U.G. 1st Semester Examination - 2021
CHEMISTRY

Course Code : BCEMCCHC102

Course Title : Physical Chemistry–I

Full Marks : 30 Time : 2 Hours

The figures in the right-hand margin indicate marks.

Candidates are required to give their answers in their own words as far as practicable.

1. Answer any **ten** questions: 1×10=10

a) Test the cyclic rule for a gas obeying the equation $p(V-b) = RT$.

b) Will there be any difference in the nature of the Maxwell's velocity distribution curve for N_2 and CO_2 gases at a particular temperature if both of them behave ideally?

c) In a certain reaction the plot of $\log t_{\frac{1}{2}} vs. \log a$ (terms have their usual significance) generates a straight line with slope = –1. State the order of the reaction.

d) Relation between mean free path (λ) and collision diameter (σ) may be written as : $\lambda = K\sigma^m \left(\frac{V}{N}\right)$; K = constant. Find 'm' by dimensional analysis.

e) Check whether the following function (φ) is a state function or not, where

$$d\varphi = \frac{p}{T^2}dp - \frac{p^2}{T^3}dT .$$

f) A zero order reaction proceeds at a constant rate— Comment.

g) At 25°C the specific rate constant for the first order reaction $A \rightarrow B$ *is* $2.0\times10^{-2}\ min^{-1}$. Find out the time, where *[A] = [B]*.

h) At very low temperature (T close to 0) an approximate empirical expression for heat capacity of a substance is given by $C_{p,m} = a + bT + \frac{c}{T^2}$, where a, b and c are independent of temperature. Give an expression for the change in enthalpy of the substance when it is heated from 0 to a temperature T.

i) Calculate the rms velocity of He gas at 27°C.

j) What do you mean by adiabetic flame temperature?

k) Write the relationship between change in internal energy and heat capacity at constant volume.

l) What do you mean by Keesom interaction?

m) Ten litres N_2 expanded reversibly and adiabetically from 10 atm to 1 atm. Final volume of the gas become 25 litres. Calculate the adiabetic work done. $\gamma_{N_2} = 1.4$

n) Give an example of a consecutive reaction.

o) Write the expression of coefficient of compressibility of a gas.

2. Answer any **five** questions: 2×5=10

a) Show that the ratio of number of molecules with root mean square velocity to the number of molecules having most probable velocity for any gas at temperature T is given by $\frac{3}{2\sqrt{e}}$.

b) One mole of a certain monoatomic gas at 25°C and at 1 atm is adiabatically and reversibly compressed to final pressure of 10atm. Evaluate final temperature and ΔU.

c) Find an expression for the Boyle temperature in terms of a, b and R of a gas obeying a

hypothetical equation of state

$$\left(p + \frac{a}{V^2\sqrt{T}}\right)\left(V - \frac{b}{\sqrt{T}}\right) = RT$$

d) A gas undergoes free expansion adiabatically untill its volume is doubled. Hence temperature of the gas decreases– justify.

e) Decomposition of ozone $2O_3 \rightleftharpoons 3O_2$ is observed to obey the rate law; rate = $K[O_3]^2/[O_2]$. Suggest a mechanism that agrees with the rate law.

f) Calculate the pressure of N_2 gas molecules at 25°C when its mean free path is 1.00 cm. $\left(\sigma_{N_2} = 3.74\text{Å}\right)$

g) Show that dU is a perfect differential.

h) Show that the work in a reversible process is greater than that in an irreversible process.

3. Answer any **two** of the following: 5×2=10

a) i) One mole of the ideal gas is expanded isothermally from (p_1, v_1) to (p_2, v_2) in two stages. First stage uses constant opposing pressure p' and second stage uses constant opposing pressure p_2. Show that the maximum value of work

produced will be $2RT\left[1-\left(\frac{p_2}{p_1}\right)^{\frac{1}{2}}\right]$ and the intermediate pressure $p' = (p_1 p_2)^{\frac{1}{2}}$.

ii) Heat of neutralization of HCl by NaOH is –57.32 kJ mol^{-1}. When 10ml of $\left(\frac{N}{10}\right)$ NH_4OH is neutralized with 20ml of $\left(\frac{N}{20}\right)$HCl, enthalpy change is –51.34 J. Calculate enthalpy of dissociation of NH_4OH.

b) i) Following is the mechanism of a unimolecular reaction.

$$A + A \xrightarrow{K_1} A + A^*$$
$$A^* + A \xrightarrow{K_2} 2A$$
$$A^* \xrightarrow{K_3} B + C\,(\text{Products})$$

Derive the expression for the rate of formation of product.

ii) Write the significance of activation energy. 3+2

c) i) Show graphically the variation of distribution of molecular velocity of gas with the increase in temperature.

ii) Express the compressibility factor using the reduced terms.

iii) Calculate using Berthelot equation the number of gms of hydrogen in a vessel of 500 cc capacity when the gas is forced in at 100 atm pressure and 127°C. (T_c = 33.2k, P_c = 12.8 atm.) 2+1+2

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