



WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 1st Semester Examination, 2019

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-1**

1. (a) Plot Maxwell's distribution function for translational kinetic energy of gas molecules at two different temperatures (consider the 3 dimensional case). 3+4+3+3
In the graph, depict the fraction of molecules possessing energies greater than a particular value ε^* .
- (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.
- (c) Binary collision frequency of a gas is $10^{28} \text{ cc}^{-1} \text{ s}^{-1}$ at NTP. Find the same when P is doubled at constant T . Does binary collision depend on T ?
- (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.

2. (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+4+3+3
- (b) 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.

$$\text{Given: } \int_0^{\infty} x e^{-ax^2} dx = \frac{1}{2a}.$$

- (c) Calculate the average time between collisions for O_2 at 25°C and 1 atm. The diameter of oxygen molecule is 2.4 \AA .
- (d) The virial equation of state in terms of P is given by

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

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?

UNIT-2

3. (a) Justify or criticize the following:

2+2+4+3+5

For a fixed change in volume, the reversible adiabatic expansion will produce the greatest drop in temperature than in an irreversible one.

- (b) Use Euler's chain or the cyclic relation to show that

$$C_V = - \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_U$$

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

- (d) For the following reaction at 25°C,



What will be heat released when 100 ml. of 2.0 M NaOH solution reacts with 100 ml. of 2.0 M HCl solution?

- (e) A body of constant heat capacity C_p , and at a temperature T_i is put in contact with a reservoir at a higher temperature T_f . The pressure remains constant while the body comes to equilibrium with the reservoir. Show that the entropy change of the universe is equal to $\Delta S = C_p[x - \ln(1+x)]$, where $x = -(T_f - T_i)/T_f$.

4. (a) Derive Kirchoff's equation.

(2+4)+6+4

The combustion of nitrogen and oxygen at 27°C occurs according to $2\text{N}_2 + \text{O}_2 = 2\text{N}_2\text{O}$. $\Delta H = 39.4 \text{ kcal}$. What will be the heat of formation at 227°C? Use the relation $C_p = a + bT$. C_p is the molar heat capacity (in cal) at constant pressure.

Gas	a (cal)	$b \times 10^3$ (in cal)
N_2	6.52	1.25
O_2	6.15	3.1
N_2O	7.0	7.1

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

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 and comment on this observation.

- (c) Show that Joule-Thomson coefficient can be written as

$$\mu_{JT} = - \frac{1}{C_p} \left\{ \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial P} \right)_T + \left[\frac{\partial(PV)}{\partial P} \right]_T \right\}$$

Hence state under what condition(s) a gas will be cooled by Joule-Thomson expansion.

UNIT-3

5. (a) For a reaction, frequency $A = 4 \times 10^{13} \text{ sec}^{-1}$ and activation energy $E_a = 98.6 \text{ kJmole}^{-1}$. If the reaction is of first order, at what temperature will its half-life be 10 minutes? 3+2+3+3

(b) State the type of reaction in each of the following:

- (i) Doubling the catalyst concentration doubles the rate of reaction.
(ii) Rate does not change with time.

(c) Possible mechanism for the reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ is the following

- (i) $\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O}_2$, rate constant k_1
(ii) $\text{N}_2\text{O}_2 \rightarrow 2\text{NO}$, rate constant k_2
(iii) $\text{N}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{NO}_2$, rate constant k_3 .

Apply steady state approximation to N_2O_2 to obtain the rate law

$$\frac{d[\text{NO}_2]}{dt} = \frac{2k_1k_3[\text{NO}]^2[\text{O}_2]}{k_2 + k_3[\text{O}_2]}$$

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



6. (a) For the mechanism: (i) $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$ (ii) $\text{C} \rightarrow \text{G} + \text{H}$. Step (ii) is the rate determining step. Given activation energies $E_1 = 120$, $E_{-1} = 96$ and $E_2 = 196 \text{ kJ/mole}$ respectively. Find the overall activation energy of the reaction. 4+4+3

(b) Draw the following plots with proper labeling of axes (i) concentration of reactant and product vs time for a reversible reaction where $k_1 < k_{-1}$, (ii) $\log k$ vs pH for an acid and base catalysed reaction.

(c) Acid hydrolysis of ester is a pseudo first order reaction and the rate constant is given by $k = \frac{1}{t} \ln \frac{V_\infty - V_0}{V_\infty - V_t}$, where V_0 , V_t and V_∞ are the volume of standard

NaOH required to neutralize the acid present at the beginning ($t = 0$), at time t and at the end of the reaction ($t = \infty$) respectively.

When the ester is 40% hydrolyzed, then show that $5V_t = 2V_\infty - 3V_0$.

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