6 ▪▪▪ Thermodynamics

Facts that Matter

● Important Terms and Definitions

System: Refers to the portion of universe which is under observation.
Surroundings: Everything else in the universe except system is called surroundings.
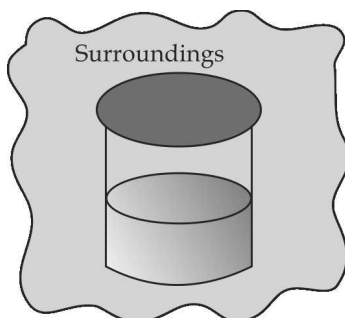The Universe = The System + The Surroundings.

Fig. 6.1 *System and the surroundings*

Open System: In a system, when there is exchange of energy and matter taking place with the surroundings, then it is called an open system.
For Example: Presence of reactants in an open beaker is an example of an open system.
Closed System: A system is said to be a closed system when there is no exchange of matter but exchange of energy is possible.
For example: The presence of reactants in a closed vessel made of conducting material.
Isolated System: In a system, when no exchange of energy or matter takes place with the surroundings, is called isolated system.
For example: The presence of reactants in a thermoflask, or substance in an insulated closed vessel is an example of isolated system.
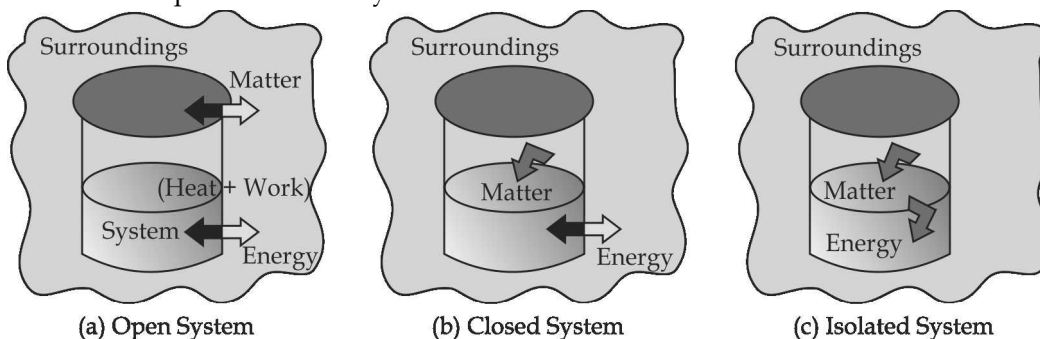

(a) Open System   (b) Closed System   (c) Isolated System
Fig. 6.2 *Open, closed and isolated system.*

Homogeneous System: A system is said to be homogeneous when all the constituents present is in the same phase and is uniform throughout the system.

For example: A mixture of two miscible liquids.

Heterogeneous system: A mixture is said to be heterogeneous when it consists of two or more phases and the composition is not uniform.

For example: A mixture of insoluble solid in water.

The state of the system: The state of a thermodynamic system means its macroscopic or bulk properties which can be described by state variables:

Pressure (P), volume (V), temperature (T) and amount (n) etc.

They are also known as state functions.

Isothermal process: When the operation is carried out at constant temperature, the process is said to be isothermal. For isothermal process, $dT = 0$

Where dT is the change in temperature.

Adiabatic process: It is a process in which no transfer of heat between system and surroundings, takes place.

Isobaric process: When the process is carried out at constant pressure, it is said to be isobaric. *i.e. $dP = 0$*

Isochoric process: A process when carried out at constant volume, it is known as isochoric in nature.

Cyclic process: If a system undergoes a series of changes and finally returns to its initial state, it is said to be cyclic process.

Reversible Process: When in a process, a change is brought in such a way that the process could, at any moment, be reversed by an infinitesimal change. The change r is called reversible.

● **Internal Energy**

It is the sum of all the forms of energies that a system can possess.

In thermodynamics, it is denoted by Δu which may change, when

- Heat passes into or out of the system
- Work is done on or by the system
- Matter enters or leaves the system.

Change in Internal Energy by Doing Work

Let us bring the change in the internal energy by doing work.

Let the initial state of the system is state A and Temp. T_A

$$\text{Internal energy} = u_A$$

On doing some mechanical work the new state is called state B and the temp. T_B. It is found to be

$$T_B > T_A$$

u_B is the internal energy after change.

∴ $$\Delta u = u_B - u_A$$

Change in Internal Energy by Transfer of Heat

Internal energy of a system can be changed by the transfer of heat from the surroundings to the system without doing work.

$$\Delta u = q$$

Where q is the heat absorbed by the system. It can be measured in terms of temperature difference.

q is +ve when heat is transferred from the surroundings to the system.

q is –ve when heat is transferred from system to surroundings.

When change of state is done both by doing work and transfer of heat.

$$\Delta u = q + w$$

First law of thermodynamics (Law of Conservation of Energy). It states that, energy can neither be created nor be destroyed. The energy of an isolated system is constant.

$$\Delta u = q + w.$$

● Work (Pressure-volume Work)

Let us consider a cylinder which contains one mole of an ideal gas in which a frictionless piston is fitted.

$$\text{Total volume of the gas} = V$$
$$\text{Pressure of the gas} = P$$
$$\text{external pressure} = P_{ex}$$

If
$$P_{ex} > P$$
$$\text{final volume} = V_f$$
$$\text{Distance moved by the piston} = l$$
$$\text{cross-sectional area of piston} = A$$
$$\text{volume change } \Delta V = l \times A = (V_f - V_i)$$

$$P = \frac{F}{A}$$
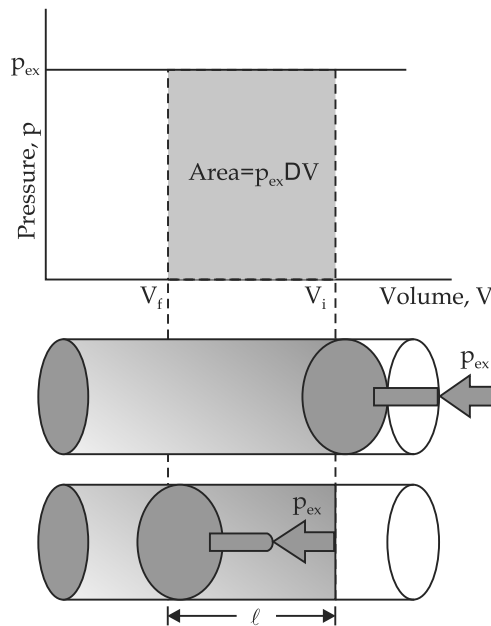
Fig. 6.3 *Work done on an ideal gas in a cylinder when it is compressed by a constant external pressure, p_{ex} (in single step) is equal to the shaded area.*

$$F = P \times A$$
$$W = F \times d. \text{ (force} \times \text{distance)}$$
$$= P_{ex} \times A \times l = P_{ex}(-AV)$$
$$W = -P \Delta V$$

−ve sign is used for work done by the system in case of expansion in volume by convertions.

If in a system volume expands from V_1 to V_2

$$W = -\int_{V_1}^{V_2} P_{ex}\, dV$$

● **Work Done in Isothermal and Reversible Expansion of Ideal Gas**

$$W_{rev.} = -\int_{V_i}^{V_f} P_{ex}\, dV = -\int_{V_i}^{V_f} (P_{in} \pm dP)\, dV$$

Since $dP \times dV$ is very small we can write,

$$W_{rev.} = -\int_{V_i}^{V_f} P_{in}\, dV$$

For ideal gas $\qquad\qquad PV = nRT$

$$P = \frac{nRT}{V}$$

Therefore, at constant temperature,

$$W_{rev.} = -\int_{V_i}^{V_f} nRT\frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

$$= -2.303\, nRT \log \frac{V_f}{V_i}$$

● **Isothermal and Free Expansion of an Ideal Gas**

For isothermal expansion of an ideal gas into vacuum $W = 0$

$$\text{Since, } P_{ex} = 0$$
$$\Delta U = 0, \quad q = 0$$

(1) For isothermal irreversible change
$$q = -W = p_{ex}(V_f - V_i)$$

(2) For isothermal reversible change

$$q = -W = nRT \ln \frac{V_f}{V_i}$$

$$= 2.303\, nRT \log \frac{V_f}{V_i}$$

For adiabatic change $\quad q = 0$
$$\Delta U = W_{ad}$$

• Enthalpy (H)

It is defined as total heat content of the system. It is equal to the sum of internal energy and pressure-volume work.

Mathematically, $\quad H = U + PV$

Change in enthalpy: Change in enthalpy is the heat absorbed or evolved by the system at constant pressure.

$$\Delta H = q_p$$

For exothermic reaction (System loses energy to Surroundings),

ΔH and q_p both are –Ve.

For endothermic reaction (System absorbs energy from the Surroundings).

ΔH and q_p both are +Ve.

Relation between ΔH and Δu.

Let us consider a general reaction $A \longrightarrow B$

Let H_A be the enthalpy of reactant A and H_B be that of the products.

$$\therefore \qquad\qquad H_A = U_A + PV_A$$
$$H_B = U_B + PV_B$$
$$\Delta H = H_B - H_A$$
$$= (U_B + PV_B) - (U_A + PV_A)$$
$$\Delta H = \Delta U + P\Delta V \; (H_B - H_A)$$
$$\Delta H = \Delta U + P\Delta V$$

At constant pressure and temperature using ideal gas law,

$$PV_A = n_A \, RT \quad \text{(For reactant } A)$$
$$PV_B = n_B \, RT \quad \text{(For product } B)$$

Thus, $\qquad PV_B - PV_A = n_B \, RT - n_A \, RT$
$$= (n_B - n_A) \, RT$$
$$P\Delta V = \Delta n_g \, RT$$
$$\therefore \qquad\qquad \Delta H = \Delta U + \Delta n_g \, RT$$

• Extensive property

An extensive property is a property whose value depends on the quantity or size of matter present in the system.

For example: Mass, volume, enthalpy etc. are known as extensive property.

• Intensive property

Intensive properties do not depend upon the size of the matter or quantity of the matter present in the system.

For example: temperature, density, pressure etc. are called intensive properties.

• Heat capacity

The increase in temperature is proportional to the heat transferred.

$$q = \text{coeff.} \times \Delta T$$
$$q = C\Delta T$$

Where, coefficient C is called the heat capacity.

C is directly proportional to the amount of substance.

$$C_m = \frac{C}{n}$$

It is the heat capacity for 1 mole of the substance.

● Molar heat capacity

It is defined as the quantity of heat required to raise the temperature of a substance by 1° (kelvin or celsius).

● Specific Heat Capacity

It is defined as the heat required to raise the temperature of one unit mass of a substance by 1° (kelvin or celsius).

$$q = C \times m \times \Delta T$$

where
$$m = \text{mass of the substance}$$
$$\Delta T = \text{rise in temperature.}$$

● Relation Between C_p and C_v for an Ideal Gas

At constant volume heat capacity = C_v
At constant pressure heat capacity = C_p
At constant volume $q_v = C_v \Delta T = \Delta U$
At constant pressure $q_p = C_p \Delta T = \Delta H$
For one mole of an ideal gas

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(RT)$$
$$\Delta H = \Delta U + R\Delta T$$

On substituting the values of ΔH and Δu, the equation is modified as

$$C_p \Delta T = C_v \Delta T + R \Delta T$$
or
$$C_p - C_v = R$$

● Measurement of ΔU and ΔH—Calorimetry

Determination of ΔU: ΔU is measured in a special type of calorimeter, called bomb calorimeter.
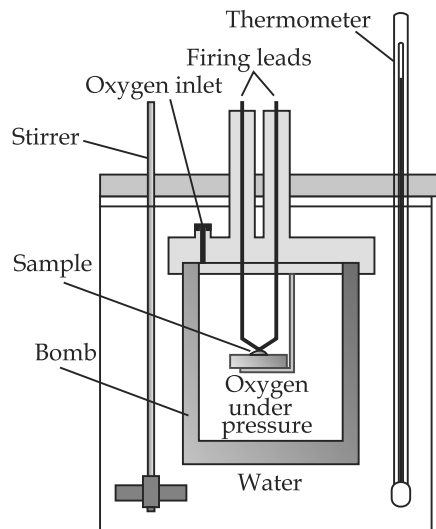

Fig. 6.4 *Bomb calorimeter*

Working with calorimeter. The calorimeter consists of a strong vessel called (bomb) which can withstand very high pressure. It is surrounded by a water bath to ensure that no heat is lost to the surroundings.

Procedure: A known mass of the combustible substance is burnt in the pressure of pure dioxygen in the steel bomb. Heat evolved during the reaction is transferred to the water and its temperature is monitored.

During the process volume remains constant

$$\Delta V = 0$$

Temperature change of the calorimeter is converted to q_v.

The value of ΔU can be calculated using the formula.

$$\Delta U = Q \times \Delta T \times \frac{M}{m}$$

Q = heat capacity of the calorimeter.
ΔT = rise in temperature.
m = mass of the substance taken
M = Molecular mass of the substance.

Determination of ΔH: At constant pressure heat evolved or absorbed is Δq_p is equal to the heat of reaction or enthalpy of reaction $\Delta_r H$.

In exothermic reaction, Δq_p and $\Delta_r H$ both will be –ve (negative).

In endothermic reaction, Δq_p and $\Delta_r H$ both will be +ve (positive).

Heat change at constant pressure can be done in a calorimeter shown in the fig. 6.5.

Enthalpy Change Δ_r H of a reaction

The enthalpy change in a chemical reaction is given by the symbol $\Delta_r H$.

$\Delta_r H$ = (Sum of enthalpies of products) – (Sum of enthalpies of reactants)

$$\Delta_r H = \sum_i a_i H_{products} - \sum_i b_i H_{reactants}$$

a_i and b_i are the stoichiometric coefficients.

Standard enthalpy of reactions: When reaction takes place at the standard state of substance the enthalpy of reaction is known as standard enthalpy.

It is denoted by $\Delta H^{\ominus}$.

Fig. 6.5 *Calorimeter for measuring heat changes at constant pressure (atmospheric pressure).*

● Enthalpy Changes During Phase Transformation

Enthalpy of fusion: Enthalpy of fusion is the heat energy or change in enthalpy when one mole of a solid at its melting point is converted into liquid state.

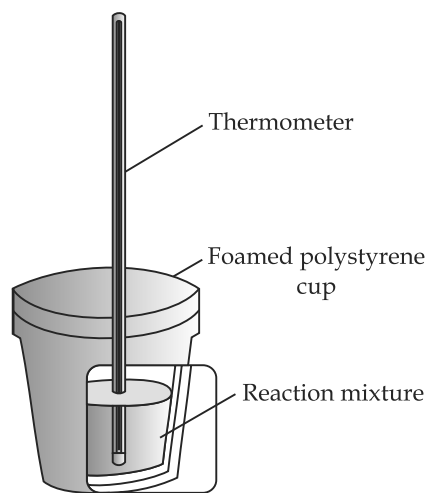**For example:** Enthalpy of fusion of ice at 273 K is 6.0 kJ mol^{-1}

$$\underset{\text{ice}}{H_2O \ (s)} \longrightarrow \underset{\text{water}}{H_2O \ (l)}$$

$\Delta_{fus} H^{\ominus} = + 6.0$ kJ mol^{-1}

Enthalpy of vaporisation: It is defined as the heat energy or change in enthalpy when one mole of a liquid at its boiling point changes to gaseous state.
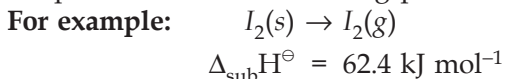
For example:

$$H_2O \ (l) \longrightarrow H_2O \ (g)$$

$\Delta_{vap} H^{\ominus} = 40.79$ kJ mol^{-1}

Enthalpy of Sublimation: Enthalpy of sublimation is defined as the change in heat energy or change in enthalpy when one mole of solid directly changes into gaseous state at a temperature below its melting point.

For example: $I_2(s) \rightarrow I_2(g)$

$$\Delta_{sub}H^{\ominus} = 62.4 \text{ kJ mol}^{-1}$$

● Standard Enthalpy of Formation

Enthalpy of formation is defined as the change in enthalpy in the formation of 1 mole of a substance from its constituting elements under standard conditions of temperature at 298K and 1 atm pressure. It is denoted as $\Delta_f H^{\ominus}$.

C (graphite s) + $2H_2$ (g) $\rightarrow CH_4$ (g)

$$\Delta_f H^{\ominus} = -74.8 \text{ kJ mol}^{-1}$$
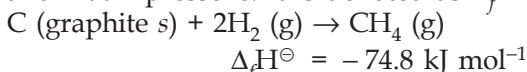
Enthalpy of Combustion: It is defined as the heat energy or change in enthalpy that accompanies the combustion of 1 mole of a substance in excess of air or oxygen.

For example: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$$\Delta_c H^{\ominus} = -890.3 \text{ kJ mol}^{-1}$$
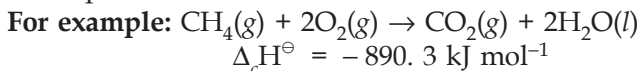
The negative sign of enthalpy change indicates that this is an exothermic reaction.
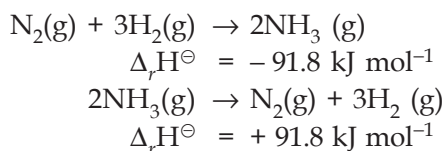
● Thermochemical Equation

A balanced chemical equation together with the value of $\Delta_r H$ and the physical state of reactants and products is known as thermochemical equation.

$$H_2(g) + \frac{1}{2}O_2 \ (g) \rightarrow H_2O(l)$$

$$\Delta_f H^{\ominus} = -286.0 \text{ kJ mol}^{-1}$$
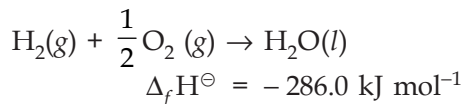
Conventions regarding thermochemical equations

1. The coefficients in a balanced thermochemical equation refer to the number of moles of reactants and products involved in the reaction.
2. The numerical value of $\Delta_r H^{\ominus}$ refers to the number of moles of substance specified by an equation.
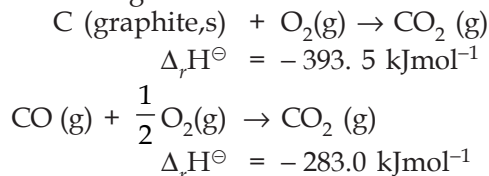3. If a chemical reaction is reversed, the value of $\Delta_r H^{\ominus}$ is reversed in sign.
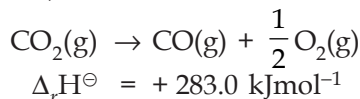   For example:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3 \ (g)$$
$$\Delta_r H^{\ominus} = -91.8 \text{ kJ mol}^{-1}$$
$$2NH_3(g) \rightarrow N_2(g) + 3H_2 \ (g)$$
$$\Delta_r H^{\ominus} = +91.8 \text{ kJ mol}^{-1}$$

● Hess's Law of Constant Heat Summation

The total amount of heat evolved or absorbed in a reaction is same whether the reaction takes place in one step or in number of steps.

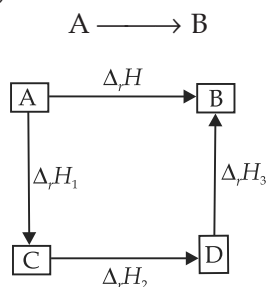Let us consider the following reactions:

$$C \text{ (graphite,s)} + O_2(g) \rightarrow CO_2 \ (g)$$
$$\Delta_r H^{\ominus} = -393.5 \text{ kJmol}^{-1}$$

$$CO \text{ (g)} + \frac{1}{2}O_2(g) \rightarrow CO_2 \ (g)$$
$$\Delta_r H^{\ominus} = -283.0 \text{ kJmol}^{-1}$$

On combining the two reactions,

$$CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g)$$
$$\Delta_r H^{\ominus} = +283.0 \text{ kJmol}^{-1}$$

In general it can be represented as,

$$A \longrightarrow B$$

- **Born-Haber Cycle**

It is not possible to determine the Lattice enthalpy of ionic compound by direct experiment. Thus, it can be calculated by following steps. The diagrams which show these steps is known as Born-Haber Cycle.

1. $\quad$ Na $(s) \longrightarrow$ Na (g)
    $\quad$ Δ sub $H^{\ominus}$ $\quad = \quad$ 108.4 kJ mol^{-1}
2. $\quad$ Na $(g) \longrightarrow$ Na$^+$ $(g) + e^-$ (g)
    $\quad$ ionization enthalpy $\Delta_i H^{\ominus} = 496$ kJ mol^{-1}
3. $\quad$ $\dfrac{1}{2}$ Cl$_2$ $(g) \longrightarrow$ Cl (g)

    $\quad$ bond dissociation enthalpy $\dfrac{1}{2} \Delta_{bond} H^{\ominus} = 121$ kJ mol^{-1}
4. $\quad$ Cl $(g) + e^-$ $(g) \longrightarrow$ Cl$^-$ (g)
    $\quad$ The electron gain enthalpy $\Delta_{eg} H^{\ominus} = -348.6$ kJ mol^{-1}
5. $\quad$ Na$^+$ (g) + Cl$^-$ $(g) \longrightarrow$ Na$^+$Cl$^-$ (s)
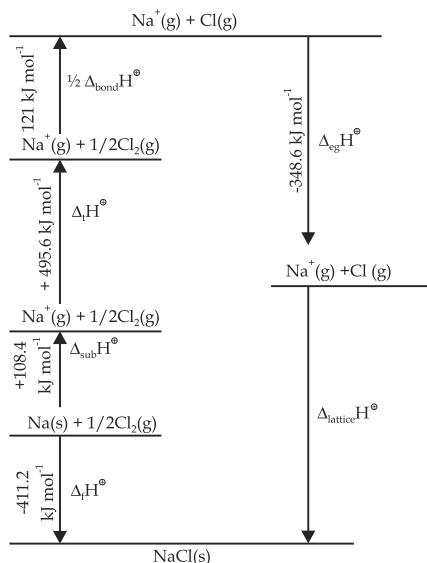
Fig. 6.6 *Enthalpy diagram for lattice enthalpy of NaCl*

Applying Hess's law

$\quad$ $\Delta_{Lattice} H^{\ominus}$ $\quad = \quad$ 411.2 + 108.4 + 121 + 496 − 348.6
$\quad$ $\Delta_{Lattice} H^{\ominus}$ $\quad = \quad$ + 788 kJ

• Spontaneity

Spontaneous Process: A process which can take place by itself or has a tendency to take place is called spontaneous process.

Spontaneous process need not be instantaneous. Its actual speed can vary from very slow to quite fast.

A few examples of spontaneous process are:
   (*i*) Common salt dissolves in water of its own.
  (*ii*) Carbon monoxide is oxidised to carbon dioxide of its own.

• Entropy (S)

The entropy is a measure of degree of randomness or disorder of a system. Entropy of a substance is minimum in solid state while it is maximum in gaseous state.

The change in entropy in a spontaneous process is expressed as ΔS

Mathematically,

$$\text{Change in entropy } (\Delta S) = \underset{\substack{\text{state} \\ \text{(product)}}}{S_{\text{final}}} - \underset{\substack{\text{state} \\ \text{(reactions)}}}{S_{\text{initial}}}$$

For reversible and isothermal process,

$$\text{Change in entropy } \Delta S = \frac{q_{reV}}{T} = \frac{\Delta H}{T}$$

When a system is in equilibrium, $\Delta S = 0$

Second law of thermodynamics: The entropy of universe is continuously increasing due to spontaneous processes taking place in it.

$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$ *i.e.,* $\Delta S_{\text{total}} > 0$

• Gibbs Energy and Spontaneity

A new thermodynamic function, the Gibbs energy or Gibbs function G, can be defined as
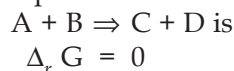
$$G = H - TS$$
$$\Delta G = \Delta H - T\Delta S$$

Gibbs energy change = enthalpy change – temperature × entropy change

ΔG gives a criteria for spontaneity at constant pressure and temperature.
   (*i*) If ΔG is negative (< 0) the process is spontaneous.
  (*ii*) If ΔG is positive (> 0) the process is non-spontaneous.

• Free Energy Change in Reversible Reaction

The criterion for equilibrium
$$A + B \Rightarrow C + D \text{ is}$$
$$\Delta_r G = 0$$

When all the reactants and products are in standard state,

$\Delta_r G^{\ominus}$ is related to the equilibrium constant of the reaction as

$$0 = \Delta_r G^{\ominus} - RT \ln K$$
$$\Delta_r G^{\ominus} = - RT \ln K$$
$$\Delta_r G^{\ominus} = - 2.303 \, RT \log K$$
$$\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$$
$$= - RT \ln K$$

Since $\Delta_r G^\ominus$ depends upon the value of $\Delta_r H^\ominus$ for strongly endothermic reactions, the value of $\Delta_r H^\ominus$ may be large and +ve. In such case K will be much smaller than 1, and the reaction is unlikely to form product in large amount.

In case of exothermic reactions $\Delta_r H^\ominus$ is large and negative and $\Delta_r G^\ominus$ is likely to be large and negative too.

In such cases, K will be much larger than 1.

Third law of thermodynamics: The entropy of a perfectly crystalline substance is zero at zero kelvin.

Words that Matter

- **Thermodynamics:** Deals with the energy changes in chemical or physical process.
- **First law of thermodynamics**

$$\Delta U = q + w \quad \text{(Where } w \text{ is the work done on the system)}$$

- **Change in internal energy and enthalpy is related as**

$$\Delta H = \Delta U + P\Delta V$$
$$\Delta H = \Delta U + \Delta n_g RT$$

  ΔH is negative for exothermic reactions and positive for endothermic reactions.
  Heat changes at constant pressure

$$\Delta H = q_p$$

- **Hess's law**

  Enthalpy change for chemical reaction can be determined by

$$\Delta_r H = \sum_f (a_i \Delta_f H_{\text{products}}) - \sum_i (b_i \Delta_f H_{\text{reactants}})$$

- **Entropy:** Is a measure of disorder or randomness.

  For a spontaneous change, total entropy change is positive.
  For Bilated system

$$\Delta U = 0, \quad \Delta S > 0$$

  Entropy change can be measured by the equation

$$\Delta S = \frac{q_{rev}}{T} \quad \text{for a reversible process.}$$

- **Gibbs energy**

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

  For a spontaneous change

$$\Delta G_{sys} < 0 \quad \text{and at equilibrium}$$
$$\Delta G_{sys} = 0$$

  Standard Gibbs energy is related to equilibrium constant by

$$\Delta_r G^\ominus = -RT \ln K$$

NCERT TEXTBOOK QUESTIONS SOLVED

Q1. *Choose the correct answer:*

A thermodynamic state function is a quantity

  (*i*) *used to determine heat changes*

  (*ii*) *whose value is independent of path*

  (*iii*) *used to determine pressure volume work*

  (*iv*) *whose value depends on temperature only.*

Ans. (*ii*) whose value is independent of path

Q2. *For the process to occur under adiabatic conditions, the correct condition is:*

    (*i*) $\Delta T = 0$ (*ii*) $\Delta p = 0$

    (*iii*) $q = 0$ (*iv*) $w = 0$

Ans. (*iii*) $q = 0$

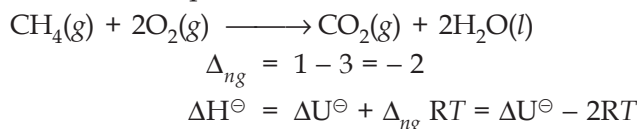**Q3.** *The enthalpies of all elements in their standard states are :*

    (*i*) unity   (*ii*) zero

    (*iii*) < 0 (*iv*) different for each element

Ans. (*ii*) zero

Q4. *$\Delta U^{\ominus}$ of combustion of methane is $- X$ kJ mol^{-1}. The value of $\Delta H^{\ominus}$ is*

    (*i*) $= \Delta U^{\ominus}$ (*ii*) $> \Delta U^{\ominus}$

    (*iii*) $< \Delta U^{\ominus}$ (*iv*) 0

Ans. The balanced chemical equation for the combustion reaction is :

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$
$$\Delta_{ng} = 1 - 3 = - 2$$
$$\Delta H^{\ominus} = \Delta U^{\ominus} + \Delta_{ng} RT = \Delta U^{\ominus} - 2RT$$

∴ $\Delta H^{\ominus} < \Delta U^{\ominus}$ or (*iii*) is the correct answer.

Q5. *The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are –890.3 kJ mol^{-1}, – 393.5 kJ mol^{-1} and – 285.8 kJ mol^{-1} respectively. Enthalpy of formation of $CH_4(g)$ will be*

    (*i*) $- 74.8$ kJ mol^{-1} (*ii*) $- 52.27$ kJ mol^{-1}

    (*iii*) $+ 74.8$ kJ mol^{-1} (*iv*) $+ 52.26$ kJ mol^{-1}

Ans. As per the available data :

    (*i*) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);$ $\Delta_C H^{\ominus} = - 890.3$ kJ mol^{-1}

    (*ii*) $C(s) + O_2(g) \longrightarrow CO_2(g);$ $\Delta_c H^{\ominus} = - 393.5$ kJ mol^{-1}

    (*iii*) $H_2(g) + 1/2O_2(g) \longrightarrow H_2O(l);$ $\Delta_c H^{\ominus} = - 285.8$ kJ mol^{-1}

The equation we aim at:

$$C(s) + 2H_2(g) \longrightarrow CH_4(g); \quad \Delta_f H^{\ominus} = ?$$
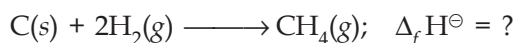
Eqn. (*ii*) + 2 × Eqn. (*iii*) – Eqn. (*i*) and the correct $\Delta_f H^{\ominus}$ value is:

$$= (- 393.5) + 2 \times (- 285.8) - (- 890.3) = -74.8 \text{ kJ mol}^{-1}$$

∴ (*i*) is the correct answer.

Q6. *A reaction, $A + B \rightarrow C + D + q$ is found to have a positive entropy change. The reaction will be*

    (*i*) *possible at high temperature*   (*ii*) *possible only at low temperature*

    (*iii*) *not possible at any temperature*   (*iv*) *possible at any temperature*

Ans. (*iv*) possible at any temperature

Q7. *In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?*

Ans.   Heat absorbed by the system, $q = 701$ J

           Work done by the system $= - 394$ J

           Change in internal energy $(\Delta U) = q + w = 701 - 394$ **= 307 J.**

Q8. *The reaction of cyanamide, $NH_2CN(s)$ with dioxygen was carried out in a bomb calorimeter and ΔU was found to be -742.7 kJ mol^{-1} at 298 K. Calculate the enthalpy change for the reaction at 298 K.*

$$NH_2CN\ (s) + 3/2O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(l)$$

Ans. $\Delta U = -742.7$ kJ mol^{-1}; $\Delta^{ng} = 2 - 3/2 = +1/2$ mol.

$R = 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1}; T = 298 K

According to the relation, $\Delta H = \Delta U + \Delta^{ng}\ RT$

$\Delta H = (-742.7\ kJ) + (1/2\ mol) \times (8.314 \times 10^{-3}\ kJ\ K^{-1}\ mol^{-1}) \times (298\ K)$

$= -742.7$ kJ $+ 1.239$ kJ $= -741.5$ **kJ.**

Q9. *Calculate the number of kJ of heat necessary to raise the temperature of 60 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24 J mol^{-1} K^{-1}.*

Ans.   No. of moles of Al (m) $= \dfrac{(60\ g)}{(27\ g\ mol^{-1})} = 2.22$ mol

Molar heat capacity $(C) = 24$ J mol^{-1} K^{-1}

Rise in temperature $(\Delta T) = 55 - 35 = 20°C = 20$ K

Heat evolved $(q) = C \times m \times T = (24\ J\ mol^{-1}\ K^{-1}) \times (2.22\ mol) \times (20\ K)$

$= 1065.6$ J $= $ **1.067 kJ**

Q10. *Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0°C to ice at $-10.0°C$. $\Delta_{fus} H = 6.03$ KJ mol^{-1} at 0°C. C_p $[H_2O(l)] = 75.3$ J mol^{-1} K^{-1}; C_p $[H_2O(s)] = 36.8$ J mol^{-1} K^{-1}.*

Ans. The change may be represented as:

$$H_2O\ (l)\ (10°C) \xrightarrow{\ \Delta H\ } H_2O(s)\ (-10°C)$$

$\Bigg\downarrow \Delta H_1 \qquad\qquad\qquad \Bigg\uparrow \Delta H_3$

$$H_2O\ (l)\ (0°C) \xrightarrow{\ \Delta H_2\ } H_2O(s)\ (0°C)$$
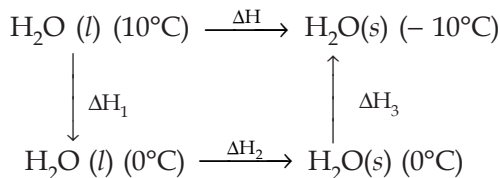
According to Hess's Law;

$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

$\Delta H_1 = 75.3$ J mol^{-1} K^{-1} (10 K) $= 753$ J mol^{-1}

ΔH_2 (solidification) $= -6.03$ kJ $mol^{-1} = -6030$ J mol^{-1}

(sign changed)

$\Delta H_3 = 36.8$ J mol^{-1} K^{-1} (-10 K) $= -368$ J mol^{-1}

$\Delta H = (753 - 6030 - 368)$ J $mol^{-1} = -5645$ J mol^{-1}

$\therefore$ $= -5.645$ **kJ** $\textbf{mol}^{-1}$.

Q11. *Enthalpy of combustion of carbon to carbon dioxide is -393.5 kJ mol^{-1}. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and oxygen gas.*

Ans. The combustion equation is:

$$C(s) + O_2(g) \longrightarrow CO_2(g);\quad \Delta_c H = -393.5\ kJ\ mol^{-1}$$
$$\text{(44 g)}$$
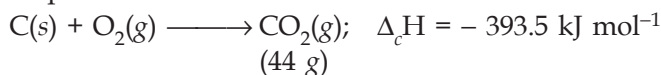
Heat released in the formation of 44g of $CO_2 = 393.5$ kJ

Heat released in the formation of 35.2 g of $CO_2 = \dfrac{(393.5\ kJ) \times (35.2\ g)}{(44\ g)} = $ **314.8 kJ**

Q12. *Calculate the enthalpy of the reaction:*
$$N_2O_4(g) + 3CO(g) \longrightarrow N_2O(g) + 3CO_2(g)$$
Given that; $\quad\quad \Delta_f HCO(g) = -110 \text{ kJ mol}^{-1};\quad \Delta_f HCO_2(g) = -393 \text{ kJ mol}^{-1}$

$\Delta_f HN_2O(g) = 81 \text{ kJ mol}^{-1};\quad \Delta_f H N_2O_4(g) = 9.7 \text{ kJ mol}^{-1}.$

Ans. Enthalpy of reaction $(\Delta_r H)$ = [81 + 3 (– 393)] – [9.7 + 3 (– 110)]

= [81 – 1179] – [9.7 – 330] = **– 778 kJ mol^{-1}**

Q13. *Given :* $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g);\ \Delta_r H^\ominus = -92.4 \text{ kJ mol}^{-1}$*. What is the standard enthalpy of formation of NH$_3$ gas?*

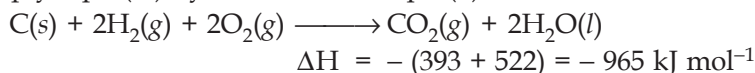**Ans.** $\Delta_f H^\ominus NH_3 (g) = -(92.4)/2 = -46.2 \text{ kJ mol}^{-1}.$

Q14. *Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the following data:*

(i) $CH_3OH(l) + 3/2\ O_2 (g) \longrightarrow CO_2 (g) + 2H_2O (l);\quad \Delta_r H^\ominus = -726 \text{ kJ mol}^{-1}$

(ii) $\quad\quad C(s) + O_2(g) \longrightarrow CO_2 (g);\quad \Delta_c H^\ominus = -393 \text{ kJ mol}^{-1}$

(iii) $\quad\quad H_2(g) + 1/2O_2(g) \longrightarrow H_2O (l);\quad \Delta_f H^\ominus = -286 \text{ kJ mol}^{-1}$

Ans. The equation we aim at ;
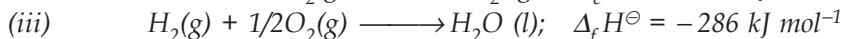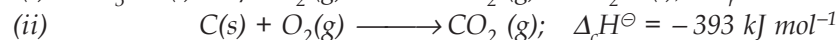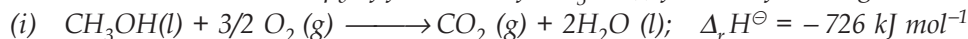
$C(s) + 2H_2(g) + 1/2O_2(g) \longrightarrow CH_3OH (l);\quad \Delta_f H^\ominus = \pm? \quad\quad\quad ... (iv)$

Multiply eqn. (*iii*) by 2 and add to eqn. (*ii*)

$C(s) + 2H_2(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$\Delta H = -(393 + 522) = -965 \text{ kJ mol}^{-1}$

Subtract eqn. (*iv*) from eqn. (*i*)

$CH_3OH(l) + 3/2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);\ \Delta H = -726 \text{ kJ mol}^{-1}$

Subtract: $C(s) + 2H_2(g) + 1/2O_2(g) \longrightarrow CH_3OH(l);\quad \Delta_f H^\ominus$ **= – 239 kJ mol^{-1}**

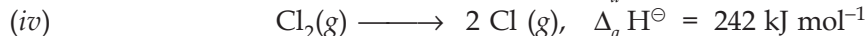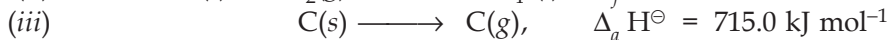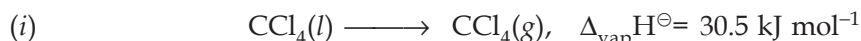**Q15.** *Calculate the enthalpy change for the process*
$$CCl_4(g) \longrightarrow C(g) + 4\ Cl(g)$$
and calculate bond enthalpy of C – Cl in $CCl_4(g)$
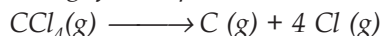
Given: $\quad\quad \Delta_{vap} H^\ominus (CCl_4) = 30.5 \text{ kJ mol}^{-1};\quad \Delta_f H^\ominus(CCl_4) = -135.5 \text{ kJ mol}^{-1}$

$\Delta_a H^\ominus (C) = 715.0 \text{ kJ mol}^{-1}$ *where $\Delta_a H^\ominus$ is enthalpy of atomisation*

$\Delta_a H^\ominus (Cl_2) = 242 \text{ kJ mol}^{-1}.$

Ans. The available data is:

(i) $\quad\quad CCl_4(l) \longrightarrow CCl_4(g),\quad \Delta_{vap}H^\ominus = 30.5 \text{ kJ mol}^{-1}$

(ii) $\quad C(s) + 2Cl_2(g) \longrightarrow CCl_4 (l),\quad \Delta_f H^\ominus = -135.5 \text{ kJ mol}^{-1}$

(iii) $\quad\quad\quad C(s) \longrightarrow C(g),\quad \Delta_a H^\ominus = 715.0 \text{ kJ mol}^{-1}$

(iv) $\quad\quad\quad Cl_2(g) \longrightarrow 2\ Cl(g),\quad \Delta_a H^\ominus = 242 \text{ kJ mol}^{-1}$

The equation we aim at is:

$CCl_4(g) \longrightarrow C(g) + 4Cl(g); \Delta H= ?$

Eqn. (*iii*) + 2 × Eqn. (*iv*) – Eqn. (*i*) – Eqn. (*ii*) gives the required equation with

$\Delta H = 715.0 + 2 (242) - 30.5 - (-135.5) \text{ kJ mol}^{-1}$

$= 1304 \text{ kJ mol}^{-1}$

Bond enthalpy of C–Cl in CCl_4 (average value) $= \dfrac{1304}{4}$ **= 326 kJ mol^{-1}.**

Q16. *For an isolated system $\Delta U = 0$; what will be ΔS?*

Ans. Change in internal energy (ΔU) for an isolated system is zero for it does not exchange any energy with the surroundings. But entropy tends to increase in case of spontaneous reaction. Therefore, $\Delta S > 0$ or positive.

Q17. *For a reaction at 298 K*

$$2A + B \longrightarrow C$$
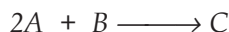
$\Delta H = 400$ kJ mol^{-1} and $\Delta S = 0.2$ kJ K^{-1} mol^{-1}.

At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range?

Ans. As per the Gibbs Helmholtz equation:

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

For $\Delta G = 0$; $\Delta H = T\Delta S$ or $T = \dfrac{\Delta H}{\Delta S}$

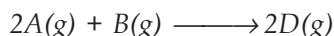$$T = \dfrac{(400 \text{ kJ mol}^{-1})}{(0.2 \text{ kJ } K^{-1}\text{mol}^{-1})} = 2000 \ K$$

Thus, reaction will be in a state of equilibrium at 2000 K and will be spontaneous above this temperature.

Q18. *For the reaction; $2Cl(g) \longrightarrow Cl_2(g)$; what will be the signs of ΔH and ΔS?*

Ans. ΔH : negative (– ve) because energy is released in bond formation

ΔS : negative (– ve) because entropy decreases when atoms combine to form molecules.

Q19. *For the reaction*

$$2A(g) + B(g) \longrightarrow 2D(g)$$
$$\Delta U^{\ominus} = -10.5 \text{ kJ and } \Delta S^{\ominus} = -44.1 \text{ Jk}^{-1}$$

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

Ans.
$$\Delta H^{\ominus} = \Delta U^{\ominus} + \Delta^{ng}RT$$
$$\Delta U^{\ominus} = -10.5 \text{ kJ}; \quad \Delta^{ng} = 2 - 3 = -1 \text{ mol}$$
$$R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}; T = 298 \text{ K}$$
$$\therefore \quad \Delta H^{\ominus} = (-10.5 \text{ kJ}) + [(-1 \text{ mol}) \times (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298\text{K})]$$
$$= -10.5 \text{ kJ} - 2.478 \text{ kJ} = -12.978 \text{ kJ}$$

According to Gibbs Helmholtz equation:
$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$
$$\Delta G^{\ominus} = (-12.978 \text{ kJ}) - (298 \text{ K}) \times (-0.0441 \text{ kJ K}^{-1})$$
$$= -12.978 + 13.112 = -12.978 + 13.142 = \textbf{0.164 kJ}$$

Since $\Delta G^{\ominus}$ is positive, the reaction is non-spontaneous in nature.

Q20. *The equilibrium constant for the reaction is 10. Calculate the value of $\Delta G^{\ominus}$; Given*

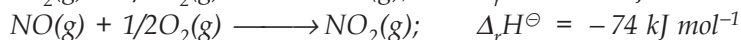$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}; T = 300 \text{ K}.$$

Ans.
$$\Delta G^{\ominus} = -RT \ln K = -2.303 \ RT \log K.$$
$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}; T = 300 \text{ K}; K = 10$$
$$\Delta G^{\ominus} = -2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times (300 \text{ K}) \times \log 10$$
$$= -5527 \text{ J mol}^{-1} = \textbf{–5.527 kJ mol}^{-1}.$$

Q21. *Comment on the thermodynamic stability of $NO(g)$ and $NO_2(g)$ given: :*

$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO(g); \qquad \Delta_r H^{\ominus} = 90 \text{ kJ mol}^{-1}$$
$$NO(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO_2(g); \qquad \Delta_r H^{\ominus} = -74 \text{ kJ mol}^{-1}$$

Ans. For NO (g) ; $\Delta_r H^{\ominus}$ = + ve : Unstable in nature

For NO_2 (g) ; $\Delta_r H^{\ominus}$ = – ve : Stable in nature

Q22. *Calculate the entropy change in surroundings when 1.0 mol of $H_2O(l)$ is formed under standard conditions. Given $\Delta H^{\ominus} = -286$ kJ mol^{-1}.*

Ans.
$$q_{rev} = (-\Delta_f H^{\ominus}) = -286 \text{ kJ mol}^{-1} = 286000 \text{ J mol}^{-1}$$

$$\Delta S_{(Surroundings)} = \frac{q_{rev}}{T} = \frac{(286000 \text{ J mol}^{-1})}{298 \text{ K}} = \textbf{959 J K}^{-1} \textbf{ mol}^{-1}.$$

MORE QUESTIONS SOLVED

I. VERY SHORT ANSWER TYPE QUESTIONS

Q1. *If $\Delta U = 0$ how are q and w related to each other?*

Ans. $\Delta U = q + w$

Q2. *When is bond energy equal to bond dissociation energy?*

Ans. For diatomic molecules e.g. H_2, O_2, Cl_2 etc. both energies are equal.

Q3. *What is the enthalpy of formation of the most stable form of an element in its standard state?*

Ans. It is zero.

Q4. *Out of diamond and graphite, which has greater entropy?*

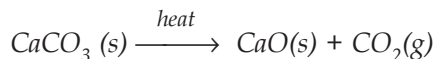**Ans.** Graphite has greater entropy since it is loosely packed.

Q5. *At what temperature entropy of a substance is zero?*

Ans. At absolute zero.

Q6. *From thermodynamic point of view, to which system the animals and plants belong?*

Ans. Open system.

Q7. *Predict the sign of ΔS for the following reaction*

$$CaCO_3 \text{ (s)} \xrightarrow{\text{heat}} CaO(s) + CO_2(g)$$

Ans. ΔS is positive.

Q8. *State Hess's law.*

Ans. The change of enthalpy of a reaction remains same whether the reaction is carried out in one step or several steps.
$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 - - -$$

Q9. *What is the enthalpy change for an adiabatic process?*

Ans. For an adiabatic process,
$$\Delta H = 0$$

Q10. *What do you mean by entropy?*

Ans. Entropy is a measure of randomness of a system.

Q11. *Give a relation between entropy change and heat absorbed or evolved for a reversible reaction occurring at temperature T.*

Ans. $$\Delta s = \frac{q_{rev}}{T}$$

Q12. *What is the condition for spontaneity in terms of free energy change?*

Ans. If ΔG is negative, process is spontaneous.
If ΔG is positive, the process is non-spontaneous.
If $\Delta G = 0$, the process is in equilibrium.

Q13. *What is an adiabatic process?*

Ans. The process in which no exchange of heat takes place between the system and the surroundings.

Q14. *What is free energy in terms of thermodynamics?*

Ans. Free energy of a system is the capacity to do work.

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

Q15. *Define extensive properties.*

Ans. Properties which depend upon the amount of the substance are called as extensive properties.

Q16. *How are internal energy change, free energy change and entropy change are related to one another?*

Ans. $\Delta G = \Delta H - T\Delta S$ (At constant pressure)

Q17. *How is entropy of a substance related to temperature?*

Ans. On increasing temperature, entropy of a substance increases.

Q18. *Define intensive properties.*

Ans. Properties which depend on the nature of the substance and not on the amount of the substance are called intensive properties.

Q19. *What is Gibbs Helmholtz equation?*

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

Where ΔG = free energy change.

ΔH = enthalpy change.

ΔS = entropy change.

Q20. *What are the units of entropy?*

Ans. SI unit of $\Delta S = JK^{-1}\,mol^{-1}$.

**Q21.** *What is a spontaneous change? Give one example.*

Ans. A process which can take place of its own or initiate under some condition.

For example: Common salt dissolves in water of its own.

II. SHORT ANSWER TYPE QUESTIONS

Q1. *When liquid benzene is oxidised at constant pressure at 300 K, the change in enthalpy is −3728 kJ. What is the change in internal energy at the same temperature?*

Ans. The chemical equation representing the oxidation of liquid benzene is :

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$$
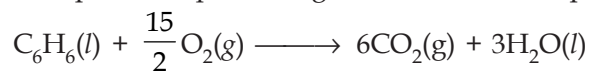
$$\Delta H = -3728kJ; \quad \Delta^{ng} = 6 - \frac{15}{2} = -\frac{3}{2}\ mol$$

$$R = 8.314 \times 10^{-3}\ kJ\ K^{-1}\ mol^{-1},\ T = 300\ K$$

According to the relation, $\Delta H = \Delta U + \Delta^{ng}RT$

$$(-3728\ kJ) = \Delta U + \left(-\frac{3}{2}mol\right)$$

$$\times (8.314 \times 10^{-3}\ kJ\ K^{-1}mol^{-1}) \times (300\ K)$$

$$(-3728\ kJ) = \Delta U - 3.7413\ kJ$$

$$\Delta U = -3728 + 3.7413 = \mathbf{-3724.2587\ kJ}$$

Q2. *The enthalpy of formation of methane at constant pressure and 300 K is − 78.84 kJ. What will be the enthalpy of formation at constant volume?*

Ans. The equation representing the enthalpy of formation of methane is:

$$C(s) + 2H_2(g) \longrightarrow CH_4(g); \quad \Delta H = -78.84\ kJ$$

$$\Delta H = 78.84\ kJ; \quad \Delta^{ng} = 1 - 2 = -1\ mol$$

$$R = 8.314 \times 10^{-3}\ kJ\ K^{-1}\ mol^{-1}; \quad T = 300\ K$$

According to the relation, $\Delta H = \Delta U + \Delta^{ng} RT$

$\Delta U = \Delta H - \Delta^{ng} RT$

$= (-78.84 \text{ kJ}) - (1 \text{ mol})$

$\times (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times 300\text{K}$

$= -78.84 - 2.49 = \mathbf{-81.35 \text{ kJ}}$

Q3. *Calculate the enthalpy change for the reaction: $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$. Given that bond energies of $H-H$, $Cl-Cl$ and $H-Cl$ bonds are 433, 244 and 431 kJ mol^{-1} respectively.*

Ans. The chemical equation for the reaction is:

$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

The enthalpy of reaction is:

$\Delta_r H = \Sigma\text{B.E. of reactants} - \Sigma\text{B.E. of products}$

$= [\text{B.E. of } H-H \text{ bond} + \text{B.E. of } Cl-Cl \text{ bond}]$

$- [2 \times \text{B.E. of } H-Cl \text{ bond}]$

$= (433 + 244) - (2 \times 431) = 433 + 244 - 862$

$= \mathbf{-185 \text{ kJ}}$

Q4. *The bond enthalpy of $H_2(g)$ is 436 kJ mol^{-1} and that of $N_2(g)$ is 941.3 kJ mol^{-1}. Calculate the average bond enthalpy of an $N-H$ bond in ammonia. Given: $\Delta_f H^{\ominus} (NH_3)$ $= -46$ kJ mol^{-1}*

Ans.
$$1/2 N \equiv N + 3/2\ H-H \longrightarrow \begin{array}{c} H \\ | \\ N-H \\ | \\ H \end{array}$$
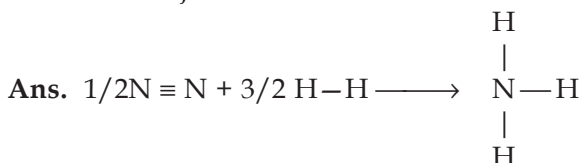
$\Delta_f H^{\ominus} (NH_3) = \text{BE of reactants} - \text{BE of products}$

$= [1/2\text{BE of the } N \equiv N \text{ bond} + 3/2 \text{ Be of } H-H \text{ bond}]$

$- [3 \text{ BE of } N-H \text{ bond}]$

$[-46 \text{ kJ mol}^{-1}] = (1/2 \times 941.3 \text{ kJ mol}^{-1} + 3/2 \times 436 \text{ kJ mol}^{-1})$

$- (3 \text{ BE of } N-H \text{ bond})$

BE of $N-H$ bond $= 1/3 (470.65 + 654.0 + 46) = \mathbf{390.2 \text{ kJ mol}^{-1}.}$

Q5. *When two moles of $C_2H_6(g)$ are burnt, 3129 kJ of heat is liberated. Calculate the heat of formation of $C_2H_6(g)$. $\Delta_f H$ for $CO_2(g)$ and $H_2O(l)$ are -393.5 and -286 kJ mol^{-1} respectively.*

Ans. The heat of combustion of $C_2H_6(g)$ per mole $(\Delta H) = \dfrac{-3129}{2} = -1564.5 \text{ kJ}.$

The combustion equation may be written as :

$$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l); \quad \Delta H = -1564.5 \text{ kJ}.$$
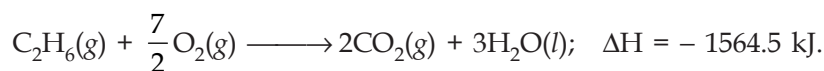
Now, $\Delta H = \Sigma\Delta_f H^{\ominus} (\text{products}) - \Sigma\Delta_f H^{\ominus} (\text{reactants})$

$= [2\Delta_f H^{\ominus} CO_2(g) + 3\Delta_f H^{\ominus} H_2O(l)]$

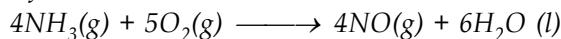$$- \left[\Delta_f H^{\ominus} C_2H_6(g) + \frac{7}{2}\Delta_f H^{\ominus} O_2(g)\right]$$

On substituting the values in the above equation

$-1564.5 = [2 \times (-393.5) + 3(-286)] - [\Delta_f H^{\ominus} C_2H_6(g) + \text{zero}]$

$-1564.5 = -787 - 858 - \Delta_f H^{\ominus} C_2H_6(g)$

or $\Delta_f H^{\ominus} C_2H_6(g) = -787 - 858 + 1564.5 = \mathbf{-80.5 \text{ kJ}.}$

Q6. *Calculate $\Delta G^{\ominus}$ for the reaction :*

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O \; (l)$$

Given that $\Delta_f G^{\ominus}$ for the formation of NH_3 (g), NO(g) and H_2O (l) are -16.8 kJ mol^{-1}, $+86.7$ kJ mol^{-1} and -237.2 kJ mol^{-1} respectively. Predict feasibility of reaction under the conditions.

Ans.
$$\Delta G^{\ominus} = \Sigma\Delta_f G^{\ominus}_{(products)} - \Sigma\Delta_f G^{\ominus}_{(reactants)}$$
$$= \{4 \text{ mol} \times 4_f G^{\ominus} \text{ NO } (g) + 6 \text{ mol} \times \Delta_f G^{\ominus} \text{ H}_2\text{O } (l)\}$$
$$- \{4 \text{ mol} \times \Delta_f G^{\ominus} \text{ NH}_3 \text{ (g) } + 5 \text{ mol} \times \Delta_f G^{\ominus} \text{ O}_2(g)\}$$
$$= [4 \text{ mol} \times (86.7 \text{ kJ mol}^{-1}) + 6 \times (-237.2 \text{ kJ mol}^{-1})]$$
$$- [4 \text{ mol} \times (-16.8 \text{ kJ mol}^{-1}) + 5 \times \text{zero}]$$
$$= (346.8 \text{ kJ} - 1423.2 \text{ kJ}) + 67.2 \text{ kJ} = -1009.2 \text{ kJ.}$$

Since $\Delta G^{\ominus}$ is negative, the reaction is feasible in the forward direction.

Q7. *Determine whether or not it is possible for sodium to reduce aluminium oxide to aluminium at 298 K.*

Given: $\Delta_f G^{\ominus} Al_2O_3(s) = -1582$ kJ mol^{-1}; $\Delta_f G^{\ominus} Na_2O$ (s) $= -377$ kJ mol^{-1}.

Ans. The reaction involved is

$$Al_2O_3(s) + 6Na(s) \longrightarrow 2Al(s) + 3Na_2O(s)$$
$$\Delta G^{\ominus} = \Sigma\Delta_f G^{\ominus} (p) - \Sigma\Delta_f G^{\ominus} (r)$$
$$= [2\Delta_f G^{\ominus} \text{ Al}(s) + 3\Delta_f G^{\ominus} \text{ Na}_2\text{O}(s)] - [\Delta_f G^{\ominus} \text{ Al}_2\text{O}(s) + 6\Delta_f G^{\ominus} \text{ Na}(s)]$$
$$= [2 \times 0 + 3 \times (-377)] - [-1582 + 6 \times 0]$$
$$= 451 \text{ kJ mol}^{-1}.$$

This means that sodium can not reduce aluminium oxide (Al_2O_3) to aluminium metal because $\Delta G^{\ominus}$ comes out to be positive.

Q8. *1 g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation C(graphite) + O_2(g) $\rightarrow$ CO_2 (g) During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm?*

Ans. Suppose q is the quantity of heat from the reaction mixture and C_v is the heat capacity of the calorimeter, then the quantity of heat absorbed by the calorimeter.

$$q = C_v \times \Delta T$$

Quantity of heat from the reaction will have the same magnitude but opposite sign because the heat lost by the system (reaction mixture) is equal to the heat gained by the calorimeter.

$$q = -C_v \times \Delta T = -20.7 \text{ kJ/ K} \times (299 - 298) \text{ K}$$
$$= -20.7 \text{ kJ}$$

(Here, negative sign indicates the exothermic nature of the reaction). Thus, ΔU for the combustion of the 1g of graphite $= -20.7$ kJ K^{-1}

For combustion of 1 mol of graphite,

$$= \frac{12.0\text{g mol}^{-1} \times (-20.7 \text{ kJ})}{1 \text{ g}}$$
$$= -2.48 \times 10^2 \text{ kJ mol}^{-1}. \quad \text{Since } \Delta ng = 0,$$
$$\Delta H = \Delta U = -2.48 \times 10^2 \text{ kJ mol}^{-1}$$

Q9. *Calculate $\Delta_r G^{\ominus}$ for conversion of oxygen to ozone, 3/2 O_2(g) $\rightarrow O_3$(g) at 298 K. If K_p for this conversion is 2.47×10^{-29}.*

Ans. We know $\Delta_r G^\ominus = -2.303\ RT \log K_p$

and $R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$

Therefore, $\Delta_r G^\ominus = -2.303\ (8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K})\ (\log 2.47 \times 10^{-29})$

$= 163000\ \text{J mol}^{-1} = 163\ \text{J mol}^{-1}$.

Q10. *Define the following:*

(i) *First law of thermodynamics.*

(ii) *Standard enthalpy of formation.*

Ans. (i) **First law of thermodynamics:** It states that energy can neither be created nor be destroyed. The energy of an isolated sytem is constant.

$$\Delta u = q + w$$

(ii) It is defined as the amount of heat evolved or absorbed when one mole of the compound is formed from its constituent elements in their standard states.

Q11. (a) *Why is the entropy of a substance taken as zero at 0K?*

(b) *Calculate ΔG and $\Delta G^\ominus$ for the reaction.*

$$A + B \rightleftharpoons C + D$$
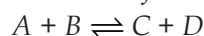
at 27°C. Equilibrium constant (K) for this reaction = 10^2

Ans. (a) From third law of thermodynamics, it can be explained that entropy of a perfectly crystalline substance is zero at zero kelvin.

(b) $\Delta G = 0$ (because the reaction is in equilibrium)

$\Delta G^\ominus = -2.303\ RT \log K$

$= -2.303 \times 8.314\ \text{JK}^{-1}\ \text{mol}^{-1} \times 300\ \text{K} \log 10^2$

$= -11.488\ \text{kJ mol}^{-1}$

Q12. *Give reason for the following:*

(a) *Neither q nor w is a state function but q + w is a state function.*

(b) *A real crystal has more entropy than an ideal crystal.*

Ans. (a) $q + w = \Delta U$

As ΔU is a state function hence, $q + w$ is a state function.

(b) A real crystal has some disorder due to the presence of defects in its structural arrangement whereas ideal crystal does not have any disorder. Hence, a real crystal has more entropy than an ideal crystal.

Q13. (a) *Under what condition, the heat evolved or absorbed in a reaction is equal to its free energy change?*

(b) *Calculate the entropy change for the following reversible process*

$$H_2O(s) \rightleftharpoons H_2O(l)\ \Delta_{fus}H\ \text{is 6.0 kJ mol}^{-1}$$

Ans. (a) $\Delta G = \Delta H - T\Delta S$

When the reaction is carried out at 0°k

or $\Delta S = 0$

$\Delta G = \Delta H$

(b) $H_2O(s) \rightleftharpoons H_2O(l)$

$\Delta_{fus}H = 6.0\ \text{kJ mol}^{-1}$

$= 6000\ \text{J mol}^{-1}$

$T_f = 0°C = (0 + 273) = 273\ \text{K}$

$$\Delta_{fus}S = \frac{\Delta_{fus}H}{T_f} = \frac{6000\ \text{J mol}^{-1}}{273\ \text{K}} = 21.98\ \text{J K}^{-1}\ \text{mol}^{-1}$$

III. LONG ANSWER TYPE QUESTIONS

Q1. (a) *What is a spontaneous process? Mention the conditions for a reaction to be spontaneous at constant temperature and pressure.*

(b) *Discuss the effect of temperature on the spontaneity of an exothermic reaction.*

Ans. (a) A process is said to be spontaneous if it takes place by itself by own or under some condition.

ΔG gives a criteria for spontaneity at constant temperature and pressure.

(b) If the temperature is so high that $T\Delta S > \Delta H$ in magnitude, ΔG will be positive and the process will be non-spontaneous.

If the temperature is made low so that $T\Delta S < \Delta H$ in magnitude, ΔG will be negative and the process will be spontaneous.

Q2. *Predict in which of the following, entropy increases/decreases.*

(i) *A liquid crystallizes into a solid*

(ii) *Temperature of a crystallize solid is raised from 0K to 115 K*

(iii) $2NaHCO_3 (s) \longrightarrow Na_2 CO_3 (s) + CO_2 (g) + H_2O (g)$

(iv) $H_2(g) \longrightarrow 2H(g)$

Ans. (i) After freezing, the molecules attain an ordered state and therefore, entropy decreases.

(ii) At 0K the constituent particles are in static form therefore, entropy is minimum. If the temperature is raised to 115 K particles begin to move and entropy increases.

(iii) Reactant, $NaHCO_3$ is solid. Thus, its entropy is less in comparison to product which has high entropy.

(iv) Here, one molecule gives two atoms. Thus, number of particles increases and this leads to more disordered form.

Q3. (a) *Why standard entropy of an elementary substance is not zero whereas standard enthalpy of formation is taken as zero?*

(b) *Under what conditions will the reaction occur, if*

(i) *both ΔH and ΔS are positive*

(ii) *both ΔH and ΔS are negative*

Ans. (a) A substance has perfectly ordered arrangement of its constituent particles only at absolute zero. When the element formed from itself, this means no heat change.

Thus, $\Delta_f H = 0$

(b) (i) If both ΔH and ΔS are positive ΔG can be – ve only if $T\Delta S > \Delta H$ in magnitude. Thus, the temperature should be high.

(ii) If both ΔH and ΔS are negative ΔG can be negative only if $T\Delta S < \Delta H$ in magnitude. Thus, the value of T should be low.

Q4. (a) *What is bond energy? Why is it called enthalpy of atomisation?*

(b) *Calculate the bond energy of $C-H$ bond, given that the heat of formation of CH_4, heat of sublimation of carbon and heat of dissociation of H_2 are*

-74.8, $+719.6$, 435.4 kJ mol^{-1} respectively.

Ans. (a) Bond energy is the amount of energy required to dissociate one mole of bonds present between the atoms in the gaseous phase. As the molecules dissociate completely into atoms in the gaseous phase therefore bond energy of a diatomic molecule is called enthalpy of atomisation.

(b)
$$C(s) + 2H_2(g) \rightarrow CH_4(g) \qquad \Delta_r H = -74.8 \text{ kJ} \qquad \text{...}(i)$$
$$C(s) \rightarrow C(g) \qquad \Delta_r H^\ominus = +719.6 \text{ kJ} \qquad \text{...}(ii)$$
$$H_2(g) \rightarrow 2H(g) \qquad \Delta_r H^\ominus = +435.4 \text{ kJ} \qquad \text{...}(iii)$$
$$C(s) + 2H_2(g) \rightarrow C(s) + 4H(g) \qquad \text{...}(iv)$$
$$C(s) + 2H_2(g) \rightarrow CH_4(g) \qquad \text{...}(v)$$

Subtract (v) from (iv) $0 = C(s) + 4H(g) - CH_4(g)$

$$\Delta_r H^\ominus = 719.6 + 2(435.4) - (-74.8)$$

or
$$CH_4(g) = C(s) + 4H(g)$$
$$\Delta H = +1665.2 \text{ kJ}$$
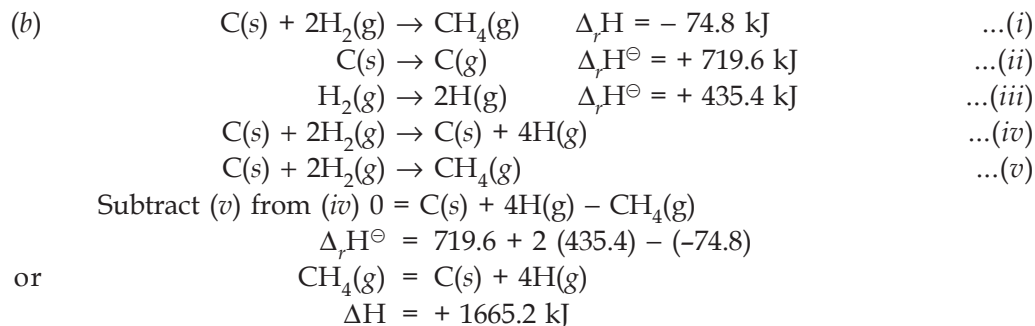
This gives the enthalpy of dissociation of four moles of C—H bonds (called enthalpy of atomisation)

Hence bond energy for C—H bond = $\dfrac{1665.2}{4}$ = 416.3 kJ mol^{-1}

IV. MULTIPLE CHOICE QUESTIONS

1. Thermodynamics is applicable to
(a) macroscopic system only
(b) microsopic system only
(c) homogeneous system only
(d) heterogeneous system only

2. An isochoric process takes place at constant
(a) temperature
(b) pressure
(c) volume
(d) concentration

3. For a cyclic process, the change in internal energy of the system is
(a) always +ve
(b) equal to zero
(c) always −ve
(d) none of the above

4. Which of the following properties is not a function of state?
(a) concentration
(b) internal energy
(c) enthalpy
(d) entropy

5. Which of the following relation is true?
(a) $C_p > C_v$
(b) $C_v > C_p$
(c) $C_p = C_v$
(d) $C_p = C_v = 0$

6. Which of the following always has a negative value?
(a) heat of reaction
(b) heat of solution
(c) heat of combustion
(d) heat of formation

7. The bond energy depends upon
(a) size of the atom
(b) electronegativity
(c) bond length
(d) all of the above

8. For an endothermic reaction.
(a) ΔH is −ve
(b) ΔH is +ve
(c) ΔH is zero
(d) none of these

9. The process depicted by the equation.
$$H_2O(s) \longrightarrow H_2O(l)$$
$\Delta H = +1.43$ kcal represents
(a) fusion
(b) melting
(c) evaporation
(d) boiling

10. Which one is the correct unit for entropy?

(a) KJ mol $\qquad$ (b) JK^{-1} mol

(c) JK^{-1} mol^{-1} $\qquad$ (d) KJ mol^{-1}

Ans.

| 1. (a) | 2. (c) | 3. (b) | 4. (a) | 5. (a) |
| 6. (c) | 7. (d) | 8. (b) | 9. (a) | 10. (c) |

V. HOTS QUESTIONS

Q1. *Why standard entropy of an elementary substance is not zero whereas standard enthalpy of formation is taken as zero?*

Ans. A substance has a perfectly ordered arrangement only at absolute zero. Hence, entropy is zero only at absolute zero. Enthalpy of formation is the heat change involved in the formation of one mole of the substance from its elements. An element formed from its constituents means no heat change.

Q2. *The equilibrium constant for a reaction is one or more if $\Delta G^{\ominus}$ for it is less than zero. Explain.*

Ans. $\Delta_r G^{\ominus}$ = –RT InK, thus if $\Delta G^{\ominus}$ is less than zero *i.e.*, it is negative, then InK will be positive and hence K will be greater than one.

Q3. *Many thermodynamically feasible reactions do not occur under ordinary conditions. Why?*

Ans. Under ordinary conditions, the average energy of the reactants may be less than threshold energy. They require some activation energy to initiate the reaction.

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