WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 1st Semester Examination, 2018

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) The expression for the distribution of molecular speed of an ideal gas is $f(c) = 4\pi c^n \left(\frac{m}{2\pi kT}\right)^{3/2} e^{\frac{mc^2}{2kT}}$. What does $f(c)dc$ signify? Using dimensional arguments show that $n = 2$ in the expression for $f(c)$. 3+3+3+4

   (b) The classical limit of molar heat capacities at constant volume for an ideal gas are about 54.041 $\text{JK}^{-1}\ \text{mol}^{-1}$. Find the atomicity and the shape of the gas molecules. [Given: $R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$].

   (c) Calculate the mean free path and binary collision frequency for oxygen molecules at 298 K and pressure of 500 Torr. [Given: molecular diameter = 3.61×10^{-10} m].

   (d) Elucidate the nature of Keesom, Debye and London interatomic forces.

2. (a) What are the necessary conditions that are to be applied on van der Waals equation to obtain the expression for critical temperature (T_C), Boyle temperature (T_B) and the inversion temperature (T_i)? [No derivation required]. 4+3+3+3

   (b) Show that the fraction of molecules of an ideal gas moving with speeds between C_{mp} and $1.0001C_{mp}$ is constant for any gas at any temperature.

   (c) At what temperature C_{rms} of He will be same with C_{av} of O_2 at 900K?

   (d) Explain why the C_v value for nitrogen is always found to be less than that of chlorine molecule at ordinary temperature.

UNIT-II

Chemical Thermodynamics

3. (a) Classify the following into extensive and intensive properties: 2+4+3+3+(2+2)

   Pressure, Free energy, Specific heat, Molar enthalpy.

   (b) Show by schematic diagrams that for the same change in state of a gas, the two stage expansion produces more work than the single stage expansion could possibly produce.

   (c) Show that for reversible adiabatic change of an ideal gas PV^{γ} = constant.

(d) Derive Gibbs-Helmholtz equation.

(e) What do you mean by inversion temperature in the Joule-Thomson process? Explain why H_2 gas shows heating effect in J-T experiment.

4. (a) Justify or criticise the following: (2+2)+(3+2)+3+4

    (i) A system must be isolated if neither heat nor matter can enter or leave the system.

    (ii) Work of expansion is maximum in case of a reversible than in an irreversible process.

(b) Show that $C_p - C_v = \left[V - \left(\frac{\partial H}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V$

Hence show that $C_p - C_v = -T\left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_P$.

(c) A reversible engine uses one mol of a Van der Waals gas as the working substance. It is connected to two heat reservoirs of temperatures 300 K and 200 K. What will be the work produced if 1000 kJ of heat is taken from the high temperature reservoir? What is the total change in entropy?

(d) Show that for a reversible cycle, using one mole of an ideal gas as working substance, $\oint \frac{dq}{T} = 0$. Comment on the result.

UNIT-III

Chemical Kinetics

5. (a) For a first order reaction A→ Products, show that the number of molecules at time "t" is given by $N_t = N_0\left(\frac{1}{2}\right)^{(t/C)}$, where "$C$" is the constant half-life time of the reaction, and N_0 is the number of molecules at the initial time $t = 0$. 3+4+4

(b) "Uni-molecular reactions are not always first order." — Justify the statement using Lindemann's mechanism.

(c) Consider the following parallel reaction of first order each:

$$A \longrightarrow Y;$$
$$A \longrightarrow Z;$$

where k_1 and k_2 are the rate constants for the formation of Y and Z respectively. In an experiment, it was found that 60% decomposition of A takes place in 20 min and analysis of product showed that 75% of Y and 25% of Z are present. Calculate k_1 and k_2.

6. (a) The slope and intercept of the plot of $\log_{10}(k)$ vs. $(1/T)$ for a first order reaction are $-5{,}500k$ and 13.5 respectively. Estimate the activation energy and the rate constant at 227°C (k is in $\sec^{-1}$). 3+3+2+3

(b) Explain the concept of Rate determining step and Steady-state Approximation with suitable example.

(c) State two limitations of the collision theory of reaction rate.

(d) State two assumptions of Classical Transition State Theory.

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