KD EDUCATION ACADEMY [9582701166] Street no. 21 A-1 Bengali colony sant nagar burari

Time : 6 Hour

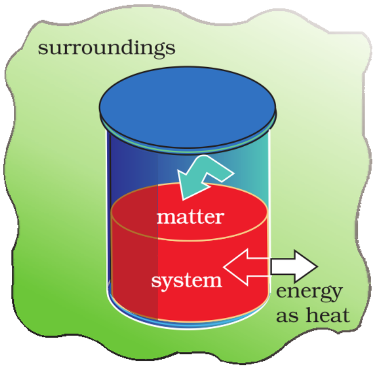
STD 11 Science Chemistry
kd 90+ ch -5 Thermodynamics

Total Marks : 170

*** Choose The Right Answer From The Given Options.[1 Marks Each]** **[34]**

1. The energy of a system available to do work is called as:
   (A) Gibbs free energy
   (B) Heat of formation
   (C) Heinsenberg uncertainty principle
   (D) Heat of vaporization

2.



   Name the type of wall used in the above figure.
   (A) Adiabatic walls.
   (B) Thermally insulating walls.
   (C) Thermally conducting walls.
   (D) None of the above.

3. The heat required to raise the temperature of a body by 1K is called:
   (A) Specific heat
   (B) Thermal capacity
   (C) Water equivalent
   (D) None of these

4. The bond dissociation energies of H_2, Cl_2, and HCl are 104, 58 and 103kcal mol^{-1} respectively. The enthalpy of formation of HCl would be:
   (A) -22kcal mol^{-1}
   (B) -44kcal mol^{-1}
   (C) +44kcal mol^{-1}
   (D) +22kcal mol^{-1}

5. Which of the following is an extensive property?
   (A) Temperature.
   (B) Density.
   (C) Gibbs free energy.
   (D) Molar volume.

6. "The change of enthalpy of a chemical reaction is the same whether the reaction takes place in one step or in several steps". This law was presented by:
   (A) Hess
   (B) La Chatelier
   (C) Kirchhoff
   (D) Lavoisier and Laplace

7. Whether a reaction is endothermic or exothermic can be indicated by:
   (A) Enthalpy change.
   (B) Entropy change.
   (C) Activation energy.
   (D) Specific heat capacity.

8. Which of the following process is non-spontaneous?
   (A) Heat flow from hot end to cool end.

(B) Water flow from higher level to lower level.

(C) Gas flow from lower pressure region to higher pressure region.

(D) Gas flow from higher pressure region to lower pressure region.

9. The enthalpy change when one mole of solute dissolves in a specified amount of solvent is called:

(A) Enthalpy of dilution. (B) Enthalpy of solution.

(C) Enthalpy of association. (D) Enthalpy of dissociation.

10. Hess’s law deals with:

(A) Heat changes in a chemical reaction.

(B) Rate of reaction

(C) Equilibrium constant

(D) Influence of pressure on volume of a gas

11. Entropy is:

(A) A thermodynamic concept. (B) A state function.

(C) Independent of path. (D) All of the above.

12. Hess's law is based on:

(A) Law of conservation of mass. (B) Law of conservation of energy.

(C) Law of active mass. (D) Both (a) and (b).

13. All natural processes are:

(A) Spontaneous (B) Non- spontaneous

(C) Exothermic (D) Endothermic

14. The volume of gas is reduced to half from its original volume. The specific heat will be ______.

(A) Reduce to half. (B) Be doubled.

(C) Remain constant. (D) Increase four times.

15. Which of the following properties is the measure of the degree of randomness or disorder in the system?

(A) Entropy. (B) Enthalpy.

(C) Internal energy. (D) None of these.

16. What is the free energy change $\triangle G$, when 1.0 mole of water at 100oC and 1 atm pressure is converted steam at 100oC and 1 atm pressure:-

(A) +540 cal (B) -9800 cal (C) +9800 cal (D) 0 cal

17. Actual flame temperature is always lower than the adiabatic flame temperature, because there is ______________:

(A) no possibility of obtaining complete combustion at high temperature.

(B) always loss of heat from the flame.

(C) both (a) and (b).

(D) neither (a) nor (b).

18. Combustion is:

(A) Exothermic reaction (B) Endothermic reaction

(C) Addition reaction (D) None of these

19.

The temperature at the bottom of a high water fall is higher than that at the top because:

(A) by itself heat flows from higher to lower temperature

(B) the difference in height causes a difference in pressure

(C) thermal energy is transformed into mechanical energy

(D) mechanical energy is transformed into thermal energy

20. If the bond energies of H-H, Br-Br and H-Br are 433, 192 and 364kJ mol^{-1}, respectively, then ΔH° for the reaction.

$H_2(g) + Br(g) \rightarrow 2HBr(g)$ is:

(A) -261kJ (B) -103kJ (C) +261kJ (D) -1031kJ

21. The most abundant element in the universe is thought to be:

(A) Hydrogen (B) Carbon (C) Oxygen (D) Nitrogen

22. Calculate the difference between C_P and C_V for 10 moles of an ideal gas.

(A) 83.14J (B) 8.314J (C) 831.4J (D) 0.831J

23. You are given a lump of an unknown metal. You perform an experiment and figure out the specific heat is close to 0.89 J/g oC. What could be the identity of the metal?

(A) Gold (B) Silver

(C) Aluminum (D) None of the above

24. Hess's law is applicable for the determination of heat of:

(A) Reaction (B) Transition

(C) Formation (D) All of the above

25. When we take acetone in a test tube it feels cold. Which reaction occurs in the process?

(A) Endothermic reaction (B) Exothermic reaction

(C) Reversible process (D) Adiabatic process

26. Maximum entropy will be in which of the following?

(A) Ice. (B) Liquid water.

(C) Snow. (D) Water vapour.

27. Which of the following endothermic processes are spontaneous?

(A) Melting of ice (B) Evaporation of water

(C) Heat of combustion (D) Both (a) and (b)

28. In a thermodynamic system working subtance is ideal gas, its internal energy is in the from of:

(A) Kinetic energy only (B) Kinetic and potential energy

(C) Potential energy (D) None of these

29. Which specific process has negative value of specific heat?

(A) Saturated vapours (B) Ice (C) Water (D) Vapours

30. For the process to occur under adiabatic conditions, the correct condition is:

(A) $\Delta T = 0$ (B) $\Delta p = 0$

(C) $q = 0$ (D) $w = 0$

31. For an ideal solution containing two liquid components A and B, the Gibbs free energy of mixing is minimum, when the molar ratio of the liquids is:

(A) 1 : 1 (B) 1 : 2

(C) 1 :10 (D) 1 : 1000

32. Which of the following is not a thermodynamic coordinate?

(A) Gas constant (R) (B) Pressure (P)

(C) Volume (V) (D) Temperature (T)

33. A liquid boils at such a temperature at which the saturated vapour pressure, as compared to atmospheric pressure, is :

(A) One-third (B) Equal (C) Half (D) Double

34. The internal energy of a piece of lead when beaten by a hammer will:

(A) Increase

(B) Decrease

(C) Remain constant

(D) Sometimes increases and sometimes decreases

*** a statement of Assertion (A) is followed by a statement of Reason (R). Choose the correct option. [2]**

35. **Notes:** In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

Assertion (A) : Spontaneous process is an irreversible process and may be reversed by some external agency.

Reason (R) : Decrease in enthalpy is a contributory factor for spontaneity.

i. Both A and R are true and R is the correct explanation of A.
ii. Both A and R are true but R is not the correct explanation of A.
iii. A is true but R is false.
iv. A is false but R is true.

36. **Notes:** In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the Choices given below each question.

Assertion (A): Combustion of all organic compounds is an exothermic reaction.

Reason (R) : The enthalpies of all elements in their standard state are zero.

i. Both A and R are true and R is the correct explanation of A.
ii. Both A and R are true but R is not the correct explanation of A.
iii. A is true but R is false.
iv. A is false but R is true.

*** Answer The Following Questions In One Sentence.[1 Marks Each] [22]**

37. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$; $\Delta H = -890 \text{kJ mol}^{-1}$
What is the calorific or fuel value of 1kg of CH_4?

38. When 430J of work was done on a system, it lost 120J of energy as heat. Calculate the value of internal energy change (ΔU) for this process.

39. What is the value of ΔG when ice and water are in equilibrium?

40. Name the state variables which remain constant in:

i. Isobaric process.
ii. Isothermal process.

41.

The standard molar entropy of $H_2O(l)$ is $70JK^{-1}mol^{-1}$. Will the standard molar entropy of $H_2O(s)$ be more, or less than $70JK^{-1}mol^{-1}$?

42. Name the thermodynamic system to which following belong:
    i. Human body.
    ii. Milk in thermos flask.

43. One mole of acetone requires less heat to vapourise than 1mol of water. Which of the two liquids has higher enthalpy of vapourisation?

44. Why is entropy of a solution higher than that of pure liquid?

45. Which one of the following is not extensive state function?
Enthalpy change, Internal energy change and Pressure.

46. Choose the correct answer.
The enthalpies of all elements in their standard states are:
    i. Unity
    ii. Zero
    iii. < 0
    iv. Different for each element.

47. Give an example of a spontaneous process which is endothermic.

48. Why does entropy increase on mixing of two gases?

49. What is the limitation of first law of thermodynamics?

50. When is the entropy of a perfectly crystalline solid zero?

51. Define standard enthalpy of formation.

52. Predict the sign of ΔS for the reaction:
$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

53. Predict the sign of entropy change for the change.
$H_2O(g) \rightarrow H_2O(l)$

54. What happens to the internal energy of the system if:
    i. Work is done on the system?
    ii. Work is done by the system?

55. At 1atm will the $\Delta_f H^\circ$ be zero for $Cl_2(g)$ and $Br_2(g)$? Explain.

56. How can you say that universe is going towards chaos?

57. If ΔG° for reversible reaction is found to be zero, what is the value of its equilibrium constant?

58. Why is standard enthalpy of formation of diamond not zero although it is an element?

*** Given Section consists of questions of 2 marks each. [24]**

59. Calculate the total entropy change, ΔS_{total} and state if the process is spontaneous, when one mole of liquid mercury Hg(l) changes to mercury vapour, Hg(g) at 298K. The molar entropy of vapourisation of Hg is $99JK^{-1}mol^{-1}$ and molar enthalpy of vapourisation is $59.1k\ J\ mol^{-1}$.

60. Derive the relationship between isothermal and free expansion of an ideal gas.

61. ΔH and ΔS for a reaction are found to be $-10000J\ mol^{-1}$ and $-33.3JK^{-1}$. Under what conditions reaction will proceed in reverse direction.

62. What is bond energy? Why is it called enthalpy of atomisation?

63. A 1.25g sample of octane (C_8H_{18}) is burnt in excess of oxygen in a bomb calorimeter. The temperature of calorimeter rises from 294.05 to 300.78K. If heat capacity of the calorimeter is 8.93kJ K^{-1}. Find heat transferred to calorimeter.

64. Consider the following reaction:
$H_2(g) + F_2(g) \rightarrow 2HF(g)$
$$\Delta H^\circ = -542 kJ,\ \Delta S^\circ = 14 JK^{-1}$$
Calculate the ΔG° value for the reaction and state if the reaction is spontaneous at 298K.

65. Establish a relationship between ΔH and ΔU in Haber's process of synthesis of ammonia assuming that gaseous reactants and products are ideal.

66. 18.0g of water completely vapourises at 100°C and 1 bar pressure and the enthalpy change in the process is 40.79kJ mol^{-1}. What will be the enthalpy change for vapourising two moles of water under the same conditions? What is the standard enthalpy of vapourisation for water?

67. Give one point to differentiate the following thermodynamic terms:
    a. Extensive properties and intensive properties.
    b. Isothermal process and isobaric process.

68. Calculate the free energy change when 1 mole of NaCl is dissolved in water at 298K. (Given, lattice energy of NaCl = -777.8kJ mol^{-1}, hydration energy = -774.1kJ mol^{-1} and $\Delta S = 0.043 kJ\ K^{-1} mol^{-1}$ at 298K).

69. The standard heat of formation of $CH_4(g)$, $CO_2(g)$ and $H_2O(g)$ are -76.2, -394.8 and -241.6kJ mol^{-1} respectively. Calculate the amount of heat evolved by burning 1m^3 of methane measured at NTP.

70. The equilibrium constant for a reaction is 10. What will be the value of $\Delta G^\ominus$? R = 8.314JK^{-1} mol^{-1}, T = 300K.

*** Given Section consists of questions of 3 marks each. [60]**

71. The heat of combustion of C_2H_6 is -368.4kcal. Calculate heat of combustion of C_2H_4, heat of combustion of H_2 is 68.32kcal mol^{-1}. ΔH for the following reaction is -37.1kcal.
$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$$

72. Two moles of an ideal gas initially at 27°C and one atmospheric pressure are compressed isothermally and reversibly till the final pressure of the gas is 10atm. Calculate q, W and ΔU for the process.

73. Calculate the number of kJ of heat necessary to raise the temperature of 60.0g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24J mol^{-1} K^{-1} .

74. In a process, 701J of heat is absorbed by a system and 394J of work is done by the system. What is the change in internal energy for the process?

75. It has been found that 221.4J is needed to heat 30g of ethanol from 15° to 18°. Calculate:
    a. specific heat capacity.
    b. molar heat capacity of ethanol.

76. Calculate the work done when 11.2g of iron dissolves in hydrochloric acid in:

i. A closed vessel.
ii. An open beaker at 25°C (Atomic mass of Fe = 56u).

77. What is meant by entropy? Predict the sign of entropy change in each of the following:
    i. H_2 (at 298K, 1atm) → H_2 (at 298K, 10atm)
    ii. H_2O (at 298K, 1atm) → H_2O (at 330K, 1atm)
    iii. $2NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O(g) + O_2(8)$
    iv. Crystallization of copper sulphate from its saturated solution.
    v. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$.

78. 10g of argon is compressed isothermally and reversibly at a temperature of 27°C from 10L to 5L. Calculate q, W, ΔU and ΔH for this process. R = 2.0cal K^{-1} mol^{-1}, log2 = 0.30, atomic weight, of Ar = 40.

79. $X(g) + 3Y(g) \rightleftharpoons 2Z(g); \Delta H = -40kJ$ and s^o of X, Y and Z are 60, 40 and 50kJ^{-1} mol^{-1} respectively. Calculate the temperature above or below which reaction become feasible?

80. How will you calculate work done on an ideal gas in a compression, when change in pressure is carried out in infinite steps?

81. How is the third law of thermodynamics useful in calculation of the absolute entropies? Calculate the value of ΔS° for the following reaction at 400K:

    $2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$

    If the value of equilibrium constant for the reaction at 400K is 1.958×10^{-4} and $\Delta H^\circ = 77.2 kJ\ mol^{-1}$ (R = 8.314J $K^{-1}mol^{-1}$).

82. i. State first law of thermodynamics.
    ii. Heat (q) and work function (w) individually are not state functions but their sum is always a state function. Why?
    iii. Define extensive property with example.

83. 1 mole of an ideal gas undergoes reversible isothermal expansion from an initial volume of V_1 to a final volume of $10V_1$ and does 10kJ of work. The initial pressure was 1×10^7Pa.
    i. Calculate V_1.
    ii. If there were 2 moles of gas, what must its temperature have been?

84. i. Classify the following processes as reversible or irreversible:
        a. Dissolution of sodium chloride.
        b. Evaporation of water at 373K and 1atm pressure.
        c. Mixing of two gases by diffusion.
        d. Melting of ice without rise in temperature.
    ii. When an ideal gas expands in vacuum, there is neither absorption nor evolution of heat. Why?

85. If the combustion of 1g of graphite produces 20.7kJ of heat, what will be molar enthalpy change? Give the significance of sign also.

86. Give the appropriate reason.
    i. It is preferable to determine the change in enthalpy rather than the change in internal energy.
    ii. It is necessary to define the 'standard state'.
    iii. It is necessary to specify the phases of the reactants and products in a thermochemical equation.

87. Given

$\mathrm{N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g); \Delta_r H^{\ominus} = – 92.4 kJ\ mol^{-1}}$

What is the standard enthalpy of formation of NH_3 gas?

88. A man takes a diet equivalent to 10000kJ per day and does work, in expending his energy in all forms equivalent to 12500kJ per day. What is change in internal energy per day? If the energy lost was stored as sucrose (1632kJ per 100g), how many days should it take to lose 2kg of his weight? (Ignore water loss)

89. 100mL of a liquid is contained in awn insulated container at a pressure of 1bar. The pressure is steeply increased to 100bar. The volume of the liquid is decreased by 1mL at this constant pressure. Find ΔH and ΔU.

90. Differentiate between the following (with examples)
    i. Open and closed system.
    ii. Adiabatic and isothermal process.
    iii. State function and path function.

* Case study based questions [8]

91. Read the passage given below and answer the following questions from (i) to (v).

$\mathrm{\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) = NH_3(g); \triangle_r H^{\ominus} = -46.1 kJmol^{-1}}$

$\mathrm{\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) = HCl(g); \triangle_r H^{\ominus} = -92.32 kJmol^{-1}}$

$\mathrm{H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l); \triangle_r H^{\ominus} = -285.8 kJmol^{-1}}$

A spontaneous process is an irreversible process and may only be reversed by some external agency.

If we examine the phenomenon like flow of Water down hill or fall of a stone on to the Ground, we find that there is a net decrease in Potential energy in the direction of change. By Analogy, we may be tempted to state that a Chemical reaction is spontaneous in a given Direction, because decrease in energy has Taken place, as in the case of exothermic Reactions. For example:

The decrease in enthalpy in passing from Reactants to products may be shown for any Exothermic reaction on an enthalpy diagram. Thus, the postulate that driving force for a Chemical reaction may be due to decrease in Energy sounds 'reasonable' as the basis of Evidence so far ! Now let us examine the following reactions:

$\mathrm{\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g); \triangle_r H^{\ominus} = +33.2 kJmol^{-1}}$

$\mathrm{C(graphite,s) + 2s(l) \rightarrow CS_2(l); \triangle_r H^{\ominus} = +128.5 kJmol^{-1}}$

Therefore, it becomes obvious that while decrease in enthalpy may be a contributory factor for spontaneity, but it is not true for all cases .

Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system. Thus heat (q) has randomising influence on the system. Temperature is the measure of average chaotic motion of particles in the system. The entropy change is inversely proportional to the temperature. $\triangle S$ is related with q and T for a reversible reaction as:

$\triangle S = \frac{q_{rev}}{T}$

The total entropy change $(\triangle S_{total})$ for the system and surrounding of a spontaneous process is given by $\triangle S_{total} = \triangle S_{system} + \triangle S_{surr} .0$

When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\triangle S = 0$. We can say that entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero. Since entropy is a state property, we can calculate the change in entropy of a reversible process by

$$\triangle \mathrm{S}_{\mathrm{sys}} = \frac{\mathrm{q}_{\mathrm{rev,rew}}}{\mathrm{T}}$$

G = H – TS

Gibbs function, G is an extensive property and a state function. The change in Gibbs energy for the system, $\triangle \mathrm{G}_{\mathrm{sys}}$ can be written as

$$\therefore \triangle \mathrm{G}_{\mathrm{sys}} = \triangle \mathrm{H}_{\mathrm{sys}} - \mathrm{T}\triangle \mathrm{S}_{\mathrm{sys}} - \mathrm{S}_{\mathrm{sys}}\triangle \mathrm{T}$$

At constant temperature, $\triangle \mathrm{T} = 0$

$$\triangle \mathrm{G}_{\mathrm{sys}} = \triangle \mathrm{H}_{\mathrm{sys}} - \mathrm{T}\triangle \mathrm{S}_{\mathrm{sys}}$$

Usually the subscript ‘system’ is dropped and we simply write this equation as

$$\triangle \mathrm{G} = \triangle \mathrm{H} – \mathrm{T}\triangle \mathrm{S}$$

Thus, Gibbs energy change = enthalpy change – temperature × entropy change, and is referred to as the Gibbs equation, one of the most important equations in chemistry. Here, we have considered both terms together for spontaneity: energy (in terms of $\triangle \mathrm{H}$) and entropy ($\triangle \mathrm{s}$, a measure of disorder) as indicated earlier. Dimensionally if we analyse, we find that $\triangle \mathrm{G}$ has units of energy because, both $\triangle \mathrm{H}$ and the $\mathrm{T}\triangle \mathrm{S}$ are energy terms, since $\mathrm{T}\triangle \mathrm{S} = (\mathrm{K})(\mathrm{J}/\mathrm{K}) = \mathrm{J}.$ Now let us consider how $\triangle \mathrm{G}$ is related to reaction spontaneity. We know, $\triangle \mathrm{S}_{\mathrm{systeam}} + \triangle \mathrm{S}_{\mathrm{surrounding}}$ If the system is in thermal equilibrium with The surrounding, then the temperature of the Surrounding is same as that of the system. Also, increase in enthalpy of the surrounding Is equal to decrease in the enthalpy of the System. Therefore, entropy change of Surroundings,

$$\triangle \mathrm{S}_{\mathrm{surr}} = \frac{\triangle \mathrm{H}_{\mathrm{surr}}}{\mathrm{T}} - \frac{\triangle \mathrm{H}_{\mathrm{sys}}}{\mathrm{T}}$$

$$\triangle \mathrm{S}_{\mathrm{total}} = \mathrm{S}_{\mathrm{sys}} + \left(- \frac{\triangle \mathrm{H}_{\mathrm{sys}}}{\mathrm{T}} \right)$$

Rearrangine the above equation:

$$\mathrm{T}\triangle \mathrm{S}_{\mathrm{total}} = \mathrm{T}\triangle \mathrm{S}_{\mathrm{sys}} - \triangle \mathrm{H}_{\mathrm{sys}}$$

For spontaneous process,

$\triangle \mathrm{S}_{\mathrm{total}} > 0$, so

$$\mathrm{T}\triangle \mathrm{S}_{\mathrm{sys}} - \triangle \mathrm{H}_{\mathrm{sys}} > \mathrm{O}$$

$$\Rightarrow -(\triangle \mathrm{H}_{\mathrm{sys}} - \mathrm{T}\triangle \mathrm{S}_{\mathrm{sys}})$$

Using equation, the above equation can Be written as:

$$-\triangle \mathrm{G} > \mathrm{O}$$

$$\triangle \mathrm{G} = \triangle \mathrm{H} - \mathrm{T}\triangle \mathrm{S}, 0$$

$$\triangle \mathrm{H}_{\mathrm{sys}}$$

Is the enthalpy change of a reaction, $\mathrm{T}\triangle \mathrm{S}_{\mathrm{sys}}$ Is the energy which is not available to Do useful work. So $\triangle \mathrm{G}$ is the net energy Available to do useful work and is thus a Measure of the ‘free energy. For this reason, it Is also known as the free energy of the reaction. $\triangle \mathrm{G}$ gives a criteria for spontaneity at Constant pressure and temperature.

If $\triangle \mathrm{G}$ is negative (< 0), the process is

b) If $\triangle \mathrm{G}$ is positive (> 0), the process is non

Entropy and Second Law of Thermodynamics – For an isolated system the change in energy remains constant. Therefore, increase in entropy in such systems is the natural direction of a spontaneous change. This, in fact is the second law of thermodynamics. Like first law of thermodynamics, second law can also be stated in several ways. The second law of thermodynamics explains why spontaneous exothermic reactions are so common. In exothermic reactions heat released by the reaction increases the disorder of the surroundings and overall entropy change is positive which makes the reaction spontaneous.

Absolute Entropy and Third Law of Thermodynamics Molecules of a substance may move in a straight line in any direction, they may spin like a top and the bonds in the molecules may stretch and compress. These motions of the molecule are called translational, rotational and vibrational motion respectively. When temperature of the system rises, these motions become more vigorous and entropy increases. On the other hand when temperature is lowered, the entropy decreases. The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics. This is so because there is perfect order in a crystal at absolute zero. The statement is confined to pure crystalline solids because theoretical arguments and practical evidences have shown that entropy of solutions and super cooled liquids is not zero at 0K. The importance of the third law lies in the fact that it permits the calculation of absolute values of entropy of pure substance from thermal data alone. For a pure substance, this can be done by summing q T rev increments from 0K to 298K. Standard entropies can be used to calculate standard entropy changes by a Hess's law type of calculation.

$\mathrm{A+B \rightleftharpoons C+D;}$ is $\triangle_{\mathrm{r}}\mathrm{G}=0$

A knowledge of the sign and Magnitude of the free energy change of a Chemical reaction allows: Prediction of the spontaneity of the Chemical reaction. Prediction of the useful work that could Be extracted from it. So far we have considered free energy Changes in irreversible reactions. Let us now Examine the free energy changes in reversible Reactions.'Reversible' under strict thermodynamic Sense is a special way of carrying out a Process such that system is at all times in Perfect equilibrium with its surroundings. When applied to a chemical reaction, the Term 'reversible' indicates that a given Reaction can proceed in either direction Simultaneously, so that a dynamic Equilibrium is set up. This means that the Reactions in both the directions should proceed with a decrease in free energy, which seems impossible. It is possible only if at equilibrium the free energy of the system is minimum. If it is not, the system would spontaneously change to configuration of lower free energy. So, the criterion for equilibrium

Gibbs energy for a reaction in which all reactants and products are in standard state, $\triangle_{\mathrm{r}}\mathrm{G}=0$ is related to the equilibrium constant of the reaction as follows:

$0=\triangle_{\mathrm{r}}\mathrm{G}^{\ominus}+\mathrm{RTlnK}$

or $\triangle_{\mathrm{r}}\mathrm{G}^{\ominus}=-\mathrm{RTlnK}$

or $\triangle_{\mathrm{r}}\mathrm{G}^{\ominus}=-2.303\mathrm{RT}\log\mathrm{K}$

We also know that

$\triangle_{\mathrm{r}}\mathrm{G}^{\ominus}=\triangle_{\mathrm{r}}\mathrm{H}^{\ominus}-\mathrm{T}\triangle_{\mathrm{r}}\mathrm{S}^{\ominus}-\mathrm{RTlnK}$

For strongly endothermic reactions, the value of $\triangle_{\mathrm{r}}\mathrm{H}^{\phi}$ may be large and positive. In such a case, value of K will be much smaller than 1 and the reaction is unlikely to form much product. In case of exothermic reactions, $\triangle_{\mathrm{r}}\mathrm{H}^{\phi}$ is large and negative, and $\triangle_{\mathrm{r}}\mathrm{G}^{\phi}$ is likely to be large and negative too. In such cases, K will be much larger than 1. We may expect strongly exothermic reactions to have a large K, and hence can go to near completion. $\triangle_{\mathrm{r}}\mathrm{G}^{\phi}$ also depends upon $\triangle_{\mathrm{r}}\mathrm{S}^{\phi}$, if the changes in the entropy of reaction is also taken into account, the value of K or extent of chemical reaction will also be affected, depending upon whether $\triangle_{\mathrm{r}}\mathrm{S}^{\phi}$ Is positive or Negative, It is possible to obtain an estimate of $\triangle\mathrm{G}^{0}$ From the measurement of $\triangle\mathrm{H}^{0}$ And $\triangle\mathrm{S}^{0}$, And then calculate K at any temperature For economic yields of the products. If K is measured directly in the Laboratory, value of $\triangle G^0$ At any other Temperature can be calculated.

- i. A spontaneous process is an ... process.
  - a. Irreversible
  - b. Reversible
  - c. Partially irreversible
  - d. Partially reversible
- ii. $\triangle S_{systeam} + \triangle S_{surrounding}$
  - a. < 0
  - b. > 0
  - c. = 0
  - d. None of above
- iii. When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\triangle S.....0.$
  - a. <
  - b. >
  - c. =
  - d. None of above
- iv. ... does not discriminate between reversible and irreversible process:
  - a. $\triangle H$
  - b. $\triangle S$
  - c. $\triangle G$
  - d. $\triangle U$
- v. $T\triangle S = \ ...$
  - a. Kg
  - b. J
  - c. M
  - d. lit

92. Read the passage given below and answer the following questions from (i) to (v).

A system in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the surroundings. The surroundings include everything other than the system. System and the surroundings together constitute the universe. The universe = The system + The surroundings However, the entire universe other than the system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighbourhood of the system constitutes its surroundings.

The wall that separates the system from the surroundings is called boundary.

Types of the System We, further classify the systems according to the movements of matter and energy in or out of the system.

1. Open System In an open system, there is exchange of energy and matter between system and surroundings. The presence of reactants in an open beaker is an example of an open system. Here the boundary is an imaginary surface enclosing the beaker and reactants.
2. Closed System In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings. The presence of reactants in a closed vessel made of conducting material e.g., copper or steel is an example of a closed system.
3. Isolated System In an isolated system, there is no exchange of energy or matter between the system and the surroundings. The presence of reactants in

a thermos flask or any other closed insulated vessel is an example of an isolated system.

The State of the System The system must be described in order to make any useful calculations by specifying quantitatively each of the properties such as its pressure (p), volume (V), and temperature (T) as well as the composition of the system. We need to describe the system by specifying it before and after the change. You would recall from your Physics course that the state of a system in mechanics is completely specified at a given instant of time, by the position and velocity of each mass point of the system. In thermodynamics, a different and much simpler concept of the state of a system is introduced. It does not need detailed knowledge of motion of each particle because, we deal with average measurable properties of the system. We specify the state of the system by state functions or state variables. The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. We can describe the state of a gas by quoting its pressure (p), volume (V), temperature (T), amount (n) etc. Variables like p, V, T are called state variables or state functions because their values depend only on the state of the system and not on how it is reached. In order to completely define the state of a system it is not necessary to define all the properties of the system; as only a certain number of properties can be varied independently. This number depends on the nature of the system. Once these minimum number of macroscopic properties are fixed, others automatically have definite values. The state of the surroundings can never be completely specified; fortunately it is not necessary to do so.

By conventions of IUPAC in chemical thermodynamics. The q is positive, when heat is transferred from the surroundings to the system and the internal energy of the system increases and q is negative when heat is transferred from system to the surroundings resulting in decrease of the internal energy of the system.

Let us consider the general case in which a change of state is brought about both by doing work and by transfer of heat. We write change in internal energy for this case as:

$$\triangle \mathrm{U} = \mathrm{q} + \mathrm{w}$$

For a given change in state, q and w can vary depending on how the change is carried out. However, $\mathrm{q} + \mathrm{w} = \triangle \mathrm{U}$ will depend only on initial and final state. It will be independent of the way the change is carried out. If there is no transfer of energy as heat or as work (isolated system) i.e., if w = 0 and q = 0, then $\triangle \mathrm{U} = 0.$ The equation i.e., $\triangle \mathrm{U} = \mathrm{q} + \mathrm{w}$ is mathematical statement of the first law of thermodynamics, which states that The energy of an isolated system is constant. It is commonly stated as the law of conservation of energy i.e., energy can neither be created nor be destroyed.

i. $\triangle \mathrm{U} = \ ....$
   a. q + w
   b. q + v
   c. q + m
   d. q + z

ii. Which of the following is not an example of state variable?
   a. Pressure
   b. Ionic radius
   c. Volume
   d. Amount

iii. $\triangle \mathrm{U} = \mathrm{q} + \mathrm{w}$ is termed as ...
   a. Third law of thermodynamics
   b. Second law of thermodynamics
   c. First law of thermodynamics
   d. None of above

iv. A … in thermodynamics refers to that part of universe in which observations are made.
  a. Universe
  b. System
  c. Surrounding
  d. Boundary

v. Which of the following is a type if system ?
  a. Open system
  b. Closed system
  c. Lsolated system
  d. All the above

* **Given Section consists of questions of 5 marks each.** **[20]**

93.
  i. A cylinder of gas supplied by a company is assumed to contain 14kg of butane. If a normal family requires 20000kJ of energy per day for cooking, how long will the cylinder last?
  ii. If the air supplied to the burner is insufficient, a portion of gas escapes without combustion. Assuming that 25% of the gas is wasted due to this inefficiency, how long will the cylinder last (Heat of combustion of butane = 2658kJ/ mol.)?

94. Derive the relationship between $\Delta \mathrm{H}$ and $\Delta \mathrm{U}$ for an ideal gas. Explain each term involved in the equation.

95.
  a. Predict the sign of the entropy change for each of the following changes:
    i. $Hg(l) \rightarrow Hg(g)$
    ii. Steam → Water
  b.
    i. Define Gibb's Energy. Give its mathematical expression. What is Gibb's energy criteria for spontaneity.
    ii. Give a brief note on the following thermodynamic terms:
      - Standard enthalpy of combustion.
      - Standard enthalpy of formation.

96. For the reaction,

$2A(g) + B(g) \rightarrow 2D(g)$

$$\Delta \mathrm{U}^{\ominus} = -10.5\mathrm{kJ} \text{ and } \Delta \mathrm{S}^{\ominus} = -44.1\mathrm{kJ}^{-1}.$$

Calculate $\Delta \mathrm{G}^{\ominus}$ for the reaction, and predict whether the reaction may occur spontaneously.

----- He who asks a question is a fool for five minutes; he who does not ask a question remains a fool forever.” — -----