# THERMODYNAMICS

- Internal energy
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- Intensive properties
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- Close, open and isolated systems
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- System and surroundings
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- Hess's law
- ΔH
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- Standard states for ΔH
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- Energy changes by work and heat
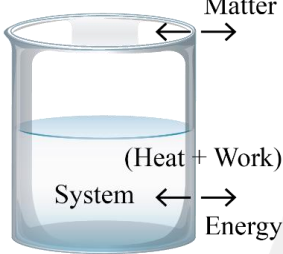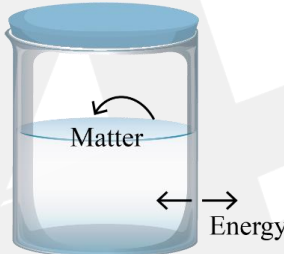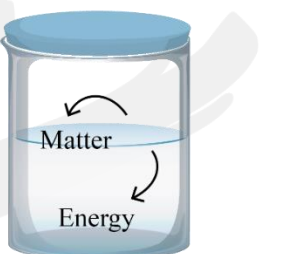- Non - spontaneous processes
- Spontaneous processes
- Entropy

# Thermodynamics

## 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.

### Universe = System + Surroundings

| Open System | Closed System | Isolated System |
|---|---|---|
| The is **exchange of energy and matter** between system and surroundings. | There is no exchange of matter but **exchange of energy** is possible between system and surroundings. | There is **no exchange** of energy or matter between the system and surroundings. |
| The presence of reactants in an **open vessel**. | The presence of reactants in a **closed vessel**. | The presence of reactants in a **closed insulated vessel**. |

**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:** 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 a 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 U which may change, when

- Heat passes into or not 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 temperature as $T_A$, Internal energy = $U_A$

On doing some mechanical work the new state is called state B and the temperature $T_B$, Internal energy = $U_B$

It is found that $T_B > T_A$.

$\therefore \quad \Delta T = T_B - T_A \quad ; \quad \Delta U = U_B - U_A$

$\therefore \quad \Delta U = U_2 - U_1 = W_{ad} \quad$ (where $W_{ad}$ is the adiabatic work)

## 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 form system to surroundings.
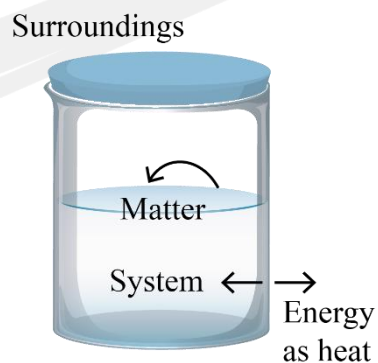
When change of state is done both by doing work and transfer of heat.

Surroundings



Matter

System ← →

Energy
as heat

A system which allows heat transfer through its boundary.

$\Delta u = q + w$

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.

$\Delta u = q + w$.

**Q.** Express the change in internal energy of a system when
(i) No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have?
(ii) No work is done on the system, but q amount of heat is taken out from the system and given to the surroundings. What type of wall does the system have?
(iii) w amount of work is done by the system and q amount of heat is supplied to the system. What type of system would it be?

**Sol:** (i) $\Delta U = w_{ad}$, wall is adiabatic
(ii) $\Delta U = -q$, thermally conducting walls
(iii) $\Delta U = q - w$, closed system.

*(Practice Questions in the end. Q. 1, 2.)*

## APPLICATION

### (A) Work (Pressure-volume Work)

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

Initial volume of gas = $V_i$

Pressure of gas = p

External pressure = $p_{ex}$     ($p_{ex} > p$)

Now, the piston is moved inward till the pressure inside becomes equal to $p_{ex}$.

Final volume of gas = $V_f$.

During this compression, the piston moves a distance = $l$.

With a cross-sectional area of the piston = A

∴     volume change = $l \times A = \Delta V$......... (1)
      ($\Delta V = V_f - V_i$)

∵     pressure = force / area

∴     force on the piston = $\mathbf{p_{ex} \times A}$
    ....... (2)

Now, w = force × displacement

    = $\mathbf{p_{ex} \times A} \times l$     (from 2)

    = $p_{ex} \times (-\Delta V)$     (from 1)

    = $- p_{ex} \times \Delta V$

    = $- p_{ex} \times (V_f - V_i)$
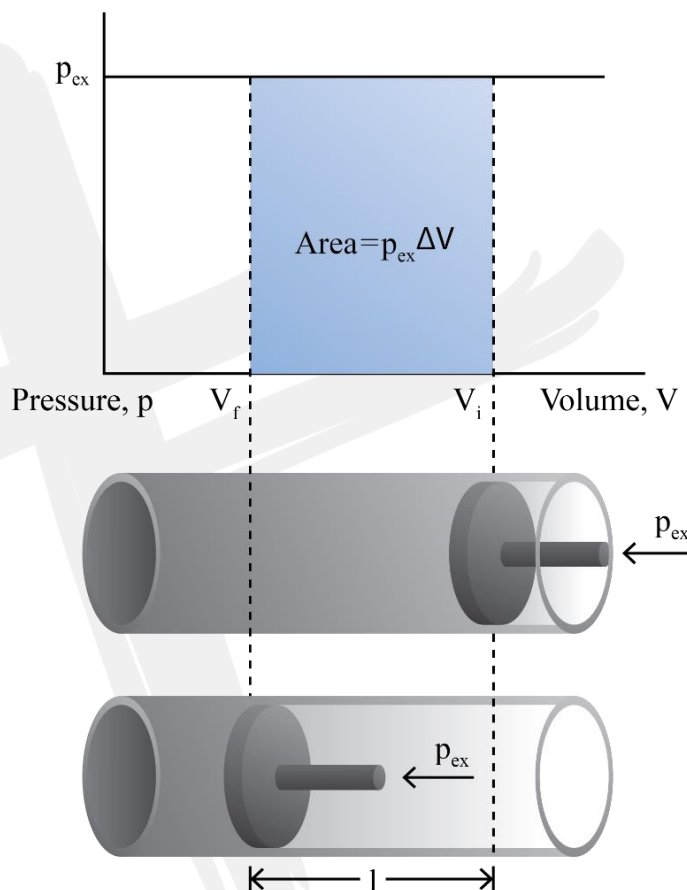


### Note

The negative sign of this expression is required to obtain conventional sign for w, which will be positive. In case of compression work is done on the system.

Where ($\Delta V$) or ($V_f - V_i$) will be always negative.

Since, negative × negative = positive

∴     sign obtained for work is positive.

If the pressure is not constant at every stage of compression, but changes in number of finite steps, work done on the gas will be summed over all the steps and will be equal to $-\sum p \Delta V$.

In such a case we can calculate the work done on the gas by the relation

$$w = -\int_{V_i}^{V_f} p_{ex}\, dV$$

In an expansion process under similar conditions, the external pressure is always less than the pressure of the system i.e., $p_{ex} = (p_{in} + dp)$.

In general case we can write, $p_{ex} = (p_{in} \pm dp)$.

Such processes are called **reversible processes**.

The expression of reversible work can be return as

$$w_{rev} = -\int_{V_i}^{V_f} p_{ex}\, dV = -\int_{V_i}^{V_f} (p_{in} \pm dp)\, dV$$

Since $dp \times dV$ is very small we can write

$$w_{rev} = -\int_{V_i}^{V_f} p_{ex}\, dV$$

Now, the pressure of the gas ($p_{in}$ which we can write as p now) can be expressed in terms of its volume through gas equation. For n mol of an ideal gas i.e., $pV = nRT$
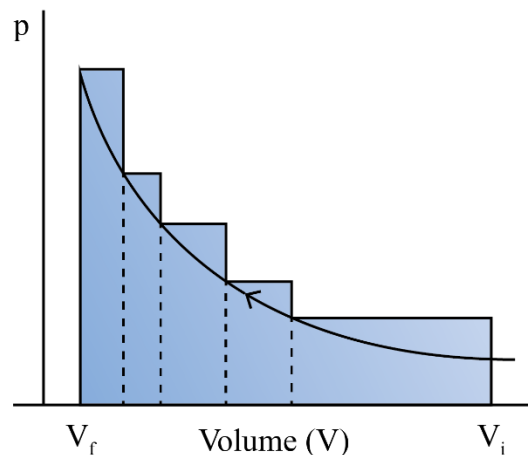
$$\Rightarrow p = \frac{nRT}{V}$$

Therefore, at constant temperature (isothermal process),

$$w_{rev} = -\int_{V_i}^{V_f} pRT\frac{dV}{V} = -nRT\int_{V_i}^{V_f} \frac{dV}{V}$$

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

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

$$= -2.303\, nRT \log \frac{V_2}{V_1} \qquad (\text{If } V_i = V_1 \text{ and } V_f = V_2)$$

## Free expansion

Expansion of a gas in vacuum ($p_{ex} = 0$) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible.

Now, we can write equation in number of ways depending on the type of processes.

Let us substitute $w = -p_{ex}\Delta V$ and we get

$$\Delta U = q - p_{ex}\,\Delta V$$

If a process is carried out at constant volume ($\Delta V = 0$), then

$$\Delta U = q_v$$

The subscript v in $q_v$ denotes that heat is supplied constant volume.

**Q.** Two litres of an ideal gas at a pressure of 10 atm expands isothermally at 25°C into a vaccum until its total volume is 10 litres. How much heat is absorbed and how much work is done in the expansion?

**Sol.** We have $q = -w = p_{ex}(10 - 2) = 0(8) = 0$

No work is done; no heat is absorbed.

## Work Done in Isothermal and Reversible Expansion of Ideal Gas

## Isothermal and Free Expansion of an Ideal Gas

For isothermal (T = constant) expansion of an ideal gas into vacuum ; $w = 0$ since $p_{ex} = 0$.
Also, Joule determined experimentally that $q = 0$ ; therefore, $\Delta V = 0$.
Equation 6.1, $\Delta V = q + w$ can be expressed for isothermal irreversible and reversible changes as follows:
1. For isothermal irreversible change $q = -w = p_{ex}(V_f - V_i)$
2. For isothermal reversible change

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

3. For adiabatic change, $q = 0$,

$$\Delta U = w_{ad}$$

## 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, $H = U + PV$

**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),

$\Delta H$ and $q_p$ both are **negative**.

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

$\Delta H$ and $q_p$ both are **positive**.

**Relation between $\Delta H$ and $\Delta U$.**

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.

$\because \qquad H_A = U_A + pV_A$

and $\qquad H_B = U_B + pV_B$

$\therefore \qquad \Delta H = H_B - H_A$

$\qquad\qquad = (U_B + pV_B) - (U_A + pV_A)$

$\qquad \Delta H = \Delta U + p\Delta V \ (H_B - H_A)$

$\qquad \Delta H = \Delta U + p\Delta V$

At the constant pressure and temperature using ideal gas law,

$\qquad pV_A = n_A \ RT$ (For reactant A)

$\qquad pV_B = n_B \ RT$ (For product B)

Thus, $\quad pV_B - pV_A = n_B \ RT - n_A RT$

$\qquad\qquad\qquad = (n_B - n_A) \ RT$

$\qquad p\Delta V = \Delta n_g \ RT$

$\qquad \Delta H = \Delta U + \Delta n_g \ RT$

**Q.** If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1bar and 100°C is 41kJ mol$^{-1}$. Calculate the internal energy change, when 1 mol of water is vapourised at 1 bar pressure and 100°C.

**Sol.** (i) The change $H_2O$ ($l$) $\rightarrow$ $H_2O$ (g)

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

or $\Delta U = \Delta H - \Delta n_g RT$, substituting the values, we get

$\Delta U = 41.00 \text{ kJ mol}^{-1} - 1 \times 8.3 \text{ J mol}^{-1}\text{K}^{-1} \times 373 \text{ K}$

$= 41.00 \text{ kJ mol}^{-1} - 3.096 \text{ kJ mol}^{-1}$

$= 37.904 \text{ kJ mol}^{-1}$ \qquad\qquad *(Practice Questions in the end. Q. 4.)*

**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 = $ coeff. $\text{x } \Delta T$

$q = C\Delta T$

Where, coefficient C is called the heat capacity.

C is directly proportional to the amount of substance.

$C_m = C/n$

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 = $ mass of the substance

$\Delta T = $ 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 $\Delta H$ and $\Delta u$, 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**

## Measurement of ΔU and ΔH : Calorimetry

We can measure energy changes associated with chemical or physical processes by an experimental technique called calorimetry.

In calorimetry, the process is carried out in a vessel called calorimeter, which is immersed in a known volume of liquid.

Knowing the heat capacity of the liquid in which calorimeter is immersed and the heat capacity of calorimeter, it is possible to determine the heat evolved in the process by measuring temperature changes.

Measurements are made under two different conditions.

(i) at constant volume, $q_v$

(ii) at constant pressure, $q_p$

### (a) ΔU Measurements

For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter. Here, a steel vessel (the bomb) is immersed in a water bath.

The whole device is called calorimeter. The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings.
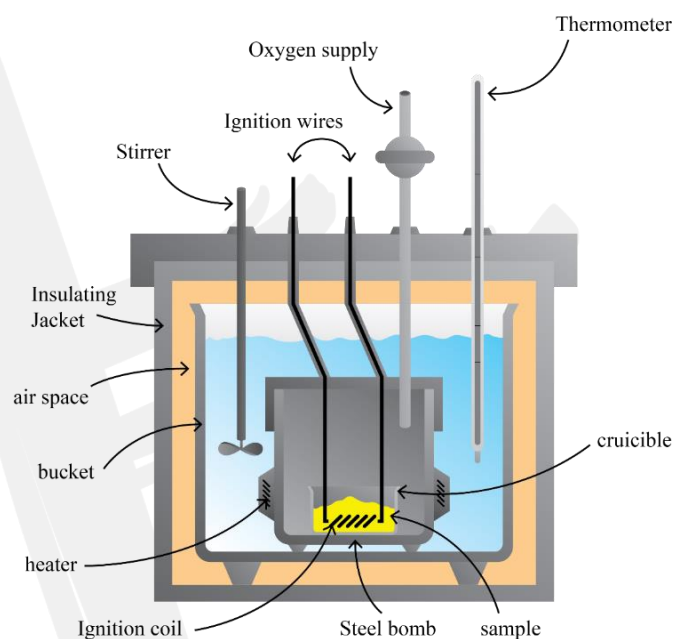


A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored.

Since the bomb calorimeter is sealed, its volume does not change i.e., the energy changes associated with reactions are measured at constant volume.

Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter.

Even for reactions involving gases, there is no work done as $\Delta V = 0$. Temperature change of the calorimeter produced by the completed reaction is then converted to $q_v$.

## (b) ΔH Measurements

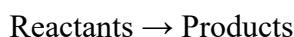Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a calorimeter.

We know that $\Delta H = q_p$ (at constant p) and, therefore, heat absorbed or evolved, qp at constant pressure is also called the heat of reaction or enthalpy of reaction, $\Delta_r H$.

In an exothermic reaction, heat is evolved, and system loses heat to the surroundings. Therefore, $q_p$ will be negative and ΔrH will also be negative.

Similarly, in an endothermic reaction, heat is absorbed, qp is positive and $\Delta_r H$ will be positive.

### Enthalpy change $\Delta_r H$ of a reaction – Reaction enthalpy

In a chemical reaction, reactants are converted into products and is represented by,

Reactants → Products



Thermometer

Foamed polystyrene cup

Reaction mixture

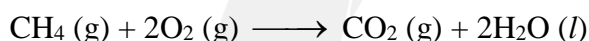Calorimeter for measuring heat changes at constant pressure (atmospheric pressure)

The enthalpy change accompanying a reaction is called the reaction enthalpy. The enthalpy change of a chemical reaction, is given by the symbol $\Delta_r H$

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

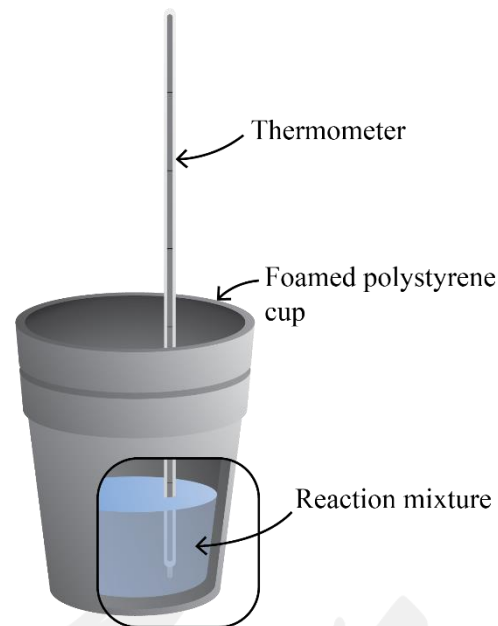$$= \sum_i a_i H_{products} - \sum_i b_i H_{reactants}$$

Here symbol $\Sigma$ (sigma) is used for summation and $a_i$ and $b_i$ are the stoichiometric coefficients of the products and reactants respectively in the balanced chemical equation. For example, for the reaction

$CH_4$ (g) + $2O_2$ (g) $\longrightarrow$ $CO_2$ (g) + $2H_2O$ (l)

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

$$= [H_m (CO_2, g) + 2H_m (H_2O, l)] - [H_m (CH_4, g) + 2H_m (O_2, g)]$$

where $H_m$ is the molar enthalpy.

**Q.** 1g 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) → $CO_2$ (g)
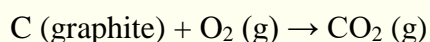
During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7 kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm?

**Sol.** Suppose q is the quantity of heat from the reaction mixture and CV 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, $\Delta U$ for the combustion of the 1 g of graphite $= -20.7 \text{ kJK}^{-1}$.

For combustion of 1 mol of graphite,

$$= \frac{12.0 \text{ g mol}^{-1} \times (-20.7\text{kJ})}{1\text{g}}$$

$= -2.48 \times 10^2 \text{ kJ mol}^{-1},$      Since $\Delta n_g = 0,$      *(Practice Questions in the end. Q. 5, 6.)*

$\Delta H = \Delta U = -2.48 \times 10^2 \text{ kJ mol}^{-1}$

## (a) Standard Enthalpy of Reactions

The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substance are in their standard states.

The standard state of a substance at a specified temperature is its pure form at 1 bar.

## (b) 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.

$$H_2O \text{ (s)} \longrightarrow H_2O \text{ (l)} ; \Delta_{fus} H^{\ominus} = 6.00 \text{ kJ mol}^{-1}$$
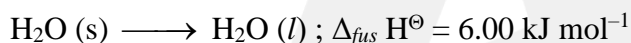
**Enthalpy of vaporisation:** It is defined as the heat energy or change in enthalpy when one mole of a liquid at its boiling point changes to gaseous state.

$$H_2O \text{ (l)} \longrightarrow H_2O \text{ (g)} ; \Delta_{vap} H^{\ominus} = +40.79 \text{ kJ mol}^{-1} \Delta_{vap} H^{\ominus}$$

**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.

## 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.

$\Delta H_r^o$ (298.15 K) and $\Delta G_r^o$ (298.15 K)

$\Delta G_r^o$ (T)

$\Delta H_r^o$ (T) and $K_p$ (298.15 K)

$K_p$ (T$_1$) and Kp (T$_2$) where T$_1$, T$_2 \neq$ T

$\Delta H_r^o$ (T) and $\Delta G_r^o$ (298.15 K)

**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.

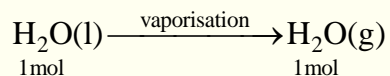$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \Delta H^{\circ} = -283 \text{ kJ}$$
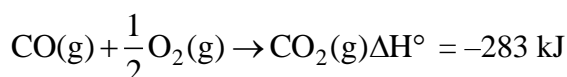
**Q.** A swimmer coming out from a pool is covered with a film of water weighing about 18g. How much heat must be supplied to evaporate this water at 298 K ? Calculate the internal energy of vaporisation at 298K.

$\Delta_{vap} H^\ominus$ for water

At 298K = 44.01 kJ mol$^{-1}$

**Sol.** We can represent the process of evaporation as

$$\underset{1\,mol}{H_2O(l)} \xrightarrow{\text{vaporisation}} \underset{1\,mol}{H_2O(g)}$$

No. of moles in 18 g $H_2O$ (l) is

$$= \frac{18g}{18\,g\,mol^{-1}} = 1\ mol$$

Heat supplied to evaporate 18g water at 298K = $n \times \Delta_{vap} H^\ominus$

$$= (1\ mol) \times (44.01\ kJ\ mol^{-1})$$

$$= 44.01\ kJ$$

(assuming steam behaving as an ideal gas).

$\Delta_{vap} U = \Delta_{vap} H^\ominus - p\Delta V = \Delta_{vap} H^\ominus - \Delta n_g RT$

$\Delta_{vap} H^v - \Delta n_g RT = 44.01$ kJ

$- (1)\ (8.314\ JK^{-1}\ mol^{-1})\ (298K)\ (10^{-3}\ kJ\ J^{-1})$

$\Delta_{vap} H^v = 44.01$ kJ $- 2.48$ kJ

$$= 41.53\ kJ$$

## 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.

Thermochemical equations

A typical chemical equation is $S + O_2 \rightarrow SO_2$

It is called a "thermochemical equation" when we add information about $\Delta H$

$$S + O_2 \rightarrow SO_2 \quad \Delta H = -296.9\ kJ$$

If we change the equation, then the $\Delta H$ also changes

$$SO_2 \rightarrow S + O_2 \quad \Delta H = +296.9\ kJ$$

If the reaction is reversed the sign is reversed

Also, if numbers in the equation change, so will the amount of energy produced/absorbed:

$$2S + 2O_2 \rightarrow 2O_2 \quad \Delta H = -593.8\ kJ$$

Conventions regarding thermochemical equations

1. The coefficient in a balanced thermochemical equation refer to the number of moles of reactants and products involved in the reaction.
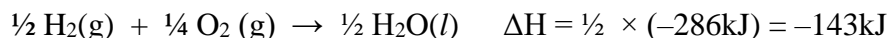
If the coefficients of the chemical equation are multiplied by some factor, the enthalpy change must also be multiplied by that same factor **(ΔH is an extensive property)**.

$$H_2(g) + \tfrac{1}{2} O_2(g) \rightarrow H_2O(l) \qquad \Delta H = 2 \times (-286kJ) = -572kJ$$

**Multiply by a factor of two:**

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad \Delta H = 2 \times (-286kJ) = -572kJ$$

**Multiply by a factor of one-half:**

$$\tfrac{1}{2} H_2(g) + \tfrac{1}{4} O_2(g) \rightarrow \tfrac{1}{2} H_2O(l) \qquad \Delta H = \tfrac{1}{2} \times (-286kJ) = -143kJ$$
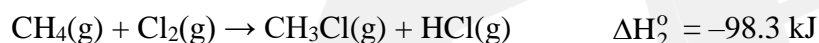
## Hess's Law of Constant Heat Summation

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. The Hess's law can also be stated as the enthalpy change for a chemical reaction is the same regardless of the path by which the reaction occurs.

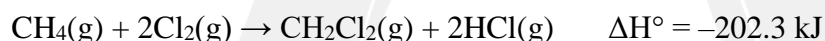For example, consider following two paths for the preparation of methylene chloride

**Path I:**

$$CH_4(g) + 2Cl_2(g) \rightarrow CH_2Cl(g) + 2HCl(g) \qquad \Delta H_1^o = -202.3 \text{ kJ}$$

**Path II:**

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g) \qquad \Delta H_2^o = -98.3 \text{ kJ}$$

$$CH_3Cl(g) + Cl_2(g) \rightarrow CH_2Cl_2(g) + HCl(g) \qquad \Delta H_3^o = -104.0 \text{ kJ}$$

Adding two steps

$$CH_4(g) + 2Cl_2(g) \rightarrow CH_2Cl_2(g) + 2HCl(g) \qquad \Delta H^\circ = -202.3 \text{ kJ}$$
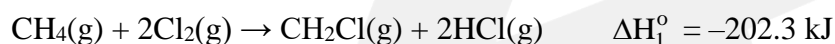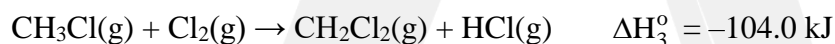
Thus, whether we follow path I or path II, the enthalpy change of the reaction is same.

$$\Delta H_1^o = \Delta H_2^o + \Delta H_3^o = 202.3 \text{ kJ}$$

## ENTHALPIES FOR DIFFERENT TYPES OF REACTIONS
### (a) Standard Enthalpy of Combustion (symbol : $\Delta_c H^\ominus$)

Standard enthalpy of combustion is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the **reactants and products** being in their standard states at the specified temperature.

Cooking gas in cylinders contains mostly butane ($C_4H_{10}$). During complete combustion of one mole of butane, 2658 kJ of heat is released. We can write the thermochemical reactions for this as:
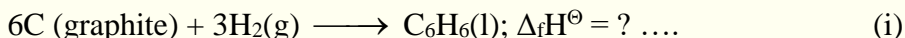
$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l); \Delta_c H^\ominus = -2658.0 \text{ kJ mol}^{-1}$$
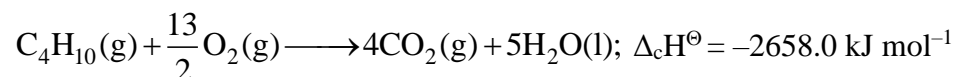
**Q.** The combustion of one mole of benzene takes place at 298 K and 1 atm. After combustion, $CO_2(g)$ and $H_2O$ (1) are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation, $\Delta_f H^\ominus$ of benzene. Standard enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are

–393.5 kJ mol$^{-1}$ and – 285.83 kJ mol$^{-1}$ respectively.

**Sol.** The formation reaction of benezene is given by :

6C (graphite) + 3H$_2$(g) $\longrightarrow$ C$_6$H$_6$(l); $\Delta_f H^\ominus$ = ? ....      (i)

The enthalpy of combustion of 1 mol of benzene is :

C$_6$H$_6$ (l) + $\dfrac{15}{2}$ O$_2$ $\longrightarrow$ 6CO$_2$ (g) + 3H$_2$O (l) ; $\Delta_c H^\ominus$ = –3267 kJ mol$^{-1}$ .... (ii)
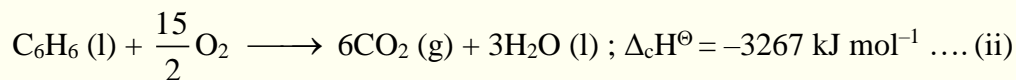
The enthalpy of formation of 1 mol of CO$_2$ (g) is :

C (graphite) + O$_2$ (g) $\longrightarrow$ CO$_2$ (g) ; $\Delta_f H^\ominus$ = –393.5 kJ mol$^{-1}$ .......      (iii)
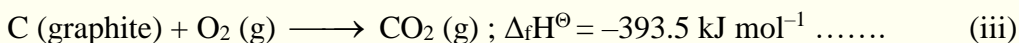
The enthalpy of formation of 1 mol of H$_2$O(l) is :

H$_2$ (g) + $\dfrac{1}{2}$ O$_2$ (g) $\longrightarrow$ H$_2$O (l) ; $\Delta_c H^\ominus$ = –285.83 kJ mol$^{-1}$ ....      (iv)
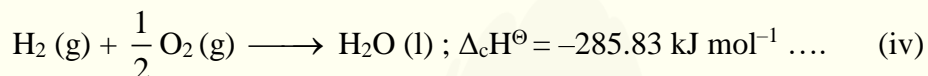
multiplying eqn. (iii) by 6 and eqn. (iv) by 3 we get:

6C (graphite) + 6O$_2$ (g) $\longrightarrow$ 6CO$_2$ (g) ; $\Delta_f H^\ominus$ = –2361 kJ mol$^{-1}$

3H$_2$ (g) + $\dfrac{3}{2}$ O$_2$ (g) $\longrightarrow$ 3H$_2$O (l) ; $\Delta_f H^\ominus$ = –857.49 kJ mol$^{-1}$
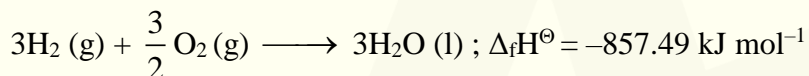
Summing up the above two equations :

6C (graphite) + 3H$_2$ (g) + $\dfrac{15}{2}$ O$_2$ (g) $\longrightarrow$ 6CO$_2$ (g) + 3H$_2$O (l) ; $\Delta_f H^\ominus$ = –3218.49 kJ mol$^{-1}$.....(v)

Reversing equation (ii);
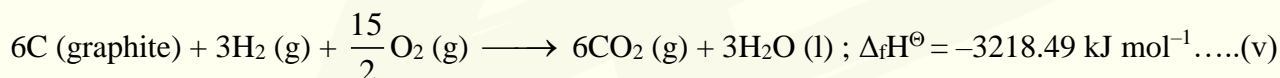
6CO$_2$ (g) + 3H$_2$O (l) $\longrightarrow$ C$_6$H$_6$ (l) + $\dfrac{15}{2}$ O$_2$ ; $\Delta_f H^\ominus$ = –3267.0 kJ mol$^{-1}$.....      (vi)
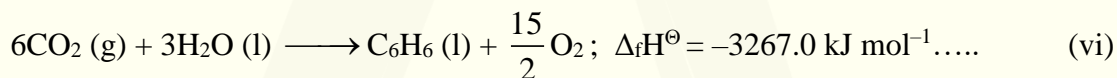
Adding equations (v) and (vi), we get

6C (graphite) + 3H$_2$ (g) $\longrightarrow$ C$_6$H$_6$ (l) ; $\Delta_f H^\ominus$ = –48.51 kJ mol$^{-1}$.....      (vii)
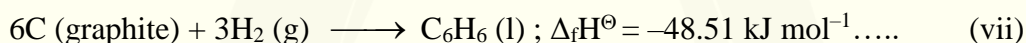
## (b) Enthalpy of Atomization (symbol: $\Delta_a H^\ominus$)

H$_2$ (g) $\longrightarrow$ 2H (g) ; $\Delta_a H^\ominus$ = 435.0 kJ mol$^{-1}$
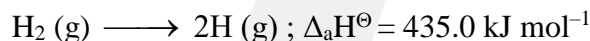
The enthalpy change in this process is known as enthalpy of atomization, $\Delta_a H^\ominus$. It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase.

## (c) Bond Enthalpy (symbol: $\Delta_{bond} H^\ominus$)

➤ Chemical reactions involve the breaking and making of chemical bonds. Energy is required to break a bond and energy is released when a bond is formed.

➤ It is possible to relate heat of reaction to changes in energy associated with breaking and making of chemical bonds. With reference to the enthalpy changes associated with chemical bonds, two different terms are used in thermodynamics.
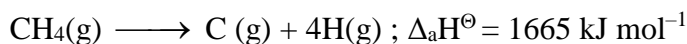
(i) Bond dissociation enthalpy

(ii) Mean bond enthalpy

**Diatomic Molecules**

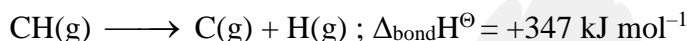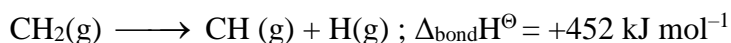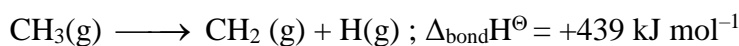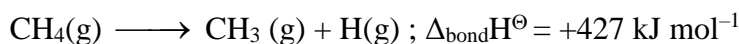H$_2$ (g) $\longrightarrow$ 2H (g) ; $\Delta_{H-H} H^\ominus$ = 435.0 kJ mol$^{-1}$

The bond dissociation enthalpy is the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gas phase.
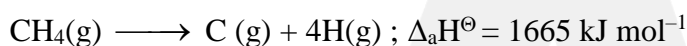
**Polyatomic Molecules**

$CH_4(g) \longrightarrow C(g) + 4H(g)$ ; $\Delta_a H^\Theta = 1665$ kJ mol$^{-1}$

In methane, all the four C – H bonds are identical in bond length and energy. However, the energies required to break the individual C – H bonds in each successive step differ :

$CH_4(g) \longrightarrow CH_3(g) + H(g)$ ; $\Delta_{bond} H^\Theta = +427$ kJ mol$^{-1}$

$CH_3(g) \longrightarrow CH_2(g) + H(g)$ ; $\Delta_{bond} H^\Theta = +439$ kJ mol$^{-1}$

$CH_2(g) \longrightarrow CH(g) + H(g)$ ; $\Delta_{bond} H^\Theta = +452$ kJ mol$^{-1}$

$CH(g) \longrightarrow C(g) + H(g)$ ; $\Delta_{bond} H^\Theta = +347$ kJ mol$^{-1}$

Therefore,

$CH_4(g) \longrightarrow C(g) + 4H(g)$ ; $\Delta_a H^\Theta = 1665$ kJ mol$^{-1}$

In such cases we use **mean bond enthalpy of C – H bond.**

For example in $CH_4$, $\Delta_{C-H} H^\Theta$ is calculated as:

$\Delta_{C-H} H^\Theta = \frac{1}{4} (\Delta_a H^\Theta) = \frac{1}{4} (1665$ kJ mol$^{-1})$

$= 416$ kJ mol$^{-1}$

### (d) Lattice Enthalpy

➤ The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

$Na^+Cl^-(s) \longrightarrow Na^+(g) + Cl^-(g)$ ; $\Delta_{lattice} H^\Theta = +788$ kJ mol$^{-1}$
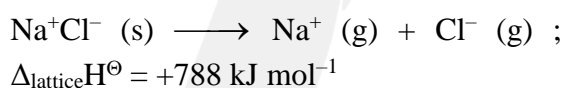
### Born-Haber Cycle

Since it is impossible to determine lattice enthalpies directly by experiment, we use an indirect method where we construct an enthalpy diagram called a **Born-Haber Cycle**.

Let us now calculate the lattice enthalpy of $Na^+Cl^-(s)$ by following steps given below :

1. $Na(s) \longrightarrow Na(g)$, sublimation of sodium metal, $\Delta_{sub} H^\Theta = 108.4$ kJ mol$^{-1}$

2. $Na(g) \longrightarrow Na^+(g) + e^{-1}(g)$, the ionization of sodium atoms, ionization enthalpy $\Delta_i H^\Theta = 496$ kJ mol$^{-1}$
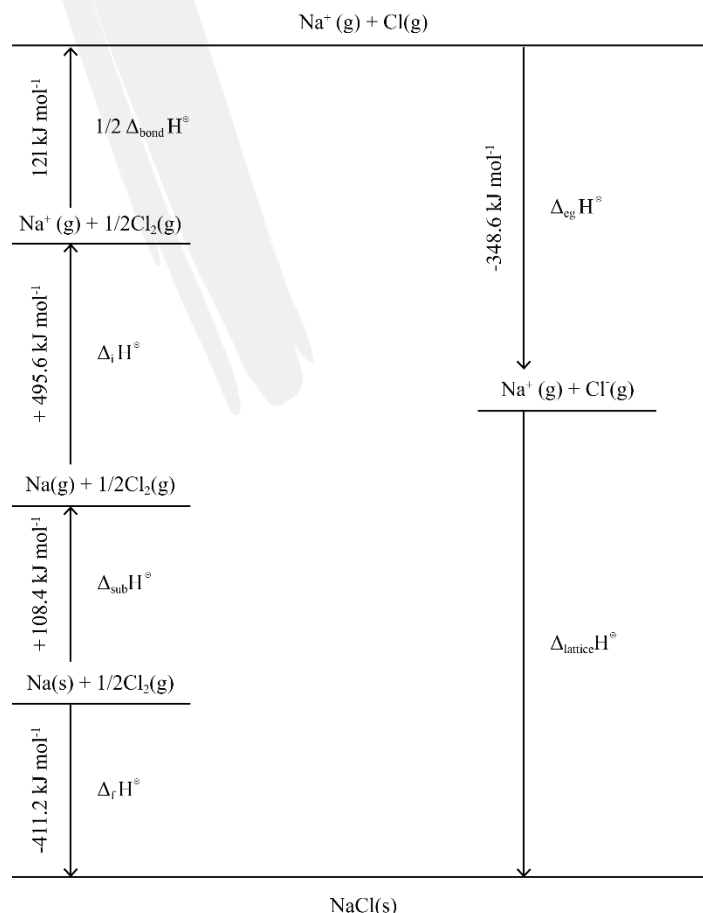
3. $\frac{1}{2} Cl_2(g) \longrightarrow Cl(g)$, the dissociation of chlorine, the reaction enthalpy is half the bond dissociation enthalpy. $\frac{1}{2}\Delta_{bond}H^{\ominus} = 121$ kJ mol$^{-1}$

4. $Cl(g) + e-1(g)$ $C\bar{l}$ (g) electron gained by chlorine atoms. The electron gain enthalpy, $\Delta_{eg}H^{\ominus} = -348.6$ kJ mol$^{-1}$.

   You have learnt about ionization enthalpy and electron gain enthalpy in Unit 3. In fact, these terms have been taken from thermodynamics. Earlier terms, ionization energy and electron affinity were in practice in place of the above terms (see the box for justification).

5. $Na^+(g) + Cl^-(g) \longrightarrow Na^+Cl^-$ (s)

   The importance of the cycle is that, the sum of the enthalpy changes round a cycle is zero. Applying Hess's law, we get,

   $\Delta_{lattice}H^{\ominus} = 411.2 + 108.4 + 121 + 496 - 348.6$
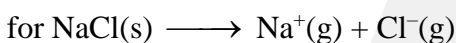
   $\Delta_{lattice}H^{\ominus} = + 788$kJ

   for NaCl(s) $\longrightarrow Na^+(g) + Cl^-(g)$

   Internal energy is smaller by 2RT (because $\Delta n_g = 2$) and is equal to +783 kJ mol$^{-1}$.

   Now we use the value of lattice enthalpy to calculate enthalpy of solution form the expression:

   $\Delta_{lattice}H^{\ominus} = 411.2 + 108.4 + 121 + 496 - 348.6$

   $\Delta_{lattice}H^{\ominus} = + 788$kJ

   for NaCl (s) $\longrightarrow Na^+(g) + Cl^-(g)$
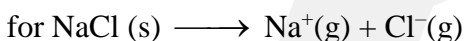
   Internal energy is smaller by 2RT (because $\Delta n_g = 2$) and is equal to +783 kJ mol$^{-1}$.

   Now we use the value of lattice enthalpy to calculate enthalpy of solution from the expression:

   $\Delta_{sol}H^{\ominus} = \Delta_{lattice}H^{\ominus} + \Delta_{hyd}H^{\ominus}$

   For one mole of NaCl(s),

   lattice enthalpy = + 788 kJ mol$^{-1}$ and $\Delta_{hyd}H^{\ominus} = -784$ kJ mol$^{-1}$ (from the literature)

   $\Delta_{sol}H^{\ominus} = + 788$ kJ mol$^{-1} - 784$ kJ mol$^{-1}$

   $\quad\quad = + 4$ kJ mol$^{-1}$

   The dissolution of NaCl(s) is accompanied by very little heat change.

**(e) Enthalpy of Solution (symbol : $\Delta_{sol}H^{\ominus}$ )**

Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent.

When an ionic compound dissolves in a solvent, the ions leave their ordered positions on the crystal lattice. These are now more free in solution. But solvation of these ions (hydration in case solvent is water) also occurs at the same time. This is shown diagrammatically, for an ionic compound, AB (s).



$$AB (s) \xrightarrow{\Delta_{sol}H^{\circ}} A^+ (aq) + B^- (aq)$$

$\Delta_{lattice}H^{\circ} \quad\quad\quad \Delta_{hyd}H^{\circ}$

$$A^+ (g) + B^- (g)$$
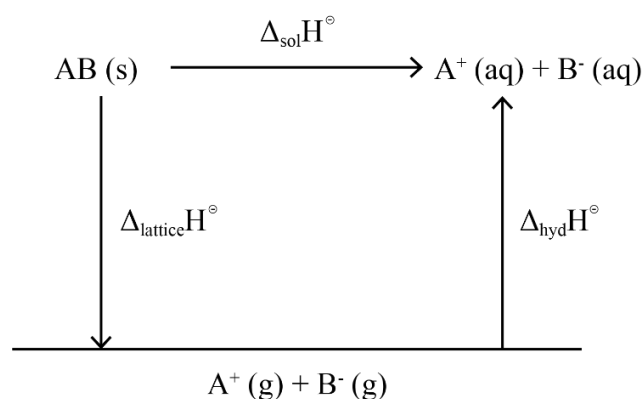
The enthalpy of solution of AB(s), $\Delta_{sol}H^{\ominus}$, in water is, therefore, determined by the selective values of the lattice enthalpy, $\Delta_{lattice}H^{\ominus}$ and enthalpy of hydration of ions, $\Delta_{hyd}H^{\ominus}$ as

$$\Delta_{sol}H^{\ominus} = \Delta_{lattice}H^{\ominus} + \Delta_{hyd}H^{\ominus}$$

**(f) Enthalpy of dilution**

The enthalpy change associated with the dilution process of a component in a solution at a constant pressure is known as enthalpy of dilution. It is defined as energy per unit mass or amount of substance.

## Second law of thermodynamics:

The state of entropy of the entire universe, as an isolated system will always increase over time, is the standard statement of the second law of thermodynamics.

➢ **Need**

The first law of thermodynamics states the conversion of energy in a process but does not explain the feasibility of the same. This point gave rise to the need for the second law of thermodynamics.

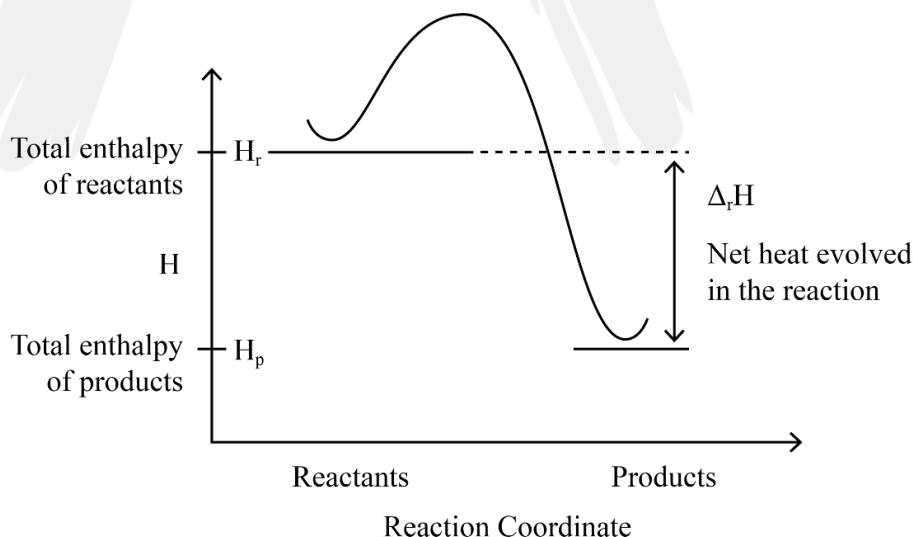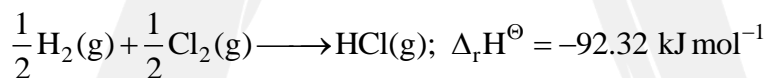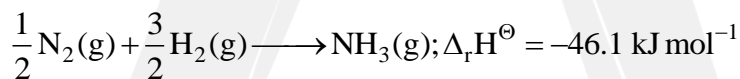## Types of processes:

➢ **Spontaneous process:**

The spontaneous process has the tendency to take place naturally and no external work is needed to carry out the same.

➢ **Non-spontaneous process:**

The non-spontaneous process is driven by external work and cannot be performed naturally.

**(a) Enthalpy change and spontaneity**

The microscopic objects proceed by decrease of energy to undergo a spontaneous process because state of lowest energy correspond to maximum stability. Similarly, chemical reactions which are exothermic in nature are spontaneous. For example

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g); \Delta_r H^{\ominus} = -46.1 \text{ kJ mol}^{-1}$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g); \ \Delta_r H^{\ominus} = -92.32 \text{ kJ mol}^{-1}$$



Now let us take another example

$$\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g); \ \Delta_r H^{\ominus} = +33.2 \text{ kJ mol}^{-1}$$

$$C(\text{graphite, S}) + 2S(l) \longrightarrow CS_2(l); \Delta_rH^{\ominus} = +128.5 \text{ kJ mol}^{-1}$$
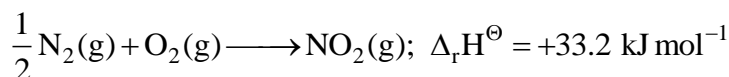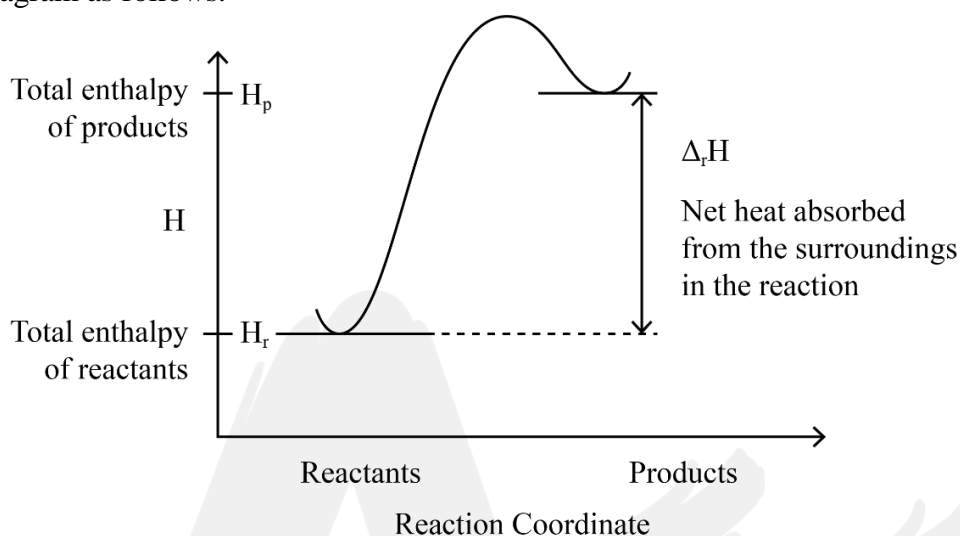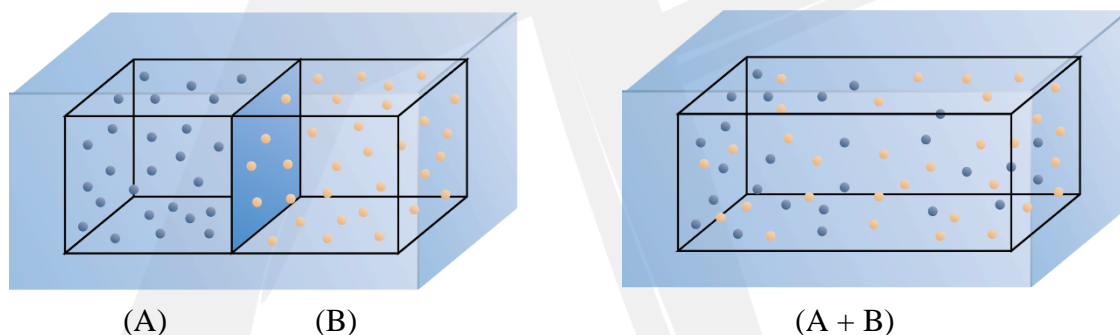
These reactions though endothermic are spontaneous. The decrease in enthalpy may be represented on enthalpy diagram as follows.



Reaction Coordinate

## (b) Entropy and spontaneity

Let us examine a case where $\Delta H = 0$ i.e., there is no change in enthalpy, but the process is still spontaneous.



(A)                (B)                                    (A + B)

Let us consider diffusion of two gases into each other in a closed container which is isolated from the surroundings as shown in the figure.

The two gases, say, gas A and gas B are represented by blue dots and yellow dots respectively and separated by a movable partition. When the partition is withdrawn, the gases begin to diffuse into each other and after a period of time, diffusion will be complete.

Let us examine the process. Before partition, if we were to pick up the gas molecules from left container, we would be sure that these will be molecules of gas A and similarly if we were to pick up the gas molecules from right container, we would be sure that these will be molecules of gas B. But, if we were to pick up molecules from container when partition is removed, we are not sure whether the molecules picked are of gas A or gas B.

Here we can say that intermixing of gases involves the increase in disorder or randomness of the system. Since every system has a tendency to attain a state of maximum stability, therefore a more disordered state may be related to more stability. Hence, the tendency of various systems to acquire a more random state may be responsible for the process.

In order to develop the criterion of spontaneity of spontaneity in terms of disorder or randomness an another thermodynamic function needs to be introduced which can be used to express disorder.

## Entropy:

As far as a chemical reaction is concerned, this entropy change can be attributed to rearrangement of atoms or ions from one pattern in the reactants to another (in the products). If the structure of the products is very much disordered than that of reactants, there will be a resultant increases in entropy.

Now let us try to quantity entropy by relating to the process to the heat involved in a process which could make entropy a thermodynamic concept. Entropy, like any other thermodynamic property such as internal energy U and enthalpy H, is a state function and $\Delta S$ is independent of path.

When the state of the system changes, the entropy also undergoes a change. This change in entropy, $\Delta S$ is $S_{final} - S_{initial}$ is defined as the ratio of heat absorbed by the system isothermally and reversibly to the temperature at which it is absorbed.

The measure of randomness or disorder in the process or a body is known as its entropy. It is a state function and is represented as S.

Spontaneous process is the process in which total randomness of the universe tends to increase. Thus,

$$\Delta S = \frac{Q_{rev}}{T}$$

For spontaneous change, $\Delta S_{Total} = \Delta S_{System} + \Delta S_{Surrounding} > 0$.

For reversible process where the entropy of the universe remains constant, Total $\Delta S_{Total} = 0$.

### Note

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

Specifically, it means that

If $\Delta S_{universe} > 0$, the reaction is spontaneous

If $\Delta S_{universe} < 0$, the reaction is non-spontaneous

If $\Delta S_{universe} = 0$, the reaction is reversible or is at equilibrium. The entropy of the system will remain constant. So, the total entropy change ($\Delta S_{total}$) for the system and surroundings of a spontaneous process is given by

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

When a system is in equilibrium, the entropy is maximum and the change in entropy, $\Delta S = 0$.

**Q.** Predict in which of the following, entropy increases/decreases :
  (i) A liquid crystallizes into a solid.
  (ii) Temperature of a crystalline solid is raised from 0 K to 115 K.
  (iii) $2NaHCO_3(s) \rightarrow Na_2CO_3 (s) + CO_2 (g) + H_2O(g)$    *(Practice Questions in the end. Q. 9.)*
  (iv) $H_2 (g) \rightarrow 2H (g)$

**Sol.** (i) After freezing, the molecules attain an ordered state and therefore, entropy decreases.
  (ii) At 0 K, the contituent particles are static and entropy is minimum. If temperature is raised to 115 K, these begin to move and oscillate about their equilibrium positions in the lattice and system becomes more disordered, therefore entropy increases.

(iii) Reactant, $NaHCO_3$ is a solid and it has low entropy. Among products there are one solid and two gases. Therefore, the products represent a condition of higher entropy.

(iv) Here one molecule gives two atoms i.e., number of particles increases leading to more disordered state. Two moles of H atoms have higher entropy than one mole of dihydrogen molecule.

**(c) Gibbs energy and spontaneity**

This gives us the most convenient parameter to judge the spontaneity of the process from the perspective of the system. At constant temperature it can be represented as;

$$\Delta G_{sys} = \Delta H - T\Delta S_{sys}$$

At constant temperature and pressure, $\Delta G = T\Delta S_{Total}$.

For process to be spontaneous, $\Delta G < 0$.

The decide the spontaneity of a process we have to consider the change in entropy of the system and surroundings which is not easy to be determined while dealing with chemical reactions. So, we need to introduce a function which could not only be applied to the system but could automatically take into account, the entropy change of surroundings i.e., it should be able to give the idea of spontaneity of process. We have seen that for a system, it is the total entropy change, $\Delta S_{total}$ which decides the spontaneity of the process. But most of the chemical reactions fall into the category of either closed systems or open systems. Therefore, for most of the chemical reaction sphere are changes in both enthalpy and entropy. Since neither decrease in enthalpy or increase in entropy alone can determine the direction of spontaneous change for these systems.

The new thermodynamic function is the Gibbs energy or Gibbs function G, as

$$G = H - TS$$

where, H = Enthalpy of the system, T = Temperature, S = Entropy of the system

We know that

$$H = U + PV$$

$$\therefore \quad G = U + PV - TS$$

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

$$\Delta G = \Delta U + \Delta(PV) - \Delta(TS)$$

If the process is carried out at constant pressure and constant temperature the terms $\Delta(PV)$ becomes $P\Delta V$ and $\Delta(TS)$ becomes $T\Delta S$. Thus, we can write

$$\Delta G_{sys} = \Delta U_{sys} + P\Delta V - T\Delta S_{sys}$$

At constant temperature ($\Delta T = 0$) and constant pressure ($\Delta P = 0$)

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

$$\therefore \quad \Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

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

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

This equation is known as Gibb;s Helmholtz equation. Gibbs equation is a very important equation in chemistry. Here we have considered both terms together for spontaneity energy (in terms of $\Delta H$) and entropy ($\Delta S$, a measure of disorder). Dimensionally, if analysed, we find that $\Delta G$ has units of energy because both $\Delta H$ and $T\Delta S$ are energy terms, since $T\Delta S = (K) (J/K) = J$.

## Gibbs energy change ($\Delta G$) and spontaneity

Let us now develop the criterion of spontaneity in terms of Gibb's energy change. As we know

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding} \qquad \ldots..(i)$$

Consider a process being carried out at constant temperature and constant pressure. Suppose heat equal to q is lost by the surroundings and gained by the system at temperature T. Then the entropy change of the surroundings is given by

$$\Delta S_{surr} = \frac{q_p}{T} \qquad \ldots…..(ii)$$

The negative sign indicates (before q) that heat has been lost by the surroundings. This lost heat by the surroundings is gained by the system at constant temperature and pressure, q represents its enthalpy change ($\Delta H$). Therefore

$$\Delta S_{surr} = \frac{-q_p}{T} = \frac{-\Delta H_{sys}}{T}$$

When this value is substituted in equation (i), we get

$$\Delta S_{total} = \Delta S_{sys} + \left( -\frac{\Delta H_{sys}}{T} \right)$$

Rearranging the above equation

$$T\Delta S_{total} = T\Delta S_{sys} - \Delta H_{sys}$$

or $\quad - T\Delta S_{total} = \Delta H_{sys} - T\Delta S_{sys}$

$$- T\Delta S_{total} = \Delta G_{sys} \qquad [\because \ \Delta G = \Delta H - T\Delta S] \qquad \ldots…..(iii)$$

For a spontaneous process, $\Delta S_{total} > 0$, so

$$T\Delta S_{sys} - \Delta H_{sys} > 0 \quad \Rightarrow \quad (\Delta H_{sys} - T\Delta S_{sys}) < 0$$

Using equation (i) the above equation can be written as

$$\Delta G < 0$$

$$\Delta G = \Delta H - T\Delta S < 0$$

Thus, for a process at a give temperature and pressure to be spontaneous the Gibbs energy of the system must decrease i.e., $\Delta G$ at constant temperature and pressure should be less than zero i.e., $\Delta G < 0$ i.e., negative.

ΔG is the net energy available to do useful work and is thus a measure of the 'free energy'. For this reason, it is also known as free energy of reaction.

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.

Summary of Gibbs energy criteria of spontaneity:

| Process | Sign of ΔS | Sign of ΔG |
|---|---|---|
| Spontaneous | Positive, $\Delta S_{total} > 0$ | Negative, $\Delta G < 0$ |
| Non-spontaneous | Negative, $\Delta S_{total} < 0$ | Positive, $\Delta G > 0$ |
| Equilibrium state | $\Delta S_{total} = 0$ | $\Delta G = 0$ |

Calculation of standard free energy of a reaction ($\Delta_r G°$) from standard free energies of formation ($\Delta_f G°$) of different reactants and products

$$\Delta_r G° = \sum \Delta_f G° \text{ (Products)} - \sum \Delta_f G° \text{ (Reactants)}$$

Relation between free energy change ($\Delta_r G$) and equilibrium constant (K) of a reaction

$$\Delta G = \Delta G° + RT \ln Q \text{ (Q = reaction quotient)}$$

At equilibrium, $\Delta G = 0$ and $Q = K$.

Hence, $\Delta G° = - RT \ln K$ or $\Delta G° = -2.303 \, RT \log K$

or $\qquad K = e^{- \Delta G° / RT}$ or $K = 10^{- \Delta G° / 2.303 \, RT}$.

Effect of temperature on the spontaneity of reaction:

| $\Delta_r H°$ | $\Delta_r S°$ | $\Delta_r G°$ | Description |
|---|---|---|---|
| − | + | − | Reaction spontaneous at all temperature |
| − | − | − (at low T) | Reaction spontaneous at low temperature |
| − | − | + (at high T) | Reaction non-spontaneous at high temperature |
| + | + | + (at low T) | Reaction non-spontaneous at low temperature |
| + | + | − (at high T) | Reaction spontaneous at high temperature |
| + | − | + (at all T) | Reaction non-spontaneous at all temperatures |

## Third law of thermodynamics:

The entropy of the system will approach a constant value as its temperature approaches absolute zero is the empirical statement of the third law of thermodynamics.

## Spontaneity

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

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

**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 $\Delta S$

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

$\Delta S$ = Overall Change in Entropy

$\Delta S_{system}$ = Change in Entropy of the system

$\Delta S_{surroundings}$ = Change in Entropy of the surroundings

$\Delta S > 0$, + entropy change, reaction is spontaneous

$\Delta S > 0$, – entropy change, reaction is nonspontaneous

Equation for the Total Change in Entropy

## 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 x entropy change $\Delta G$ gives a criteria for spontaneity at constant pressure and temperature, (i) If $\Delta G$ is negative ($< 0$) the process is spontaneous.

(ii) If $\Delta G$ is positive ($> 0$) the process is non-spontaneous.

Free Energy Change in Reversible Reaction

**Q.** 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 $2.47 \times 10^{-29}$.

**Sol.** We know $\Delta_r G^{\ominus} = -2.303\ RT \log K_p$ and R = 8.314 $JK^{-1}\ mol^{-1}$

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

= 163000 J $mol^{-1}$

= 163 kJ $mol^{-1}$.         *(Practice Questions in the end. Q. 10,11,12.)*

**Notes End**

# Ab Phod Do!

## Some Important Questions

**Q1.** Choose the correct answer. A thermodynamic state function is a quantity

(i) used to determine heat changes                          **[NCERT Exercise]**

(ii) whose value is independent of path

(iii) used to determine pressure volume work

(iv) whose value depends on temperature only

**Ans. (ii)** A quantity which is independent of path.

**Reason:**

Functions like pressure, volume and temperature depends on the state of the system only and not on the path.

**Q2.** The enthalpies of all elements in their standard states are:          **[NCERT Exercise]**

(i) Unity                                      (ii) Zero

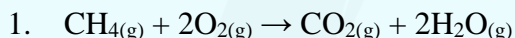(iii) $< 0$                                     (iv) Different for every element

**Ans:** (ii) Zero

**Q3.** The enthalpy of combustion of methane, graphite and dihydrogen at 298K are,

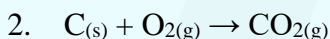$-890.3$ kJ mol$^{-1}$ $- 393.5$ kJ mol$^{-1}$, and $-285.8$ kJ mol$^{-1}$ respectively.          **[NCERT Exercise]**

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

1.  $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$

    $\Delta H = - 890.3$ kJ mol$^{-1}$

2.  $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

    $\Delta H = - 393.5$ kJ mol$^{-1}$

3.  $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$

    $\Delta H = - 285.8$ kJ mol$^{-1}$

    $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$
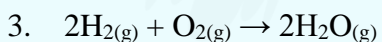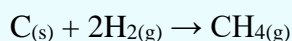
    $\Delta_f H_{CH_4} = \Delta_c H_c + 2\Delta_f H_{H_2} - \Delta_f H_{CO_2}$

    $= [-393.5 + 2(-285.8) - (-890.3)]$ kJ mol$^{-1}$

    $= -74.8$kJ mol$^{-1}$

**Q4.** 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?          **[NCERT Exercise]**

**Ans:** As per Thermodynamics 1$^{st}$ law,

$\Delta U = q + W(i)$;

ΔU internal energy = heat

W = work done

W = –594 J (work done by system)

q = +801 J (+ve as heat is absorbed)

Now,

ΔU = 801 + (–594)

ΔU = 207 J

**Q5.** Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24 J mol$^{-1}$ K$^{-1}$. **[NCERT Exercise**

**Ans:** Expression of heat (q),

q = mCPΔT; …….. (a)

ΔT = Change in temperature

c = molar heat capacity

m = mass of substance
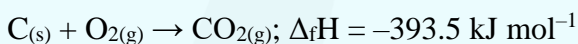
From (a)

$q = \left(\dfrac{60}{27} \text{mol}\right) (24 \text{ mol}^{-1}\text{K}^{-1})(20\text{K})$

q = 1066.67 J = 1.067 KJ

**Q6.** Enthalpy of combustion of carbon to $CO_2$ is –393.5 kJ mol$^{-1}$. Calculate the heat released upon formation of 35.2 g of $CO_2$ from carbon and dioxygen gas. **[NCERT Exercise]**

**Ans:** Formation of carbon dioxide from di-oxygen and carbon gas is given as:

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta_f H$ = –393.5 kJ mol$^{-1}$

1 mole $CO_2$ = 44g

Heat released during formation of 44g $CO_2$ = –393.5 kJ mol$^{-1}$

Therefore, heat released during formation of 35.2g of $CO_2$ can be calculated as

$= \dfrac{-393.5\text{kJ mol}^{-1}}{44\text{g}} \times 35.2\text{g}$ = –314.8 kJ mol$^{-1}$

**Q7.** Given $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ ; $\Delta_r H°$ = –92.4 kJ mol$^{-1}$. What is the standard enthalpy of formation of $NH_3$ gas? **[NCERT Exercise]**

**Ans:** "Standard enthalpy of formation of a compound is the enthalpy that takes during the formation of 1 mole of a substance in its standard form, form its constituent elements in their standard state."

Dividing the chemical equation given in the question by 2, we get

$(0.5) N_{2(g)} + (1.5)H_{2(g)} \rightarrow 2NH_{3(g)}$
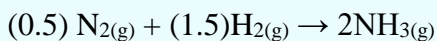
Therefore, Standard Enthalpy for formation of ammonia gas

$= (0.5) \Delta_r H^\ominus$

$= (0.5) (-92.4 \text{ kJ mol}^{-1})$

$= -46.2 \text{ kJ mol}^{-1}$

**Q8.** Calculate the enthalpy change for the process $CCl_{4(g)} \rightarrow C_{(g)} + 4Cl_{(g)}$ and determine the value of bond enthalpy for C – Cl in $CCl_{4(g)}$. **[NCERT Exercise]**

$\Delta_{vap}H^\ominus (CCl_4) = 30.5 \text{ kJ mol}^{-1}$.

$\Delta_f H^\ominus (CCl_4) = -135.5 \text{ kJ mol}^{-1}$.

$\Delta_a H^\ominus (C) = 715 \text{ kJ mol}^{-1}$.

$\Delta_a H^\ominus$ is a enthalpy of atomization

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

**Ans:** "The chemical equations implying to the given values of enthalpies" are: **[NCERT Exercise]**

(1) $CCl_{4(l)}$ à $CCl_{4(g)}$; $\Delta_{vap}H^\ominus = 30.5 \text{ kJ mol}^{-1}$

(2) $C_{(s)}$ à $C_{(g)}$; $\Delta_a H^\ominus = 715 \text{ kJ mol}^{-1}$

(3) $Cl_{2(g)}$ à $2Cl_{(g)}$; $\Delta_a H^\ominus = 242 \text{ kJ mol}^{-1}$

(4) $C_{(g)} + 4Cl_{(g)}$ à $CCl_4(g)$; $\Delta_f H^\ominus = -135.5 \text{ kJ mol}^{-1}$ $\Delta H$ for the process $CCl_{4(g)}$ à $C_{(g)} + 4Cl_{(g)}$ can be measured as:

$\Delta H = \Delta_a H^\ominus (C) + 2\Delta_a H^\ominus(Cl_2) - \Delta_a H^\ominus - \Delta_f H$

$= (715 \text{ kJ mol}^{-1}) + 2(\text{kJ mol}^{-1}) - (30.5 \text{ kJ mol}^{-1}) - (-135.5 \text{ kJ mol}^{-1})$

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

The value of bond enthalpy for C – Cl in $CCl_{4(g)}$

$= \dfrac{1304}{4} \text{kJ mol}^{-1} = 326 \text{ kJ mol}^{-1}$

**Q9.** For the reaction at 298K 2A + B → C **[NCERT Exercise]**

$\Delta H = 400 \text{ kJ mol}^{-1}$

$\Delta H = 0.2 \text{ kJ mol}^{-1}$

At what temperature will the reaction become spontaneous considering $\Delta S$ and $\Delta H$ to be constant over the temperature range?

**Ans:** Now,

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

Let, the given reaction is at equilibrium, then $\Delta T$ will be:

$T = (\Delta H - \Delta G) \dfrac{1}{\Delta S} \quad \dfrac{\Delta H}{\Delta S}$ ; $(\Delta G = 0$ at equilibrium)

$= 400 \text{ kJ mol}^{-1} / 0.2 \text{ kJ mol}^{-1} \text{ K}^{-1}$

Therefore, $T = 2000K$

Thus, for the spontaneous, $\Delta G$ must be –ve and $T > 2000K$.

**Q10.** For the reaction $2A_{(g)} + B_{(g)} \rightarrow 2D_{(g)}$             **[NCERT Exercise]**

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

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

**Ans:** $2A_{(g)} + B_{(g)} \rightarrow 2D_{(g)}$

$\Delta n_g = 2 - 3 = -1$ mole

Putting value of $\Delta U^{\ominus}$ in expression of $\Delta H$:

$\Delta H^{\ominus} = \Delta U^{\ominus} + \Delta n_g RT$

$= (-10.5 \text{ kJ}) - (-1) (8.314 \times 10^{-3} \text{kJ K}^{-1} \text{ mol}^{-1}) (298K)$

$= -10.5 \text{ kJ} - 2.48 \text{ kJ}$

$\Delta H^{\ominus} = -12.98$ kJ

Putting value of $\Delta S^{\ominus}$ and $\Delta H^{\ominus}$ in expression of $\Delta G^{\ominus}$:

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$
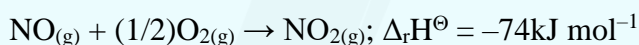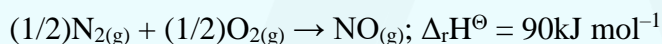
$= -12.98 \text{kJ} - (298K) (-44.1 \text{ JK}^{-1})$

$= -12.98 \text{kJ} + 13.14 \text{ kJ}$

$\Delta G^{\ominus} = 0.16 \text{kJ}$

As, $\Delta G^{\ominus}$ is positive, the reaction won't occur spontaneously.

**Q11.** Comment on the thermodynamic stability of NO(g), given,          **[NCERT Exercise]**

$(1/2)N_{2(g)} + (1/2)O_{2(g)} \rightarrow NO_{(g)}$; $\Delta_r H^{\ominus} = 90$kJ mol$^{-1}$

$NO_{(g)} + (1/2)O_{2(g)} \rightarrow NO_{2(g)}$; $\Delta_r H^{\ominus} = -74$kJ mol$^{-1}$

**Ans:** The +ve value of $\Delta_r H$ represents that during $NO_{(g)}$ formation from $O_2$ and $N_2$, heat is absorbed.

The obtained product, $NO_{(g)}$ is having more energy than reactants. Thus, $NO_{(g)}$ is unstable.

The –ve value of $\Delta_r H$ represents that during $NO_{2(g)}$ formation from $O_{2(g)}$ and $NO_{(g)}$, heat is evolved.

The obtained product, $NO_{2(g)}$ gets stabilized with minimum energy.

Thus, unstable $NO_{(g)}$ converts into stable $NO_{2(g)}$.

**Q12.** Calculate the entropy change in surroundings when 1.00 mol of $H_2O(l)$ is formed under standard conditions. $\Delta_f H^{\circ} = -286$ kJ mol$^{-1}$.        **[NCERT Exercise]**

**Ans:** $\Delta_r H^{\ominus} = -286$kJ mol$^{-1}$ is given so that amount of heat is evolved during the formation of 1 mole of $H_2O(l)$.

Thus, the same heat will be absorbed by surrounding $Q_{surr} = +286$ kJ mol$^{-1}$.

Now, $\Delta S_{surr} = Q_{surr}/7$

$= \dfrac{286 \text{kJmol}^{-1}}{298K}$

Therefore, $\Delta S_{surr} = 959.73$ J mol$^{-1}$ K$^{-1}$.

**Ab Phod Do!**