WEST BENGAL STATE UNIVERSITY

B.Sc. Honours Part-I Examination, 2021

CHEMISTRY

PAPER: CEMA-II

Time Allotted: 2 Hours

Full Marks: 50

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.

CEMAT-12-PA

Answer any *two* questions taking one from each Unit

Unit-I

1. (a) The number of gas molecules of mass m having speed in the range c and $c +$ dc is given as $dN = Ac^2 e^{-\frac{mc^2}{2k_BT}} dc$. 3

Obtain an expression for 'A'. What is the unit of 'A'?

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

(b) The mass of each molecule of a Maxwellian gas is 5.18×10^{-23} g. Find the average momentum of the gas molecules at 27°C. 2

(c) Calculate the frequency of nitrogen-nitrogen collisions in one cubic centimeter of air at 1 bar and 20°C. Assume that 80% of the molecules are nitrogen molecules. 4

The collision cross section of nitrogen molecule is $4.5\times10^{-19}\ \text{m}^2$.

(d) The principle of equipartition of energy predicts the value of heat capacity ratio $\gamma (\gamma = C_p/C_V)$ for $H_2(g)$ more accurately at 110 K compared to that at 10 K. The Boyle temperature of $H_2(g)$ is 110 K. Comment on the result. 2

(e) The mean free path of an ideal gas at 27°C and 1.0 atm is 10^{-5} cm. Suppose the gas is taken to a high altitude where the pressure is only 100 mm of Hg. Calculate the temperature at which the gas will have the same mean free path at the high altitude. 2

2. (a) Write down Maxwell's expression for the distribution of molecular speeds in three dimensions and derive the expression for the number of molecules with translational kinetic energies greater than ε', assuming $\varepsilon' >> kT$. 5

(b) Find the dimension of $1/(\sigma^2 n\bar{c})$ where σ, n and $\bar{c}$ are the collision diameter, number of molecules per unit volume and mean speed of molecules respectively. 2

(c) Show schematically the Maxwellian distribution of speed of gas molecules. Indicate on the plot the following. 4

(i) most probable, rms and average speed (relative values)

(ii) fraction of molecules having speed greater than a certain value (c say)

How will be the plot be different for CO_2 and He at the same value of temperature?

(d) Find an expression for the number of molecules striking the unit area of wall of container per unit time. 2

Unit-II

3. (a) The Lennard-Jones potential is expressed as $U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$, where r is the internuclear separation. Find an expression for the minimum value of the internuclear separation (r_{min}) in terms of σ and hence show that the minimum value of the potential energy is $U(r_{min}) = -\varepsilon$. 3

(b) Calculate the change in surface energy when two identical mercury droplets of diameter 2 mm merge to form one drop (assume the process to be isothermal). Surface tension of mercury = 490 dyne cm^{-1}. 3

(c) For the He gas, P_c = 2.24 atm and T_c = 5.2 K. Calculate the radius of the molecule of helium gas. 3

(d) The virial equation in terms of $\bar{V}$ ($\bar{V}$ is molar volume) is given as: 3

$$Z = 1 + \frac{B_{2V}(T)}{\bar{V}} + \frac{B_{3V}(T)}{\bar{V}^2} + ...$$

Where, Z is the compressibility factor. Express the van-der Waals equation for a gas in terms of the virial equation and hence justify that in the limit of every low pressure or very high temperature the behavior of the gas approaches ideality.

4. (a) Draw schematically the PV vs P isotherms for N_2 stating the characteristic features at temperatures below, above and at T_B. 3

(b) The second virial coefficient of methane can be approximated by the empirical equation $B(T) = a + be^{-c/T^2}$, where $a = -0.1993$ bar^{-1}, $b = 0.2002$ bar^{-1} and $c = 1131\,K^2$. 3

What is the Boyle temperature for methane?

(c) Glycerol flows faster at higher temperatures. — Explain. 3

(d) Find the numerical value of compressibility factor (Z) of a gas that obeys the equation of state $P(V - nb) = nRT$. The pressure and temperature are such that $V/n = 10b$. 3

CEMAT-12-PB

Answer any *two* questions taking one from each Unit

Unit-I

5. (a) For a fixed change in volume, the reversible adiabatic expansion will produce the maximum drop in temperature than the irreversible one. Justify or criticize. 2

(b) The temperature of an ideal gas, with constant heat capacity, is changed from T_1 to T_2 by a constant pressure process and by a constant volume process, then $\Delta S_P = \Delta S_V$ (ΔS refers of the gas). Justify or criticize. 3

(c) Prove that: $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$ and hence find the condition when $C_P = C_V$. Give one example of such a system. 4

(d) Explain whether the heat of an uncatalysed reaction is different from that of a catalysed reaction at a given temperature. When will be the heat of a reaction independent of temperature? 4

6. (a) Justify or criticize any one of the following statements: 2

(i) $\Delta H = q$ for a process in which the initial and final pressures are same but the pressure is not constant throughout.

(ii) Any adiabatic process must be isentropic.

(b) Show that $\left(\frac{\delta \alpha}{\delta p}\right)_T + \left(\frac{\delta \beta}{\delta T}\right)_P = 0$, where α is the coefficient of thermal expansion and β is the compressibility factor. 2

(c) Using a suitable thermodynamic equation of state evaluate the quantity $\left(\frac{\partial U}{\partial V}\right)_T$ for an ideal gas and a van-der Waals gas. Comment on the results. 4

(d) 1 mole of an ideal gas is subject to undergo a reversible cycle involving the following steps: 5

Step 1: Isothermal expansion at temperature T_1 from $p_1, V_1 \rightarrow p_2, V_2$

Step 2: Isochoric change of state from $p_2, T_1 \rightarrow p_3, T_2$ $(p_3 < p_2)$

Step 3: Adiabatic compression from $p_3, V_2, T_2 \rightarrow p_1, V_1, T_1$.

(i) Represent the cycle on a properly labeled p-V diagram.

(ii) Elucidate the expression for work-done for each step.

(iii) Show that the efficiency of the cycle is $\eta = 1 - \frac{T_1 - T_2}{T_1 \ln(T_1/T_2)}$.

Unit-II

7. (a) A first order reaction is 20% complete in 15 minutes at 300 K. The same reaction is 39% complete in 10 minutes at 320 K. Calculate the energy of activation (E_A). Will the result (the value of E_A) differ if the reaction be of second order? 4

(b) A catalyst increases the rate of the forward reaction by 10%. Calculate the change of rate (increase / decrease) of the backward reaction. 2

(c) Consider the following process 4

	A	$\rightleftharpoons$ B
$t=0$	a	0
$t=t$	$a-x$	x

Find x as a function of t and find also the value of x as $t \to 0$ and $t \to \infty$.

(d) It is customary, in the study of kinetics of a reaction, to "chill" the reaction by adding an aliquot of the reaction mixture in a *large volume* of *cold water*. Explain why these two conditions are used. 2

8. (a) Write the Arrhenius equation for the variation of rate constant with temperature. Show plots of (i) k *vs* T and (ii) $\log k$ *vs* $1/T$. 2

(b) Draw schematically the energy profile for an exothermic reaction and indicate (i) the activation energy for the forward and the backward reactions, (ii) ΔH of the reaction, (iii) effects of addition of a positive catalyst. 3

(c) (i) The rate constant (k) of a reaction is given as a function of temperature(T) as follows. 2

$$\log k = +2.1 - \frac{2.5}{T} + 0.5 \log T$$

Find the value of the activation energy of the reaction.

(ii) Find the time for completion for a second order reaction. 2

(d) Explain the term entropy of activation $(\Delta S^{\neq})$. Comment on the sign of $\Delta S^{\neq}$. 3

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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