

(c) Show that for an ideal gas $\left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V = nR/T$ (stating the appropriate conditions involved therein). 2

(d) In reversible adiabatic expansion of an ideal gas, the volume expansion is exactly compensated by the drop of temperature. Justify or criticize. 2

(e) Derive and explain Clausius inequality. 3

(f) Show that an isochor has greater slope than an isobar on a $T-S$ diagram for a reversible change of state. 2

(g) The latent heat of fusion of ice at 0°C is 1440 cal/mol and the heat capacity of ice is 8.5 cal/mol. Calculate the latent heat of fusion of ice at –20°C. 2

4\. (a) Two Carnot engines (having efficiencies η_1 and η_2) are connected in series in a manner that the heat released by the first is absorbed by the second. Prove that the efficiency of this combination is given as $\eta_{\text{net}} = \eta_1 + \eta_2 - \eta_1\eta_2$. Comment on the physical significance of the result that $|\eta_{\text{net}}| < |\eta_1 + \eta_2|$. 3

(b) Using an appropriate form of thermodynamic equation of state explicitly show that 2

$\mu_{JT} = \frac{V}{C_p}(T\alpha - 1)$ and hence show that $T_i = \frac{1}{\alpha_i}$ where T_i is the inversion temperature and α_i is the coefficient of thermal expansion at T_i (μ_{JT} denotes the Joule-Thomson coefficient).

(c) An ideal gas is made to undergo the following cycle involving the reversible steps 3

(i) isobaric expansion at p_2

(ii) adiabatic expansion to p_1 where $p_1 < p_2$

(iii) isobaric compression at p_2

(iv) adiabatic compression to the initial state.

Represent the cycle on a P vs. V and a T vs. S diagram (provide proper justification of your answer).

(d) One mole of an ideal gas expands isothermally at 27°C from 100 atmospheres to 1 atmosphere pressure. Calculate the work done if the process is carried out 4

(i) irreversibly in a single stage

(ii) irreversibly in two stages when the intermediate pressure is 50 atm

(iii) reversibly.

What conclusion can you draw from the results?

(e) At NTP, 2.8 L of oxygen were mixed with 19.6 L of Hydrogen. Calculate the change of entropy. 2

(f) At 20°C the heat of solution of anhydrous copper sulfate in a large excess of water is – 15,500 cal/mol, and that of copper sulfate pentahydrate is 2,550 cal/mol. Calculate the heat of the following reaction at 20°C. 2

$$CuSO_4\,(s) + 5\,H_2O\,(l) \rightarrow CuSO_4 \cdot 5\,H_2O(s)$$

UNIT-III

5. (a) By measuring the rate constant of a catalyzed reaction how can you experimentally verify whether it is homogeneous catalyzed or not? Explain. 2

(b) At 30°C the half-life for the decomposition of N_2O_5 is 5.5 h and it is independent of the initial pressure of the gas. Comment on the order of the reaction. Calculate (i) the rate constant and (ii) the time required for 90% decomposition. 2

(c) For the consecutive reaction (assume each step to be of first-order) 3

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

plot the variation of concentrations of different species with time when

(i) $k_1 = 2k_2$

(ii) $k_2 = 2k_1$

(iii) $k_2 = 10k_1$.

(d) Derive Michaelis Menten equation of enzyme catalysis. 4

6. (a) Explain primary kinetic salt effect with examples. 3

(b) An unimolecular reaction behaves kinetically as first-order in the limit of high pressure and kinetically as second-order in the limit of low pressure. Justify or criticize. 3

(c) For any reaction rise of temperature will inevitably cause enhancement of reaction rate. Justify or criticize. 2

(d) For a reaction $A \rightleftharpoons B \rightleftharpoons C$, show from kinetic point of view that $\frac{[C]_{eq}}{[A]_{eq}} = \frac{k_1 k_2}{k_{-1} k_{-2}}$. 3

Here k_1 and k_{-1} are the rate constants for forward and backward reaction of $A \rightleftharpoons B$ and k_2 and k_{-2} are the rate constants for forward and backward reaction of $B \rightleftharpoons C$.

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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