

B.Sc. 1st Semester (Honours) Examination, 2020-2021

CHEMISTRY

Course ID: 11412

Course Code: SHCHEM/102/C-2

Course Title: Physical Chemistry-I

Time: 1 Hour 15 Minutes

Full Marks: 25

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* of the following questions: 1×5 = 5
- (a) What is the unit of rate constant for a third order reaction?
 - (b) In Vander Waals equation, what are the dimensions of the constant 'a' and 'b'?
 - (c) Classify each of the following properties as intensive or extensive:
 - (i) Entropy (ii) surface tension (iii) pressure (iv) number of moles.
 - (d) A first order reaction is never theoretically complete. - Explain.
 - (e) Comment - ΔW and ΔQ are meaningless.
 - (f) Give an example of autocatalysis.
 - (g) Two Vander Waals gas have the same value of 'b' but different 'a' values. Which of these would occupy greater volume under identical condition?
 - (h) How does mean free path depends on temperature?
2. Answer *any two* of the following questions: 5×2 = 10
- a) How does the rate constant depend on temperature? What is its value when $T \rightarrow \infty$?
How is the activation energy determined graphically? 1+2+2 = 5
 - b) Prove that, $C_p - C_v = \frac{\alpha^2 VT}{\beta}$, Hence show that $C_p \geq C_v$. Terms have their usual meaning. 3+2 = 5
 - c) Starting from Maxwell distribution of molecular speed, obtained the expression of *rms* speed. Calculate the root mean square velocity of CO_2 at 27°C ? 3+2 = 5

- d) Write Joule's criteria of ideality. Show that $(\partial H/\partial P)_T = 0$ is a better criterion of ideality than $(\partial U/\partial V)_T = 0$. Define Joule-Thomson coefficient. $(2+2+1)+4+1 = 5$

3. Answer *any one* of the following questions: $10 \times 1 = 10$

- a) (i) Write the integrated rate equation for the elementary reaction $A+B \rightarrow$ product, when the initial concentrations of A and B, respectively 'a' and 'b' are (I) different ($a \neq b$) and (II) same ($a=b$).

(ii) Show that the 2nd result may be directly obtained from the 1st form under the limit $b \rightarrow a$, given that $\ln(1+X) = X$ as $X \rightarrow 0$.

(iii) Show also that when one of the reactant is taken in excess the second order reaction (I) turns into first order reaction.

(iv) Prove that the work done in an isothermal reversible expansion of n moles of an ideal gas is greater than to that of a real gas. $(1+1)+2+2+4 = 10$

- b) (i) Derive expressions for the critical constants of a gas using van der Waal's equation of state. Write the units of 'a' and 'b' in van der Wall's equation.

(ii) The formation of molecules having speed in the range of u to $u + du$ of a gas of molar mass M at temperature T is the same as that of the gas of molar mass 2M at temperature T/2. - Explain.

(iii) For a certain gas, the Vander Waals constants are $a = 6.69 \text{ atm-litre}^2 \text{ mole}^{-2}$ and $b = 0.057 \text{ litre mole}^{-1}$. What will be the maximum work performed in the expansion of 2 moles of gas from 4 to 40 litres at 300 K? $4+2+4 = 10$
