LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034



B.Sc. DEGREE EXAMINATION – **CHEMISTRY**

THIRD SEMESTER - NOVEMBER 2022

UCH 3503 - THERMODYNAMICS

| Date: 03-12-2022 | Dept. No. | Max. : 100 Marks |
|---------------------------|-----------|------------------|
| Time: 09:00 AM - 12:00 NO | ON | |

| | SECTION A | | | |
|------|--|--------------------|--------------------|--|
| Ansv | ver ALL the Questions in one or two sentences | | | |
| 1. | Fill in the blanks | $(5 \times 1 = 5)$ | | |
| a) | The of an ideal gas is proportional to its absolute temperature. | K1 | CO1 | |
| b) | If the heat of formation of CO_2 is -94 kcal mol^{-1} , then the enthalpy of CO_2 is | K1 | CO1 | |
| c) | For an isochoric process, $\Delta S_v = \underline{\qquad} \ln (T_2/T_1)$. | K1 | CO1 | |
| d) | The equilibrium constant is affected by change in | K 1 | CO1 | |
| e) | The expression for rotational partition function (q _{rot}) is | K 1 | CO1 | |
| 2. | . Choose the correct answer | | $(5 \times 1 = 5)$ | |
| a) | In the ideal gas equation PV = nRT (i) n is the number of molecules of a gas (ii) n is the number of moles of a gas (iii) P is the pressure of the one mole of a gas (iv) V is the volume of one mole of a gas | K1 | CO1 | |
| b) | Heat of reaction is independent of (i) temperature (ii) pressure (iii) physical state (iv) path adopted | K1 | CO1 | |
| c) | If a process is both endothermic and spontaneous, then (i) $\Delta S > 0$ (ii) $\Delta S < 0$ (iii) $\Delta H < 0$ (iv) $\Delta G > 0$ | K1 | CO1 | |
| d) | $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$; $\Delta H = +ve$, the reaction (i) increases by pressure (ii) occurs at 1000 atm pressure (iii) occurs at high temperature (iv) occurs at high pressure and temperature | K1 | CO1 | |
| e) | describes the quantum state of individual particle in the system. K1 C | | | |
| | (i) microstate (ii) macrostate iii) thermodynamic (iv) equilibrium | | | |
| 3. | Choose the correct answer | | $(5 \times 1 = 5)$ | |
| a) | Which among the following is not an intensive property? (i) boiling point (ii) refractive index (iii) Molarity (iv) volume | K2 | CO1 | |
| b) | For an ideal gas, Joule-Thomson coefficient is (i) positive (ii) negative (iii) zero (iv) infinity | K2 | CO1 | |
| c) | Unit of molar entropy is (i) J K ⁻¹ mol ⁻¹ (ii) J mol ⁻¹ (iii) J K mol ⁻¹ (iv) J ⁻¹ K ⁻¹ mol ⁻¹ | K2 | CO1 | |
| d) | Le Chatelier's principle is applicable to | K2 | CO1 | |
| e) | The value of ln 10! is (i) 230 (ii) 13 (iii) 23 (iv) 130 | K2 | CO1 | |

| 4. | Mat | ch the following | | (5 x | 1 = 5) |
|------|--|---|------|--------|--------|
| a) | At c | onstant volume - $K_{\mathrm{f}} = K_{\mathrm{r}}$ | | K2 | CO1 |
| b) | A reaction has a $+\Delta G$ - Boyle's law | | | K2 | CO1 |
| c) | At equilibrium - $q = 0$ | | K2 | CO1 | |
| d) | In adiabatic process - Isochoric | | K2 | CO1 | |
| e) | At c | onstant temperature - Non-spontaneous process | | K2 | CO1 |
| | | SECTION B | | 1 | |
| Ansv | ver an | y TWO of the following | (2 | x 10 = | 20) |
| 5. | (a) | Discuss the different types of molecular velocities. | (5) | K3 | CO2 |
| | (b) | Calculate the pressure exerted by one mole of carbon dioxide gas in a $1.32~\rm dm^3$ vessel at 48°C using van der Waals gas. The van der constants are a = $3.59~\rm dm^3$ atm mol ⁻² and b = $0.0427~\rm dm^3$ mol ⁻¹ , R= $0.08206~\rm dm^3$ atm K ⁻¹ mol ⁻¹ . | (5) | K3 | CO2 |
| 6. | (a) | Show that $C_p - C_v = R$. | (5) | К3 | CO2 |
| | (b) | (b) Obtain the following expression for Joule-Thomson coefficient: (5) K3 CO2 $\mu_{JT} = \frac{dT}{dP} = -\frac{(\partial H/\partial P)_T}{C_P}$ | | | |
| 7. | | Derive K_p and K_c for $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$. Using Le Chatelier's principle, explain the effect of pressure on the above equilibrium. | (10) | К3 | CO2 |
| 8 | (a) | Derive any one Maxwell's relations between thermodynamic quantities. | (5) | K3 | CO2 |
| | (b) | State and explain Nernst heat theorem. | (5) | K3 | CO2 |
| | | SECTION C | | | |
| Ansv | ver an | y TWO of the following | (2 | x 10 = | 20) |
| 9. | (a) | Explain the effect of temperature on Maxwell's distribution of molecular velocities. | (5) | K4 | CO3 |
| | (b) | Derive Kirchoff's equation. | (5) | K4 | CO3 |
| 10. | | With the help of Carnot cycle, Show that $w = q_2 (T_2-T_1)/T_2$. | (10) | K4 | CO3 |
| 11. | (a) | Write any two applications of bond energy. | (5) | K4 | CO3 |
| | (b) | Show the relationship between K_p and K_c . Calculate K_p for the given reaction having K_c value of 49 mol dm ³ at 27°C. $2SO_3(g) \Rightarrow 2SO_2(g) + O_2(g)$ | (5) | K4 | CO3 |
| 12. | | List the major assumptions of Maxwell-Boltzmann statistics. Explain the relation between energy and partition function. | (10) | K4 | CO3 |
| | | SECTION D | | | |
| | | y ONE of the following | | x 20 = | , |
| 13. | (a) | Explain the principle of equipartition of energy. | (5) | K5 | CO4 |
| | (b) | State the Hess's law of constant heat summation. Explain its applications. | (10) | K5 | CO4 |
| | (c) | Derive Gibbs-Helmholtz equation. | (5) | K5 | CO4 |
| 14. | (a) | Write notes on thermodynamic probability and macrostate. | (5) | K5 | CO4 |
| | (b) | State the Planck and Lewis-Randall formulations of third law of thermodynamics. | (5) | K5 | CO4 |

| | (c) | Explain Van't Hoff reaction isotherm. The standard free energy change ΔG^o of a reaction at 298 K is 28.5 kJ. Calculate the value of the equilibrium constant (K_{eq}). | (10) | K5 | CO4 |
|-----|--|---|------|----|-------|
| | | SECTION E | | | |
| Ans | Answer any ONE of the following $(1 \times 20 = 20)$ | | | | = 20) |
| 15. | (a) | Summarize the postulates of kinetic theory of gases and derive the expression for kinetic gas equation. | (8) | K6 | CO5 |
| | (b) | Write short notes on the following: (i) Exact and inexact differentials (ii) Concept of enthalpy | (7) | K6 | CO5 |
| | (c) | Show that $P_1V_1^{\gamma} = P_2V_2^{\gamma}$. | (5) | K6 | CO5 |
| 16. | (a) | Explain the thermodynamic working principle of a refrigerator. | (5) | K6 | CO5 |
| | (b) | Write in detail the effect of temperature and pressure on the following equilibrium using Le Chatelier's principle: $N_2O_4(g) \rightleftharpoons 2NO_2\left(g\right) \qquad ; \Delta H = +59.0 \text{ kJ}$ | (5) | K6 | CO5 |
| | (c) | Write the steps involved in the determination of absolute entropy of solids, liquids and gases? | (10) | K6 | CO5 |

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