

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: $1 \times 10 = 10$
- Test the cyclic rule for a gas obeying the equation $p(V-b) = RT$.
 - 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?
 - 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.
 - Relation between mean free path (λ) and collision diameter (σ) may be written as :

$$\lambda = K\sigma^m \left(\frac{V}{N} \right); K = \text{constant. Find 'm' by}$$

dimensional analysis.

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

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

- 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 $2.0 \times 10^{-2} \text{ min}^{-1}$. 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 adiabatic 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 adiabatically from 10 atm to 1 atm. Final volume of the gas become 25 litres. Calculate the adiabatic 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: $2 \times 5 = 10$

- 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 10 atm. 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 until 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. ($\sigma_{N_2} = 3.74\text{\AA}$)
- 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: $5 \times 2 = 10$

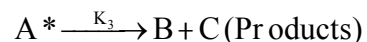
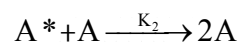
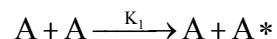
- a) i) One mole of the ideal gas is expanded isothermally from (p_1, v_1) to (p_2, v_2) in two stages. First stage uses constant opposing pressure p' and second stage uses constant opposing pressure p_2 . Show that the maximum value of work

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 $-57.32 \text{ kJ mol}^{-1}$. 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.



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 . ($T_c = 33.2\text{k}$, $P_c = 12.8 \text{ atm}$.)

2+1+2