THERMODYNAMICS

Topic: 1

Concepts of thermodynamics with definitions, First law of thermodynamics, derivation of mathematical equation of First Law and its applications

VERY SHORT ANSWER QUESTIONS

1. Explain "System" and "Surroundings".

System: A small part of the universe chosen for thermodynamic study is called system.

Surroundings: The remaining part of the universe in contact with the system is known as surroundings.

Universe = System + Surroundings..

2. Name three intensive properties.

Ans. Intensive properties: Properties of a system which are independent of the amount of the material in the system.

Ex: Density pressure, temperature, boiling point, etc.,

3. **Name three extensive properties**.

Ans. Extensive properties: Properties of a system which depend on the total amount of the material present in the system.

Ex: Mass, volume, internal energy, Gibbs energy etc,.

SHORT ANSWER QUESTIONS

1. State first law of thermodynamics.

First law of thermodynamics: The law of conservation of energy is taken as the first law of thermodynamics**.**

Statements:

i) "Energy can neither be created nor destroyed, although it can be transformed from one form to another"

ii) "It is impossible to construct perpetual motion machine of first kind"

iii) “The total energy of the system and surroundings is constant”

2. Give the mathematical formulation of first law of thermodynamics.

Mathematical form of 1 law of thermodynamics:

Let a system in state “A” of internal energy E_A absorb form the surroundings a certain amount of heat (Q) and undergo a change in its to “B” let the internal energy in the state ‘B’ is E_B. If ‘W’ is the work done by the system in the process, the increase in internal energy (ΔE) of the system is given by the equation,

$$\Delta E = E_B - E_A$$

From first law, net gain of energy (Q – W) must be equal to ΔE

$$\Delta E = (E_B - E_A) = (Q - W)$$

(or) $$Q = \Delta E + W$$

For infinitesimally small changes $q = \Delta E + W$

This is mathematical form of I law of thermodynamics.

LONG ANSWER QUESTIONS

1. State and explain first law of thermodynamics.

Ans. First law of thermodynamics:

The law of conservation of energy is taken as the first law of thermodynamics.

Statements:

i) “Energy can neither be created nor destroyed, although it can be transformed from one form to another”.

ii) “it is impossible to construct a perpetual motion machine of first kind (which Producework without consuming energy)”.

iii) “the total energy of the system and surroundings is constant”.

Mathematical form:

Let a system in state “A”, of internal energy E_A absorb from the surroundings acertain amount of heat (Q) and undergo a change in its state to B. Let the internal energy in the state

B is $E_{B.}$ If "W" is the work done by the system in the process, the increase in internal energy ΔE of the system is given by the equation, $\Delta E = E_B - E_{A.}$

$$\text{System - (A)}, E_{A.} \xrightarrow{Q} \text{System - (A)}, E_B$$

From first law, net gain of energy (Q-W) must be equal to ΔE

$$\Delta E = (E_B - E_A). = (Q-W)$$

(or) $Q = \Delta E + W$

For infinitesimally small changes $\boxed{q = \Delta E + W}$

$\therefore$ q = increase in internal energy + energy used in doing work.

Above equation is mathematical form of I law of thermodynamics.

2. What are extensive and intensive properties? Give examples.

Ans. Measurable (or) macroscopic properties such as mass, pressure, volume, temperature, surface tension, viscosity etc., can be subdivided into two categories as below:

i) **Extensive properties:** The properties whose magnitude depends upon the quantity of matter present in the system are called extensive properties. Examples of such properties are mass, volume, heat capacity, internal energy, entropy, heat content, Gibbs free energy etc. These properties change with quantity of matter present in the system. These properties are additive in nature.

ii) **Intensive properties**: The properties which do not depend upon the quantity of matter present in the system are called intensive properties.

Examples of such properties are density, molar volume, molar entropy, molar heat capacity surface tension, viscosity, specific heat, refractive index, pressure, temperature, boiling point, freezing point, vapour pressure etc. These properties depend only on the nature of the substance.

THERMODYNAMICS

Topic: 2

Heat capacities, Specific Heats, exothermic and endothermic processes, Enthalpy of bond dissociation, combustion, neutralization, formation, atomization, sublimation, phase transition, ionization and dilution.

VERY SHORT ANSWER QUESTIONS

1. Explain enthalpy?

Enthalpy (H): "Enthalpy is the amount of heat exchanged by a system with its surroundings at constant pressure and temperature"

Enthalpy is state function. Thus, the magnitude to enthalpy change depends only upon the enthalpies in the initial and final states.

$$\Delta H = [H_{products} - H_{reactants}]$$

2. What is heat capacity? Explain.

Ans. Heat capacity (C): "Heat capacity of a substance is defined as the amount of heat required to raise its temperature through one degree"

Heat capacity (C) is a state function. Hence to evaluate 'C' the conditions such as volume or constant pressure have to be specified in order to define the path. Thus there are two different types of heat capacities. These are:

i) Heat capacity at constant volume (C_v)

ii) Heat capacity at constant pressure (C_p).

3. What is thermo chemical equation? Give one example.

Ans: Thermo chemical equation: The chemical equation in which heat change accompanying a reaction is also numerically specified with proper sign by ΔH (or) ΔE by the side of the equation are known as thermo chemical equation.

Ex: $C_{(graphite)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)}$; $\Delta H = -393.5$ kJ

$C_{(rhombic)} + O_{2\,(g)} \longrightarrow SO_{2\,(g)}$; $\Delta H = -297.5$ kJ

SHORT ANSWER QUESTIONS\

2. State second law of thermodynamics.

Ans. II law of thermodynamics:

Statements:

i) " It is impossible for a self acting machine unaided by any external agency to convert heat from a body at low temperature to a body at higher temperature".

ii) " All spontaneous processes are thermodynamically irreversible and entropy of the system increases in all spontaneous processes."

iii) "For any spontaneous process taking place in an isolated system, the change in entropy (ΔS) is positive".

3. What is entropy?

Ans. Entropy: is taken as a measure of disorder of molecules (or) randomness of system.
Greater the disorder of molecules in a system, the higher is the entropy.
Entropy is a state function. It depends on the temperature, pressure of the system.
For a spontaneous process in an isolated system the entropy change is positive.

LONG ANSWER QUESTIONS

1. Give the criteria for spontaneity if it occurs on its own without intervention of any external agency of any kind.

Ans. Spontaneous reaction:

A Process is said to be spontaneous if it occurs on its own without intervention of any external agency of any kind.

All natural processes are spontaneous.

Entropy increases in all spontaneous processes.

Change in entropy "(ΔS) = positive" is a condition but is not necessary and sufficient condition for the spontaneous nature of a reaction.

Change in enthalpy "(ΔH) = negative" may be a condition but not a necessary and sufficient condition for the spontaneous nature of a reaction.

At this juncture, “Gibbs” introduced another thermodynamic function which involves both enthalpy (H) and entropy (S) functions. This is known as free energy function (G). This is given by the equation, G = H – TS. ‘G’ is now referred as Gibbs energy’ (or) Gibbs function.

ΔG_{sys} is negative “for spontaneous reactions (or) processes. Thus the spontaneity of a reaction and the algebraic signs of ΔH, ΔS, ΔG and the magnitude of ‘T’ can be related as follows:

ΔH	**ΔS**	**ΔG**	**Nature of the reaction**
-	+	-	Spontaneous at all ‘T’ values.
+	-	+	Non - Spontaneous at all ‘T’ values.
-	-	-	Spontaneous at low ‘T’ values.
-	-	+	Non - Spontaneous at high ‘T’ values.
+	+	+	Non - Spontaneous at low ‘T’ values.
+	+	-	Spontaneous at high‘T’ values.

3. Explain the terms with examples.
i)Heat of formation, ii) Heat of combustion and iii) Heat of solution.

Ans. i) Heat of formation (ΔH_f):

Definition: The amount of heat evolved (or) absoubed during the formation of one mole of the compound at constant temperature from the constituent elements in the standard state is heat formation.

Ex: $\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \longrightarrow NO(g)$, $\Delta H = +90.04$ kj (endothermic compound)

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$, $\Delta H = -286.21$ kj (exothermic compound)

Compounds which liberate heat in their formation reaction from the constituent elements are called exothermic compounds. For this reactions, ΔH_f = (-) ve

Compounds which absorb heat in the formation reaction from the constituent elements are called endothermic compounds. For this reactions, ΔH_f = (+) ve

ii) Heat of combustion:

Definition: The heat evolved when one mole of a substance is completely burnt at constant volume in excess of oxygen.

Ex: $C(s) + O_2(g) \longrightarrow CO_2(g)$, $\Delta H = -393.5$ kj

$CH_4(g) + O_2(g) \longrightarrow CO_2(g) + 2\ H_2O(g)$, $\Delta H = -890.8$ kj

Combustion is a process of burning a chemical compound at high temperatures in presence of excess of O_2 (or) air at constant volume and at high pressures.

Combustion process is always an exothermic process.(ΔH = -ve)

iii) Heat of solution: The amount of heat evolved (or) absorbed when 1 mole of a solute is dissolved completely in large excess of solvent is called heat of solution.

(or)

The change of enthalpy when a solution containing 1 mole of a solute is diluted from one concentration to another.

Ex: $Kcl(s) + aq \longrightarrow Kcl(aq)$, $\Delta H = +19.75$ kj

This is measured per mole of solute. If solvent is water then it is called enthalpy of dilution.

4. What is the heat of neutralization? How does its value change with the chemical nature of the acid and base: Give examples?

Ans. Heat of neutralization: The amount of heat evolved when a gram - equivalent of an acid reacts with a gram equivalent of a base to form salt and water is called Heat of neutralization.

Ex: $HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H2O$; $\Delta H = -57.3$ kj

The ionic form of the above reaction is

$H^+_{(aq)} + Cl^-_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)} + H_2O$

$\therefore$ The net change is $H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O$

$\therefore$ The amount of heat evolved when 1 mole of water is formed from 1 mole H^- ions is called Heat of neutralization.

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O\ (L)$$

Process is always exothermic. The amount of heat evolved depends on the chemical nature of the acid and the base.

Strong acid + strong base: $HCl_{(aq)} + Na^+_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O(L)$, $\Delta H = -57.3$ kj

Heat of neutralization of a strong acid against strong base is always constant (-57.32 kj). It is because in dilute solutions all strong acids and bases ionise completely and thus heat of neutralization in such cases is actually the heat of formation of H_2O from H^+ & OH^- ions (i.e.,) $H^+ + OH^- \rightarrow H_2O$; $\Delta H = -57.32$kj.

Strong acid + weak base: $HCl_{(aq)} + NH_4OH_{(aq)} \rightarrow NH_4Cl_{(aq)} + H_2O$; $\Delta H = -57.34$ kj

Heat of neutralization of weak base a against strong acid is always less than (-57.32 kj). Because apart of evolved heat is used up to ionise weak base (NH_4OH)

Heat of neutralization between NH_4OH and HCl involves the following reactions:

a) $NH_4OH \xrightarrow{+ H_2O} NH^+_4 + OH^-$, $\Delta H_1 = + 5.98$ kj

b) $H^+ + Cl^- + NH^+_4 + OH^- \longrightarrow NH^+_4 + Cl^- + H_2O$, $\Delta H_2 = -57.32$ kj

(or) $H^+ + OH^- \longrightarrow H_2O$ (after cancelling common ions)

$\therefore$ The heat of neutralization of NH_4OH + HCl, $\Delta H = \Delta H_1 + \Delta H_2 = + 5.98 + (57.32)$,

$$\Delta H = -51.34 \text{ kj}$$

Weak acid + strong base: $CH_3COOH_{(aq)} + NaOH_{(aq)} \longrightarrow CH_3COONa_{(aq)} + H_2O$ (l)

$$\Delta H = -55.23\text{kj}$$

Heat of neutralization of weak acid against strong base is always less than –57.32 kj because of a part of heat evolved is used up to ionise weak acid (CH_3COOH).

Heat of neutralization between CH_3COOH and NaOH involves the following reactions.

a) $CH_3COOH \xrightarrow{+H_2O} CH_3COO^- + H^+, \quad \Delta H_1 + 2.09kj$

b) $Na^+ + OH^- + CH_3COO^- + H^+ \longrightarrow CH_3COO^- + Na^+ + H_2O$, $\Delta H_2 = -57.32$ kj

(or) $OH^- + H^+ \longrightarrow H_2O$ (cancelling the common ions)

∴ The heat of neutralization of $CH_3COOH + NaOH$, $\Delta H = \Delta H_1 + \Delta H_2 = +2.09 - 57.32$;

$= 55.23kj$

Weak acid + weak base:

$CH_3COOH_{(aq)} + NH_4OH_{(aq)} \longrightarrow CH_3COONH_{4\,(aq)} + H_2O$

$\Delta H = -49.25kj$. Heat of neutralization of weak acid against weak base is always less than –57.32 kj because of a part of heat evolved is used up to ionise weak acid (CH_3COOH).and weak base (NH_4OH)

Heat of neutralization between CH_3COOH and NH_4OH involves the following reactions:

a) $CH_3COOH \xrightarrow{H_2O} CH_3COO^- + H^+, \quad \Delta H_1 + 2.09kj$

b) $NH_4OH \xrightarrow{+H_2O} +NH^+_4, + OH^- \quad \Delta H_2 = +5.98kj$

c) $CH_3COO^- + H^+ + NH^+_4, + OH^- \longrightarrow CH_3COO^- + NH^+_4, + H_2O$, $\Delta H_3 = -57.32kj$

(or) $H^+ + OH^- \longrightarrow H_2O$ (after cancelling the common ions)

∴ Heat of neutralization of $CH_3COOH + NH_4OH$, $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

$= +2.09 + 5.98 - 57.32$; $\Delta H = -49.25$ kj

THERMODYNAMICS

Topic: 3

Thermo chemical equations and Hess's law, its applications

VERY SHORT ANSWER QUESTIONS

1. Explain enthalpy?

Enthalpy (H): "Enthalpy is the amount of heat exchanged by a system with its surroundings at constant pressure and temperature"

Enthalpy is state function. Thus, the magnitude to enthalpy change depends only upon the enthalpies in the initial and final states.

$$\Delta H = [H_{products} - H_{reactants}]$$

2. What is heat capacity? Explain.

Ans. Heat capacity (C): "Heat capacity of a substance is defined as the amount of heat required to raise its temperature through one degree"

Heat capacity (C) is a state function. Hence to evaluate 'C' the conditions such as volume or constant pressure have to be specified in order to define the path. Thus there are two different types of heat capacities. These are:

i) Heat capacity at constant volume (C_v)

ii) Heat capacity at constant pressure (C_p).

3. What is thermo chemical equation? Give one example.

Ans: Thermo chemical equation: The chemical equation in which heat change accompanying a reaction is also numerically specified with proper sign by ΔH (or) ΔE by the side of the equation are known as thermo chemical equation.

Ex: $C_{(graphite)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)}$; $\Delta H = -393.5$ kJ

$C_{(rhombic)} + O_{2\,(g)} \longrightarrow SO_{2\,(g)}$; $\Delta H = -297.5$ kJ

4. State Hess's law?

Ans. Hess's law: The total heat change in a reaction is the same whether the chemical reaction takes place in one single step or in several steps.

5. What is Gibbs energy?

Gibbs energy (G): The amount of energy available from a system which can be put to useful work at constant temperature and pressure is called Gibb's energy.

For explaining the criteria for spontaneity of a reaction, Gibb's introduced thermodynamic function which involved both enthalpy (H) and entropy (S) functions. This is known as free energy function (G)

This is given by the equation, $G = H - TS$

Where 'G' is known as Gibbs energy (or) Gibbs function.

SHORT ANSWER QUESTIONS

1. State second law of thermodynamics.

Ans. II law of thermodynamics:

Statements:

i) "It is impossible for a self acting machine unaided by any external agency to convert heat from a body at low temperature to a body at higher temperature".

ii) " All spontaneous processes are thermodynamically irreversible and entropy of the system increases in all spontaneous processes."

iii) "For any spontaneous process taking place in an isolated system, the change in entropy (ΔS) is positive".

2. What is entropy?

Ans. Entropy: is taken as a measure of disorder of molecules (or) randomness of system.
Greater the disorder of molecules in a system, the higher is the entropy.
Entropy is a state function. It depends on the temperature, pressure of the system.
For a spontaneous process in an isolated system the entropy change is positive.

LONG ANSWER QUESTIONS

1. State Hess's law of constant heat summation and explain it with an example.

Ans: Hess's law states that the total amount of heat evolved or absorbed in a chemical reaction is always same whether the reaction is carried out in one step (or) in several steps.

Illustration: This means that the heat of reaction depends only on the initial and final stages and not on the intermediate stages through which the reaction is carried out. Let us consider a reaction in which A gives D. The reaction is brought out in one step and let the heat of reaction be ΔH.

$A \longrightarrow D : \Delta H$

Suppose the same reaction is brought out in three stages as follows –

$A \longrightarrow B : \Delta H_1$

$B \longrightarrow C : \Delta H_2$

$C \longrightarrow D : \Delta H_3$

The net heat of reaction is $\Delta H_1 + \Delta H_2 + \Delta H_3$.

According to Hess law $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

Ex: Consider the formation of CO_2. It can be prepared in two ways.

1) **Direct method:** By heating carbon in excess of O_2.

$$C(s) + O_2 (g) \longrightarrow CO_2(g) ; \Delta H = -393.5kj$$

2) **Indirect method:** Carbon can be converted into CO_2 in the following two steps.

$$C(s) + \frac{1}{2} O_2 (g) \longrightarrow CO_2(g); \Delta H_1 = -110.5kj$$

$$C(g) + \frac{1}{2} O_{2.}(g) \longrightarrow CO_2(g);\ \Delta H_2 = -283.02kj$$

Total $\Delta H = -393.52kj$

The two ΔH values are same.

2. Give the applications of Hess's law of constant heat summation with examples.

Ans: Applications of Hess's law:

1) It is used in the indirect determination of heat of formation of intermediate compounds which are unstable (or) which cannot be isolated.

Ex: Heat of formation (ΔH) of CO, cannot be directly determined but it is obtained indirectly using Hess's law from the following reactions.

$$C + O_{2.} \longrightarrow CO_2\ ;\ \Delta H_1 = -393.52kj$$

$$CO + \frac{1}{2} O_{2.} \longrightarrow CO_2\ ;\ \Delta H_2 = -283.02kj$$

ΔH of CO formation $= (\Delta H_1 - \Delta H_2) = -393.52 - (-283.02)$

$\Delta H = -110.50$ kj

3) Heat of reactions which are slow can be easily calculated.

Ex: Transformation of α –sulphur to β – sulpur is slow and the heat change of the transformation cannot be measured experimentally easily. But it can be calculated from the heats of combustion of
α –sulphur and β – sulphur as shown below.

$$S(\alpha) + O_{2.} \longrightarrow SO_2\ ;\ \Delta H_1 = -297.5kj$$

$$S(\beta) + O_{2.} \longrightarrow SO_2\ ;\ \Delta H_2 = -300.0kj$$

$\therefore S(\alpha) \longrightarrow S(\beta)$, $\Delta H = (\Delta H_1 - \Delta H_2) = -297.5 - (-300) = +2.5kj$

(or) S (β) ——> S (α), $\Delta H = -2.5$kj

4) Determination of lattice energy (U) of NaCl (Born – Haber Cycle):

The lattice energy is calculated from the thermo chemical data as follows:

$$Na_{(s)} + \frac{1}{2} Cl_2(g) \longrightarrow Na^+ + Cl^-, \ \Delta H = -410.5\text{kj (direct step)}$$

But (in multi steps) $Na_{(s)} \longrightarrow Na_{(g)}$, $\Delta H_1 = +108.7$kj/mol

$Na_{(g)} \longrightarrow Na^+_{(g)} + e^-$, $\Delta H_2 = +492.82$ kj/mol

$\frac{1}{2} Cl_2(g) \longrightarrow Cl(g)$, $\Delta H_3 = +119.55$ kj/mol

$Cl(g) + e^- \longrightarrow Cl^-(g)$, $\Delta H_4 = -361.59$ kj/mol

$Na^+_{(g)} + Cl^-(g) \longrightarrow Na^+ Cl^-(S)$, $\Delta H_5 = -U$ kj

But (from Hess's law) $\Delta H = (\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - U)$

$$-410.5 = 108.7 + 492.82 + 119.55 - 361.59 - U$$

$$U = -769.96\ (\approx 770)\ \text{kj/mol}$$

5. How are thermodynamic systems classified?

Ans: For the purpose of thermodynamic study, we divide the entire universe mainly in to two parts. They are –

System: A small part of the universe chosen for thermodynamic study is called system.

Surroundings: The remaining part of the universe in contact with the system is known as surroundings

Types of systems: The systems are classified into three types. These are:

a) Open system: A system which can exchange matter as well as energy with the surroundings is called an open system.

Ex: Evaporation of water from a beaker presents as open system.

Here vapours of water (matter) go into the atmosphere and heat (energy) required is absorbed by water from the surroundings.

b) Closed system: A system which may exchange energy but not matter with surroundings is called a closed system.

Ex: Consider boiling of water in a closed metallic vessel. Here, heat is transferred from the burner (surroundings) to the system. Steam remains inside the vessel. Thus, matter is not exchanged.

c) Isolated system: A system which can neither exchange matter nor energy with the surroundings is called an isolated system.

Ex: Take some water in an insulated vessel and put a small piece of sodium metal in it. An exothermic reaction takes place. Neither hydrogen gas (matter) nor heat (energy) is transferred to the surroundings.

6. What are C_p and C_v?

Ans: Heat capacity (C): Heat capacity (C) of a substance is defined as the amount of heat required to raise its temperature through one degree.

(or)

It is the ratio of heat absorbed (q) to the resulting increase in temperature (dT).

$$\therefore \quad C \quad \frac{q}{dT}$$

Heat capacity (C) is a state function. Hence to evalute 'C', the conditions such as volume or constant pressure have to be specified in order to define the path. Thus there are two different types of heat capacities. These are :

i) Heat capacity at constant volume (C_v)

ii) Heat capacity at constant pressure (C_p)

From first law of thermodynamics,

$$q = dE + W = dE + P \,.\, dV \quad (\because W = PV)$$

$$\therefore \quad C \quad \frac{q}{dT} = \frac{dE + P \cdot dV}{dT}$$

If the absorption of heat takes place at constant volume, C_v (i.e.,) dV = 0

$$\therefore \quad C_v = \frac{q_v}{dT} = \frac{\partial E + O}{\partial T} = \frac{[\partial E]}{[\partial T]_v}$$

$$\therefore \quad C_v = \frac{[\partial E]}{[\partial T]_v}$$

Definition for "C_v": Heat capacity of a system at constant volume (C_v) may be defined as rate of change of internal energy with temperature at constant volume.

If heat is absorbed by the system at constant pressure, heat capacity is denoted by "C_p" and is called heat capacity at constant pressure.

$$C_P = \frac{q_P}{dT} = \frac{[\partial E]}{[\partial T]_P} + P \frac{[\partial v]}{[\partial T]_P} \qquad \text{----------(1)}$$

But $H = E + PV$

Differentiating this equation w.r.to T at constant pressure, we get

$$\frac{[\partial H]}{[\partial T]_p} = \frac{[\partial E]}{[\partial T]_p} + \frac{[\partial v]}{[\partial T]_p} \qquad \text{----------(2)}$$

From equations (1) and (2) , we get

$$C_p = \left[\frac{\partial H}{\partial T}\right]_p$$

Definition for C_p: Heat capacity of a system at constant pressure (C_p) may be defined as rate of change of enthalpy with temperature at constant pressure.

THERMODYNAMICS

Topic: 4

Spontaneous processes and criteria for spontaneity, entropy as a state function.

VERY SHORT ANSWER QUESTIONS

1. State Hess's law?

Ans. Hess's law: The total heat change in a reaction is the same whether the chemical reaction takes place in one single step or in several steps.

2. What is Gibbs energy?

Gibbs energy (G): The amount of energy available from a system which can be put to useful work at constant temperature and pressure is called Gibb's energy.

For explaining the criteria for spontaneity of a reaction, Gibb's introduced thermodynamic function which involved both enthalpy (H) and entropy (S) functions. This is known as free energy function (G)

This is given by the equation, $G = H - TS$

Where 'G' is known as Gibbs energy (or) Gibbs function.

3. What is Gibbs equation?

Ans. Gibbs equation: For explaining the criteria for spontaneity of a reaction, Gibbs introduced thermodynamic function which involved both enthalpy (H) and entropy (S) functions. This is known as free energy function (G).
This is given by the equation, $G = H - TS$

Where 'G' is known as Gibbs energy (or) Gibbs function.

$$\Delta G = \Delta H - T\Delta S$$

SHORT ANSWER QUESTIONS

1. What is entropy?

Ans. Entropy: is taken as a measure of disorder of molecules (or) randomness of system. Greater the disorder of molecules in a system, the higher is the entropy. Entropy is a state function. It depends on the temperature, pressure of the system. For a spontaneous process in an isolated system the entropy change is positive.

2. **Define Gibbs energy.**

Ans: Gibbs energy ΔG: The amount of energy available from a system which can be put to useful work at constant temperature and pressure is called Gibb's energy.

For explaining the criteria for spontaneity reaction, Gibb's introduced thermodynamics function which involved both enthalpy (H) and entropy (S) functions. This is known as free energy function (G:)

This is given by the equation $G = H - TS$

Where 'G' is known as Gibbs energy (or) Gibbs function.

$$\Delta G = \Delta H - T\Delta S$$

ΔG_{sys} = negative for spontaneous reactions ($\Delta G < 0$)

ΔG_{sys} = positive for non – spontaneous reactions ($\Delta G > 0$)

ΔG_{sys} = Zero for equilibrium reactions ($\Delta G = 0$)

3. State third law of thermodynamics.

Ans. Third law of thermodynamics: "The entropy of a pure and perfectly crystalline substance is zero at the absolute zero of a temperature (-273^0C)

$$S_{\lim T \to 0} = 0$$

This law imposes a limitation on the value of entropy.

$$S_T = \int_0^T \frac{Cp}{T}\,dT$$

Thus entropy (S) of a substance at any temperature is calculated if the temperature dependence of '^{Cp}' is known as in evaluating absolute entropy of any substance.

Importance of this law: One of the most important applications of third law is the calculation. Of entropy changes in chemical reactions.

4. What is the importance of third law?

Ans: Importance of III law:

i) It imposes a limitation on the value of entropy

ii) Used in the calculation of entropy changes in chemical reactions.

iii) The overall (or) total entropy change (ΔS_{total}) must be positive for any spontaneous process (or) reaction.

$$\Delta S_{total} = \{ \Delta S_{sys} + \Delta S_{surrounding} \} > 0$$

5. What is absolute entropy?

Ans: Absolute entropy (S^o): The entropy per mole amount of substance (or) ion in its standard state (i.e.,) at 298 K and 1 atm, pressure is called absolute entropy.

Ex:

Substance	Value of S^o ($JK^{-1} mol^{-1}$)
C (graphite)	5.7
C (diamond)	2.4
C (gas)	198
H_2O(liquid)	69.9
H_2O(gas)	188.8

Absolute entropy (S^o) is calculated using C_v value.

6. State and explain first law of thermodynamics.

Ans: I law of thermodynamics: The law of conservation of energy is taken as the first law of thermodynamics.

Statements:

i) "Energy can neither be created nor destroyed, although it can be transformed from one form to another".

ii) "It is impossible to construct a perpetual motion machine of first kind"

iii) "The total energy of the system and surroundings is constant".

Mathematical form of law of thermodynamics is

$q = \Delta E + W$

q = amount of heat absorbed by the system from surroundings

ΔE = increase in internal energy

W = work done

7. State and explain the significance of second law.

First law is unable to predict the feasibility of the change (or) direction of the change. The process which takes place on its own without any external agency is called spontaneous process.
All natural processes are spontaneous and thermodynamically irreversible.

. Second law of thermodynamics:

i) "It is impossible to construct a machine in cycles which transforms heat from a lower temperature to higher temperature region without intervention of any external agency"

ii) "Heat cannot flow from a colder body to a hotter body on its own".

iii) "All spontaneous processes are thermodynamically irreversible and entropy of system increases in all spontaneous processes".

8. Explain the terms 'entropy', 'Gibbs energy', with suitable examples.

Ans: Entropy (S): Entropy is taken as a measure of disorder of molecules (or) randomness of the system. Greater the disorder of molecules in a sytem, the higher is the entropy.

$$S_{gas} < S_{liquid} > S_{solid}$$

For a spontaneous process in an isolated system the entropy change is positive.

Gibbs energy (G): The amount of energy available from a system which can be put to useful work at constant temperature and pressure is called Gibb's energy.

For explaining the criteria for spontaneity of a reaction, Gibb's introduced thermodynamics function which involved both enthalpy (H) and entropy (S) functions. This is given by the equation,

$$G = H - TS$$

Where 'G' is known as Gibbs energy (or) Gibbs function.

9. What are the criteria for the spontaneous nature of chemical reaction? Give examples.

The spontaneity of a reaction and the algebraic signs of ΔH, ΔS, ΔG and the magnitude of 'T' can be related as follows.

ΔH	ΔS	ΔG	Nature of reaction
-	+	-	Spontaneous at all T values
-	-	-	Spontaneous at low T values
+	+	-	Spontaneous at high T values

All natural processes are spontaneous.

Ex: 1. Flowing of water from high level to low level
2. Expansion of gas from high pressure zone to low pressure zone
3. Flowing of heat from hot body to cold body.

LONG ANSWER QUESTIONS

1. What are C_p and C_v?

Ans: Heat capacity (C) : Heat capacity (C) of a substance is defined as the amount of heat required to raise its temperature through one degree.

(or)

It is the ratio of heat absorbed (q) to the resulting increase in temperature (dT).

$$\therefore \quad C \quad \frac{q}{dT}$$

Heat capacity (C) is a state function. Hence to evaluate 'C', the conditions such as volume or constant pressure have to be specified in order to define the path. Thus there are two different types of heat capacities. These are:

i) Heat capacity at constant volume (C_v)

ii) Heat capacity at constant pressure (C_p)

from first law of thermodynamics,

$$q = dE + W = dE + P \cdot dV \quad (\because W = PV)$$

$$\therefore C \frac{q}{dT} = \frac{dE + P \cdot dV}{dT}$$

If the absorption of heat takes place at constant volume, C_v (i.e.,) dV = 0

$$\therefore C_v = \frac{q_v}{dT} = \frac{\partial E + O}{\partial T} = \frac{[\partial E]}{[\partial T]_v}$$

$$\therefore C_v = \frac{[\partial E]}{[\partial T]_v}$$

Definition for "C_v" : Heat capacity of a system at constant volume (C_v) may be defined as rate of change of internal energy with temperature at constant volume.

If heat is absorbed by the system at constant pressure, heat capacity is denoted by "C_p" and is called heat capacity at constant pressure.

$$C_P = \frac{q_P}{dT} = \frac{[\partial E]}{[\partial T]_P} + P \frac{[\partial v]}{[\partial T]_P} \qquad \text{----------(1)}$$

But $H = E + PV$

Differentiating this equation w.r.to T at constant pressure, we get

$$\left[\frac{\partial H}{\partial T}\right]_p = \left[\frac{\partial E}{\partial T}\right]_p + \left[\frac{\partial v}{\partial T}\right]_p \qquad \text{----------(2)}$$

From equations (1) and (2), we get

$$C_p = \left[\frac{\partial H}{\partial T}\right]_p$$

Definition for C_p: Heat capacity of a system at constant pressure (C_p) may be defined as rate of change of enthalpy with temperature at constant pressure.

2. How do you explain the spontaneous nature of an endothermic reaction? Illustrate with an example.

Ans. In endothermic reactions, Reactants on conversion into products go to higher energy state and temperature of the system falls. As a consequence, heat flows from surroundings into the system, the entropy of the surroundings decreases. If the disorder of the system raises sufficiently high and overall entropy increases is positive.

Total entropy change is positive: The reaction will be spontaneous an endothermic reaction is spontaneous only if the entropy of the system increases enough to overcome the decrease in entropy of the surroundings.

3. State and explain enthalpy and internal energy in terms of a substance.

Ans. Enthalpy (H) : Enthalpy is the amount of heat exchanged by a system with its surroundings at constant pressure and temperature.

Mathematically, change in enthalpy $\Delta H = \Delta E + P.\Delta V$

Enthalpy is state function. Thus, the magnitude of enthalpy change depends only upon the enthalpies in the initial and the final states.

$$\Delta H = [H_{products} - H_{reactants}]$$

Internal energy (E): “The total energy stored in the substance at constant temperature and pressure is called its internal energy (E)”. It is a state function and is an extensive property

Internal energy change (ΔE) is considered as the difference between the internal energies of products and reactants.

$$\Delta E = (E_p - E_r)$$

In any path taken (Q – W) is equal to ΔE.

Where Q = heat and W = work.

THERMODYNAMICS

Topic: 5

Gibbs free energy, concept, applications to spontaneous and non-spontaneous processes

VERY SHORT ANSWER QUESTIONS

1. What is Gibbs energy?

Gibbs energy (G): The amount of energy available from a system which can be put to useful work at constant temperature and pressure is called Gibb's energy.

For explaining the criteria for spontaneity of a reaction, Gibb's introduced thermodynamic function which involved both enthalpy (H) and entropy (S) functions. This is known as free energy function (G)

This is given by the equation, $G = H - TS$

Where 'G' is known as Gibbs energy (or) Gibbs function.

2. What is Gibbs equation?

Ans. Gibbs equation: For explaining the criteria for spontaneity of a reaction, Gibbs introduced thermodynamic function which involved both enthalpy (H) and entropy (S) functions. This is known as free energy function (G).
This is given by the equation, $G = H - TS$

Where 'G' is known as Gibbs energy (or) Gibbs function.

$$\Delta G = \Delta H - T\Delta S$$

SHORT ANSWER QUESTIONS

1. How are ΔH and ΔE related for a gaseous equilibrium reaction? What is (ΔH – ΔE) for

$CaCO_3$ (s) $\longrightarrow$ CaO (s) + CO_2 (g) ?

Relation between ΔH and ΔE for gaseous reactions is

$$\Delta H = \Delta E + \Delta n\, RT$$

Δn = [total no. of molecules of gaseous products] – [total no. of molecules of gaseous reactants]

R = gas constant

T = temperature in kelvin scale ($t^oc + 273$)

Solutions:

$CaCO_3$ ——> CaO + CO_2
(s) (s) (g)

$\Delta n = [(1 + 0) – 0] = 1$ (∵ only gaseous molecules are taken into consideration)

$\therefore \Delta H = \Delta E + \Delta n RT$

$\Rightarrow \Delta H – \Delta E = \Delta n RT$

But $\Delta n = 1$

$\therefore (\Delta H – \Delta E) = 1 \times RT = RT$

$\therefore \Delta H – \Delta E) = RT$

2. Define and explain “heat of formation” of a compound.

Ans: Heat of formation (ΔH_f) : The amount of heat evolved (or) absorbed during the formation of one mole of the compound at constant temperature from the constituent elements in the standard state is heat of formation.

Ex: ½ N_2 (g) + ½ O_2 (g) ——> NO (g), $\Delta H = + 90.04$kj

H_2 (g) + ½ O_2 (g) ——> H_2O (l), $\Delta H = – 286.21$ kj

Compounds which liberate heat in their formation reaction from constituent elements are called exothermic compounds.

For this reactions, ΔH_f = negative

Compounds which absorb heat in the formation reaction from the constituent elements are called endothermic compounds.

For this reactions, ΔH_f = positive.

3. Define and explain "heat of reaction".

Ans. Heat of reaction: The heat of reaction is the quantity of heat evolved or absorbed at constant temperature when the reactants of a reaction undergo complete transformation into the products as per the stoichiometric equation.

Heat of reaction = Heat content of products – Heat content of reactants
(or) Heat of reaction = enthalpy of products – enthalpy of reactants

(or) $\Delta H = H_p - H_g$

Ex : i) $N_2(g) + 3H_2(g) \longrightarrow NH_3(g)$, $\Delta H = -92kj$

ii) $2SO_2 + O_2 \longrightarrow 2SO_3$, $\Delta H = -189kj$

LONG ANSWER QUESTIONS

10. Explain Gibbs energy, enthalpy, entropy

Ans: Enthalpy (H): Enthalpy is the amount of heat exchanged by a system with its surroundings at constant pressure and temperature.

The energy change taking place at constant pressure and at a constant temperature is called enthalpy change (ΔH).

Mathematically $\Delta H = \Delta H + P.\Delta V$. When ΔE = Internal energy change.

Enthalpy is state function. Thus, the magnitude of enthalpy change depends only upon the enthalpies in the intial and the final states.

$$\Delta H = [H_{\text{products}} - H_{\text{reacants}}]$$

For gaseous reactions, $\Delta H = \Delta E + \Delta nRT$

Entropy(S): Entropy is taken as a measure of disorder of molecules (or) randomness of the system. It depends on the temperature, pressure of the state.

Entropy change, $\Delta S = \frac{q_{rev}}{T}$ [q_{rev}= heat absorbed by the system isothermally and reversibly at T]

For a spontaneous process in an isolated system the entropy change is positive.

(ΔS = positive)

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

Gibbs energy (ΔG): The amount of energy available from a system which can be put to useful work at constant temperature and pressure is called Gibb's energy. For explaining the criteria for spontaneity of a reaction, Gibb's introduced thermodynamic function which involved both enthalpy (H) and entropy (S) functions. This is known as free energy function (G). This is given by the equation, G = H – TS.

Where 'G' is known as Gibbs energy (or) Gibbs function.

$\Delta G = \Delta H - T\Delta S$

ΔG_{sys} = negative for spontaneous reactions ($\Delta G < 0$)

ΔG_{sys} = positive for non – spontaneous reactions ($\Delta G > 0$)

ΔG_{sys} = Zero for equilibrium reactions ($\Delta G = 0$)

SELECTED NUMERICALS WITH PROBLEMS

1. The bond enthalpy of $H_{2(g)}$ is 436kj/mole.The bond enthalpy of $N_{2(g)}$ is 941.3 kj/mole.
What is the bond enthalpyof N–H in $NH_{3(g)}$?NH_3 formationenergy – 46.0 kj/mole

Sol: $N_{2(g)} \longrightarrow 2N_{(g)}$; ΔH^0 = 941.3 kj/mole

$H_{2(g)} \longrightarrow 2H_{(g)}$; ΔH^0 = 436 kj/mole

$$\frac{1}{2} N_{2(g)} + \frac{3}{2} H_{2(g)} \rightarrow NH_{3(g)}; \quad \Delta H^0 = 460 kj/mole$$

$$\therefore \quad \frac{1}{2} N_{2(g)} \longrightarrow 1N_{(g)} ; \quad \Delta H = \frac{941.3}{2} = 470.7 \text{ kJ}$$

$$\frac{3}{2} H_{2(g)} \longrightarrow 3H \; ; \qquad \Delta H = 4.36 \times \frac{3}{2} = \frac{1308}{2} = 654 \text{ kJ}$$

$$\frac{1}{2} N_{2(g)} \longrightarrow \frac{3}{2} H_{2(g)} \rightarrow N_{(g)} + 3H \; ; \quad \Delta H = 1124.7 \text{ kJ} \quad \text{---------(a)}$$

$$\text{But} \quad \frac{1}{2} N_{2(g)} + \frac{3}{2} H_{2(g)} \rightarrow NH_{3(g)} \; ; \quad \Delta H = -46.0 \text{ kj/mole} \quad \text{---------(b)}$$

Subtracting (b) from (a)

$NH_{3(g)} \longrightarrow N_{(g)} + 3H_{(g)} = 1124.7 - (-46.0) = 1170.7$

Dividing by 3, we have bond dissociation energy of N – H bond

$$= \frac{1170.7}{3} = 390.2 \text{ kj/mole}$$

2. In combustion reaction of methane to give Co_2 and H_2O: the relation betweeen ΔH and ΔE is

Sol: $CH_{4(g)} + 2O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2H_2O_{(g)}$

$\Delta H = \Delta E \qquad \because \Delta n = 3 - 3 = 0$

3. Calculate the ionization enthalpy of NH_4OH from ΔH of neutralization of (HCl + NaOH) (– 57.4 kJ), HCl + NH_4OH (– 51.46 kJ)

Sol: ΔH of ($HCl + NH_4OH$) ΔH of (HCl + NaOH)

$= \Delta H$ of ionization NH_4OH

$\Delta H = \{(-51.46) - (-57.40)\}$ kJ

$\Delta H = \{57.40 - 51.46\} = 5.94$ kJ

4. Calculate the difference between ΔH and ΔE for the reaction at 527^0C in k. Cal.
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2\,NH_{3(g)}$

Sol: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2\,NH_{3(g)}$

$\Delta n = \{2 - (1+3)\} = -2$

$\Delta H = \Delta E + \Delta n\,(RT)$; $T = 527 + 273 = 800K$

$(\Delta H - \Delta E) = \Delta n\,(RT) = (-2) \times (2 \times 10^{-3}) \times 800$ k.cals

$= -2 \times 2 \times 10^{-3} \times 10^{2} \times 8$

$= -32 \times 10^{-1} = -3.2$ k.cals

5. What is ΔE for the reaction in kJ.$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ at 327^0C if ΔH is–393.5 kJ

Sol: $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$

$\Delta n = (1 - 1) = 0$ [$\because$C = solid]

$T = 327^0C + 273 = 600$ K

$R = 8.3 \times 10^{-3}$ kJ

$\Delta H = \Delta E + \Delta n\ RT$

$= \Delta E + 0 \times R \times T = \Delta E$

$\therefore\ \Delta E = -393.5$ kJ

6. ΔH for the reaction. $H_{2(g)} + Cl_{2(g)} \longrightarrow 2\ HCl_{(g)}$ is – 184.6 kJ . What is heat of formation of HCl

Sol: Heat of formation is ΔH for 1 mole

$$\therefore \Delta H = -\frac{184.6}{2} = -92.3 \text{ kJ}$$

7. The heat evolved when 10 grms of CH_4 is burnt in excess O_2 is 558.6 kJ. Calculate heat of combustion of CH_4.

Sol: Heat of combustion of CH_4. is heat evolved when 16g of CH_4 is burnt in an excess oxygen.

For 10gms ——> – 558 .6 kJ of heat is evolved.

$$16 \text{ gms} \longrightarrow -\frac{558.6}{10} \times 16 = -893.76 \text{ kJ heat is evolved.}$$

8. Calculate ΔH For C $_{(graphite)}$ → C $_{(diamond)}$ from the equations.

$C_{(graphite)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)}$; ΔH = 393.5 kJ

$C_{(diamond)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)}$; ΔH = 395.4 kJ

Sol: $C_{(graphite)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)}$; ΔH = 393.5 kJ

$C_{(diamond)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)}$; ΔH = 395.4 kJ

On substraction $C_{(graphite)} - C_{(diamond)} = -393.5 - (-395.4)$

ΔH = + 1.9 kJ

9. **Heat of reaction for $HCl_{(aq)} + NaOH \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$ ΔH = –57.3 kJ. Heat of reaction for $HCl_{(aq)}$ $NH_4OH_{(aq)} \longrightarrow NH_4Cl_{(aq)} + H_2O_{(l)}$; ΔH = –51.46 kJ. Calculate heat of ionization of $NH_4OH_{(aq)}$.**

Sol: Heat ionization of NH_4OH

[Heat of neutralization of (NH_4OH + HCl) – Heat of neutralization of (NaOH + HCl)]

= 51.46 kJ – (– 57.3)

$= 57.3 - 51.46 = +5.84$ kJ

IMPORTANT QUESTIONS

I. Long answer questions.

1. Give the criteria for spontaneity of a reaction.
2. What is the heat of neutralization? How does its value changes with the chemical nature of the acid and base? Give reasons.
3. State Hess's law of constant heat formation and explain it with an example.
4. What is Cp and Cv ?

II. Short answer questions.

1. State first law of thermodynamics
2. State second law of thermodynamics
3. Define Gibbs energy.
4. What is absolute entropy?
5. Explain the terms 'entropy', 'Gibb's Free energy' with examples.
6. State and explain enthalpy and internal energy in terms of a substance.
7. Define and explain heat of formation of a compound.

III. Very short answer questions.

1. Define and explain heat of a reaction.
2. Name three intensive properties.
3. Name three extensive properties.
4. What is heat capacity? Explain.
5. What is Gibb's equation?