## LOYOLA COLLEGE (AUTONOMOUS), CHENNAI - 600034

B.Sc. DEGREE EXAMINATION - CHEMISTRY

THIRD SEMESTER - NOVEMBER 2022
UCH 3503 - THERMODYNAMICS

Date: 03-12-2022
Time: 09:00 AM - 12:00 NOON

## SECTION A

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


| 4. | Match the following |  |  | ( $5 \times 1=5$ ) |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| a) | At constant volume | - $\quad \mathrm{K}_{\mathrm{f}}=\mathrm{K}_{\mathrm{r}}$ |  | K2 | CO1 |
| b) | A reaction has a $+\Delta \mathrm{G}$ | Boyle's law |  | K2 | CO1 |
| c) | At equilibrium | - $\quad \mathrm{q}=0$ |  | K2 | CO1 |
| d) | In adiabatic process | - Isochoric |  | K2 | CO1 |
| e) | At constant temperature | - Non-spontaneous process |  | K2 | CO1 |
| SECTION B |  |  |  |  |  |
| Answer any TWO of the following |  |  | $(2 \times 10=20)$ |  |  |
| 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 $1.32 \mathrm{dm}^{3}$ vessel at $48^{\circ} \mathrm{C}$ using van der Waals gas. The van der constants are $\mathrm{a}=3.59 \mathrm{dm}^{3} \mathrm{~atm} \mathrm{~mol}^{-2}$ and $\mathrm{b}=0.0427 \mathrm{dm}^{3} \mathrm{~mol}^{-1}, \mathrm{R}=0.08206 \mathrm{dm}^{3}$ $\operatorname{atm} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$. | (5) | K3 | CO 2 |
| 6. | (a) | Show that $\mathrm{C}_{\mathrm{p}}-\mathrm{C}_{\mathrm{v}}=\mathrm{R}$. | (5) | K3 | CO 2 |
|  | (b) | Obtain the following expression for Joule-Thomson coefficient: $\mu_{J T}=\frac{d T}{d P}=-\frac{(\partial H / \partial P)_{T}}{C_{P}}$ | (5) | K3 | CO 2 |
| 7. |  | Derive $\mathrm{K}_{\mathrm{p}}$ and $\mathrm{K}_{\mathrm{c}}$ for $2 \mathrm{NH}_{3}(\mathrm{~g}) \rightleftharpoons \mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g})$. Using Le Chatelier's principle, explain the effect of pressure on the above equilibrium. | (10) | K3 | CO 2 |
| 8 | (a) | Derive any one Maxwell's relations between thermodynamic quantities. | (5) | K3 | CO 2 |
|  | (b) | State and explain Nernst heat theorem. | (5) | K3 | CO2 |
| SECTION C |  |  |  |  |  |
| Answer any TWO of the following |  |  | $(2 \times 10=20)$ |  |  |
| 9. | (a) | Explain the effect of temperature on Maxwell's distribution of molecular velocities. | (5) | K4 | $\mathrm{CO} 3$ |
|  | (b) | Derive Kirchoff's equation. | (5) | K4 | $\mathrm{CO} 3$ |
| 10. |  | With the help of Carnot cycle, Show that $\mathrm{w}=\mathrm{q}_{2}\left(\mathrm{~T}_{2}-\mathrm{T}_{1}\right) / \mathrm{T}_{2}$. | (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 $\mathrm{K}_{\mathrm{c}}$ value of $49 \mathrm{~mol} \mathrm{dm}{ }^{3}$ at $27^{\circ} \mathrm{C}$. $2 \mathrm{SO}_{3}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})$ | (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 |  |  |  |  |  |
| Answer any ONE of the following |  |  | ( $1 \times 20=20$ ) |  |  |
| 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 | CO 4 |
|  | (c) | Derive Gibbs-Helmholtz equation. | (5) | K5 | CO4 |
| 14. | (a) | Write notes on thermodynamic probability and macrostate. <br> State the Planck and Lewis-Randall formulations of third law of thermodynamics. | (5) | K5 | CO 4 |
|  | (b) |  | (5) | K5 | CO4 |

## SECTION E

## Answer any ONE of the following

$(1 \times 20=20)$

| 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: <br> (i) Exact and inexact differentials <br> (ii) Concept of enthalpy | (7) | K6 | CO 5 |
|  | (c) | Show that $\mathrm{P}_{1} \mathrm{~V}_{1}{ }^{\gamma}=\mathrm{P}_{2} \mathrm{~V}_{2}{ }^{\gamma}$. | (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: $\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}_{2}(\mathrm{~g}) \quad ; \Delta \mathrm{H}=+59.0 \mathrm{~kJ}$ | (5) | K6 | CO5 |
|  | (c) | Write the steps involved in the determination of absolute entropy of solids, liquids and gases? | (10) | K6 | CO 5 |

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