West Bengal State University

B.A./B.Sc./B.Com (Honours, Major, General) Examinations, 2014

PART – I

CHEMISTRY — HONOURS

Paper – II

Duration : 2 Hours] [Full Marks : 50

The figures in the margin indicate full marks.

***Use separate answer script for each Group* CEMAT-12 PA & CEMAT-12 PB.**

CEMAT-12-PA

Answer any *two* questions taking *one* from each Unit.

UNIT – I

1. a) Elucidate the concept of temperature according to the kinetic theory of gases. 2

b) The equation for the distribution of velocity of a gas in one dimension is given by the equation $\frac{dn_u}{n} = Ae^{-Bu^2}du$. Hence find the value of A and B.

[Given, $\int_0^\infty e^{-bx^2}dx = \frac{1}{2}\sqrt{\frac{\pi}{b}}$ and $\int_0^\infty x^n e^{-bx^2}dx = \frac{1}{4}\sqrt{\frac{\pi}{b^3}}$] 2 + 2

c) Molecular diameter of CO is 3·19 Å. At 27°C and 100 mm of Hg pressure, what would be (i) collision frequency and (ii) mean free path ? 2 + 2

d) Explain the effect of change of pressure on the viscosity coefficient of a gas at constant temperature. 3

2. a) Find the fraction of molecules in a gas that have $v_x^2 > \frac{kT}{m}$. Show that this fraction is the same for all gases at all temperatures. 4

b) State the principle of 'equipartition of energy'. The value of $\gamma = (C_p / C_v)$ for a non-linear molecule A_xB is found to be 1·167. Assuming ideal behaviour, find the value of x. 2 + 2

c) A 10 litre capacity metallic container with 0·1 gm-mole of H_2 gas in it has a leakage hole of radius 0·02 mm. The average velocity of H_2 molecule in the container is 350 m sec^{-1} at 298 K. How many hydrogen molecules escape through the hole per minute ? 3

d) For N_2 at 350 K and 2·00 atm, find the number of molecular collisions with a container wall of area 1·00 cm^2 that occur in 1·00 s. 2

UNIT – II

3. a) If compressibility factor Z for a van der Waals gas be 1·000054 at 273 K and 1 atm and the Boyle temperature be 107 K, calculate neglecting higher terms of P the values of a, b and molecular diameter. 4

b) i) A solution of known surface tension is given. How will you use it to determine the radius of a fine capillary tube ? 2

ii) At 25°C the surface tension of water and mercury are 72·8 and 486·5 dynes/cm respectively, while the interfacial tension between the two is 415 dynes/cm. Will water spread over mercury ? 2

c) A gas obeys equation $P(V - b) = RT$.

i) Is it possible to liquefy the gas ? Justify your answer.

ii) Show that the gas does not have the Boyle temperature. 2 + 2

4. a) Write down the van der Waals equation in the virial form. Hence deduce the expression for the Boyle temperature from the second virial coefficient. 4

b) Find the terminal velocity of a rain drop of radius 0·01 cm falling through air of viscosity coefficient = $1 \cdot 85 \times 10^{-4}$ poise. Neglect the density of air compared to that of water (1 gm cm^{-3}). 2

c) A spherical air bubble is created within a liquid of surface tension 72 dynes cm^{-1}. If the volume of the bubble is $\pi/6$ cm^3, calculate the excess pressure inside the bubble. 3

d) Viscosities of a liquid at 20°C and 40°C are $4 \cdot 09 \times 10^{-3}$ poise and $3 \cdot 41 \times 10^{-3}$ poise respectively. Calculate the activation energy of flow. 3

CEMAT-12-PB

Answer any *two* questions taking *one* from each Unit.

UNIT – I

1. a) C_p is independent of pressure for an ideal gas. Justify or criticize. 2

b) The coefficient of thermal expansion of H_2O is 2×10^{-4} per gm per °C. 200 gms of H_2O at 25°C is heated to 50°C under 2 atms external pressure. Calculate W, ΔH and Q. Given the density of H_2O at 25°C is 0·9970 gm cm^{-3} and C_p = 75·3 J $mol^{-1}K^{-1}$. 4

c) Show that : (i) $\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

(ii) $C_p - C_v = \left[V - \left(\frac{\partial H}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V$. 2 + 2

d) Show that $\mu_{JT} = \frac{V}{C_p}(\alpha T - 1)$, where μ_{JT} is the Joule-Thomson coefficient and α is the temperature coefficient of volume expansion. 3

2. a) A Carnot engine operates between two fixed temperatures and uses 1 mole of an ideal gas as the working substance. State how the efficiency will be affected when each of the following changes are carried out independently :

i) The amount of the gas is doubled

ii) The ideal gas is replaced by one mole of a van der Waals gas

iii) The engine is run in reverse cycle

iv) One step of the cycle is made irreversible. 4

b) Classify the following into extensive and intensive properties :

(i) Molar volume, (ii) Viscosity, (iii) Entropy, (iv) Osmotic pressure. 2

c) The heat of formation of NH_3 at 298 K is $-11{\cdot}0$ cal mol^{-1}. Calculate the heat of the reaction, $N_2 + 3H_2 \rightarrow 2NH_3\ (g)$ at 400 K.

[Given, $C_{p_{N_2}} = 6{\cdot}5 + 10^{-3}\ T$ cal $mol^{-1}\ K^{-1}$

$C_{p_{H_2}} = 6{\cdot}5 + 9 \times 10^{-4}\ T$ cal $mol^{-1}\ K^{-1}$

$C_{p_{NH_3}} = 8{\cdot}04 + 7 \times 10^{-4}\ T + 5{\cdot}1 \times 10^{-6}\ T^2$ cal $mol^{-1}\ K^{-1}$] 4

d) One mole of an ideal gas initially at 300 K is expanded adiabatically into vacuum to double its volume. Calculate the final temperature, ΔH, ΔS of the gas. 3

UNIT – II

3. a) The stoichiometry of a reaction indicates the order of a reaction. Justify or criticize. 2

b) The rate constant for the hydrolysis of ethyl acetate by sodium hydroxide is 0·1075 lit mol^{-1} sec^{-1} at 25°C. If the initial concentration of both the ester and alkali be 0·04 mol lit^{-1}, then calculate the fraction of ester that will be hydrolysed in 10 mins. 3

c) Graphically represent the plot of $\log k$ *vs* pH for a homogeneous acid catalysed reaction and comment on the intercept on the $\log k$ axis. 3

d) The bimolecular decomposition in gaseous phase $2HI \rightarrow H_2 + I_2$, assuming collision diameter 3·5 nm and activation energy 183·9 kJ mol^{-1} for the reaction, calculate the rate constant at 700 K and 1 atm pressure. [Neglect steric factor, $M_{HI} = 128 \times 10^{-3}$ kg mol^{-1}, 1 atm = 101325 Pa] 4

4. a) Find the time required for the decomposition of $\frac{n-1}{n}$ th fraction of the initial amount of A undergoing a first order reaction $2A \rightarrow$ Products. 3

b) Based on the mechanism

$NO(g) + O_2(g) \rightleftharpoons NO_3(g)$ (fast equilibrium)

$NO_3(g) + NO(g) \rightarrow 2NO_2(g)$ (slow)

for the reaction, $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$, show that rate law is of the form $\frac{1}{2}\frac{d[NO_2]}{dt} = K_{obs}[NO]^2[O_2]$. 3

c) What do you mean by primary salt effect ? Write an equation and plot to show the variation of rate constant with ionic strength of the reaction : $S_2O_8^{2-} + 2I^- \rightarrow I_2 + 2SO_4^{2-}$. 1 + 2

d) Show that for a first order reaction, the time required for 99·9% completion of the reaction is almost ten times the time for 50% completion. 3