2020

CHEMISTRY (Honours)

Paper : CEMH-DC-T2

(Physical)

(CBCS)

Full Marks : 25 Time : Two Hours

The figures in the margin indicate full marks.
Candidates are required to give their answers in their own words as far as practicable.

1. Answer any *five* questions : 1×5=5

(a) Which of the following gas molecules has the longest free path under the same conditions of temperature and pressure?

(i) O_2

(ii) H_2

(iii) N_2

(iv) Cl_2

(b) Same quantity of heat is supplied to three reversible engines working between heat reservoirs with the source temperatures of T_1, T_2, T_3 respectively and the sink temperature T K. If $T_1 > T_2 > T_3$ then the maximum work available will be in the order

(i) $W_1 > W_2 > W_3$

(ii) $W_3 > W_2 > W_1$

(iii) $W_1 > W_2 < W_3$

(iv) $W_1 = W_2 = W_3$

(c) ΔS of an endothermic reaction is + *ve*. The reaction is

(i) feasible at all temperature

(ii) feasible when $T\Delta S > \Delta H$

(iii) feasible when $\Delta H > T\Delta S$

(iv) not at all feasible

(d) The order of the slope of S vs T plot of Ar, N_2 and O_3 gas at constant pressure at a particular temperature is —

(i) $Ar > N_2 > O_3$

(ii) $N_2 > Ar > O_3$

(iii) $N_2 > O_3 > Ar$

(iv) $O_3 > N_2 > Ar$

(e) The unit of pre-exponential factor (A) for a 1st order reaction is —

(i) s^{-1}

(ii) $l\ mol^{-1}\ s^{-1}$,

(iii) $mol\ l^{-1}\ s^{-1}$

(iv) none of the above

(f) The compressibility factor Z at ordinary temperature and pressure is in the order

(i) $CO_2 > H_2 > N_2$

(ii) $N_2 > H_2 > CO_2$

(iii) $H_2 > N_2 > CO_2$

(iv) $CO_2 > N_2 > H_2$

2. Answer any *four* questions : 2×4=8

(a) Show that $\overline{(c-\bar{c})^2} \geq 0$ where $\bar{c}$ is the average speed.

(b) Can we liquify a van der Waals' gas for which $a = 0$? Justify your answer.

(c) For a certain gas T_c = 304.20K, P_C = 72.8 atm, Hence calculate van der Waals' constants a and b for the gas.

(d) Show graphically that w is not a state function.

(e) When 1 mole of solid naphthalene was burnt in oxygen gas to produce CO_2 gas at constant volume, at 25°C the heat involved (Qv) was found to be –1227 kcal. Calculate ΔH for the reaction, assuming it to be independent of pressure.

(f) Calculate $\left(\frac{\partial C_v}{\partial V}\right)_T$ for an ideal gas.

(g) For a reaction A $\longrightarrow$ products, plot of 1/[A] vs time is a straight line with positive slope. What is the order of the reaction?

(h) Thespecific rate constant for the second order neutralization of nitropropane by a base is given by

$$\log k = 11.899 - 3163/T$$

where concentration is in mol l^{-1} and time in min. Initial concentration of both the reactants is 0.005(M). Calculate E and $t_{1/2}$ at 25°C.

3. Answer any *two* questions : 2×6=12

(a) (i) An ideal gas is enclosed in a cylinder at a pressure of 2 atm and temperature, 300 K. The average time between two successive collisions is 6×10^{-8}s. If the pressure is doubled and the temperature is increased to 500 K, what will be the average time between two successive collisions? 3

(ii) Explain why the equipartition principle predicts more correct value of heat capacity for *He* than *HCl* at room temperature. 2

(iii) If $\bar{V}$ is the molar volume of a gas and $\bar{V}_{id}$ is the molar volume in ideal condition then what does $\bar{V} / \bar{V}_{id}$ mean? 1

(b) (i) In case of a gas which obeys the equation $P(V–b) = RT$, show that $\left(\frac{\partial H}{\partial P}\right)_T = 0$, is a better criterion for ideality of a gas. 3

(ii) Efficiency of a Carnot's engine working between 127°C and t°C (where $t > 127$) is 0.5. Calculate t and the heat rejected to the surrounding when work done by the engine per cycle is 100*J*. 3

(c) (i) A certain reaction takes place in three steps with rate constants k_1, k_2 and k_3 and activation energies E_1, E_2, E_3. If overall rate constant $k = k_1k_3/k_2$, show that overall activation energy $E = E_1–E_2+E_3$. 3

(ii) For a particular reaction at constant temperature plot of reciprocal of reactant concentration 1/[A] versus time is a straight line with a slope of 4×10^{-2} 1 $mol^{-1}s^{-1}$. Find the time required for 1 (M) reactant to decrease to 0.25 (M). 3

(d) (i) Two spherical vessels A and B of the same volume contain hydrogen and oxygen respectively at the same temperature and pressure. Find the ratio between the average momentum of the molecules. 2

(ii) Calculate the change in entropy experienced by 2 moles of an ideal gas on being heated from a pressure of 5 atmosphere at 50°C to a pressure of 1 atmosphere at 100°C. Given $C_P = 9.88$ cal $mol^{-1}deg^{-1}$. 2

(iii) Zero order reactions cannot be elementary — explain. 2