5. THERMODYNAMICS

It is a branch of science that deals with the relation between heat and work. *Chemical thermodynamics is a branch of chemistry that deals with the heat changes associated with chemical reactions.*

System and Surroundings

System is the part of the universe which is under observation or investigation. The part of the universe except system is called surroundings. The system and surroundings are separated by a boundary which may be real or imaginary.

System + surroundings → Universe

Types of systems

Depending on the ability to exchange energy and matter with the surroundings, systems are classified into three types:

1. **Open system**: It is a system that can exchange both energy and matter with the surroundings. E.g. Hot water taken in an open vessel.
2. **Closed system**: It is a system that can exchange only energy and not matter with the surroundings. E.g. Hot water taken in a closed vessel.
3. **Isolated system**: It is a system that cannot exchange both energy and matter with the surroundings. E.g. Hot water taken in a thermos flask.

Depending on the number of particles, systems are of two types:

1. **Microscopic system**: It is a system that contains a few number of particles.
2. **Macroscopic system**: It is a system that contains a large number of particles.

The properties of a macroscopic system are called **macroscopic properties**. The important macroscopic properties are: temperature (T), pressure (p), volume (V), length (l), breadth (b), height (h), internal energy (U), enthalpy (H), entropy (S), Gibb's energy (G) etc.

Macroscopic properties can be divided into two:

1. *Extensive properties*: These are properties which depend on the amount of matter present in the system. Or, these are the properties which change when a system is divided.

E.g.: Volume (V), length (l), breadth (b), height (h), internal energy (U), enthalpy (H), entropy (S), Gibb's energy (G), heat capacity (C) etc.

2. *Intensive properties*: These are properties which are independent of the amount of matter present in the system. Or, these are the properties which do not change when a system is divided.

E.g. : Temperature (T), pressure (p), molar volume (V_m), density, refractive index, molar heat capacity, viscosity, surface tension etc.

State and Path functions:

A function or a property that depends only on the initial and final state of a system and not on the path followed is called a state function.

E.g. for state functions: temperature (T), pressure (p), volume (V), internal energy (U), enthalpy (H), entropy (S), Gibb's energy (G) etc.

Path functions: These are properties which depend on the path followed also.

E.g. heat (q) and work (w).

Thermodynamic process

A thermodynamic process is the method (path) by which a state change occurs in a system. The different types of thermodynamic process are:

1. **Isothermal process**: It is a process that occurs at constant temperature. For this process, $\Delta T = 0$ but $q \neq 0$. Here the system exchanges heat energy with the surroundings, in order to keep the temperature constant.
2. **Isobaric process**: It is a process that occurs at constant Pressure. For such a process, $\Delta p = 0$
3. **Isochoric process**: It is a process that occurs at constant volume. For such a process, $\Delta V = 0$
4. **Adiabatic process**: It is a process that occurs at constant heat energy. Here no heat enters into or leaves from the system. For such a process, $q = 0$ but $\Delta T \neq 0$
5. **Cyclic process**: It is a process that takes place in a cyclic manner. Here the system undergoes a series of changes and finally returns to its initial state. For such a process, $\Delta U = 0$ and $\Delta H = 0$
6. **Reversible process**: Every process is associated with two types of forces – driving force and opposing force. Driving force favours the process while opposing force opposes it. *If the driving and opposing forces are differed by an infinitesimally small quantity the process takes place in both directions. Such a process is called reversible process.*

   A reversible process proceeds infinitely slowly by a series of equilibrium states such that the system and the surroundings are always in equilibrium with each other.
7. **Irreversible process**: If the driving and opposing forces are differed by a large quantity, then the process takes place in only one direction. Such a process is called irreversible process.

Heat and Work

Heat: It is a form of energy. Heat flows from a hot body to a cold body, when there is a thermal contact between the two. When a body absorbs heat, its energy increases and when it evolves heat, its energy decreases. Thus by international convention, when heat is absorbed by a system, q becomes $^{+}$ve and when heat is evolved by a system q becomes $^{-}$ve.

Work: In thermodynamics, there are two types of work – expansion work and non-expansion work.

1. Expansion work (w_{exp}): It is related to gaseous systems. It is the product of pressure (p) and change in volume (ΔV). i.e., expansion work (w_{exp}) = $-p\Delta V$

   For irreversible process, (w_{exp}) = $-p\Delta V$ and

   For reversible process, (w_{exp}) = $-2.303nRT \log \frac{V_2}{V_1}$
2. Non-expansion work ($w_{non\text{-}exp}$): It is related to electrochemical cells. It is the product of potential difference (E) and charge (Q). i.e., $w_{non\text{-}exp} = E \times Q$

By international convention, w becomes $^{+}$ve, when work is done *on* the system and w becomes $^{-}$ve, when work is done *by* the system.

Expression for pressure-volume work

Consider a cylinder fitted with a frictionless piston and contains one mole of an ideal gas.

Let the total volume of the gas is V_1 and pressure of the gas inside is p.

If external pressure is p_{ex} which is greater than p, piston is moved inward till the pressure inside becomes equal to p_{ex}. Let this change took place in a single step and the final volume be V_2 .

During this compression, let the piston moves a distance l and its cross-sectional area is A.

Then, volume change, $\Delta V = l \times A = (V_2 - V_1)$.

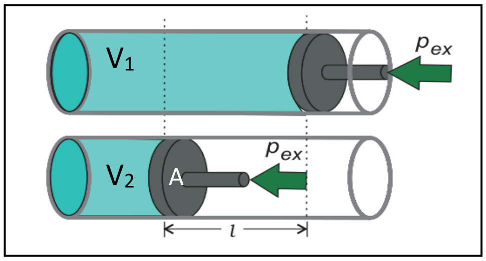
We know that pressure = Force/Area

Therefore, force on the piston = $p_{ex}.A$

If w is the work done on the system by movement of the piston,

then w = force × distance = $p_{ex}.A.l$

$$= p_{ex}(-\Delta V) = -p_{ex}\Delta V = -p_{ex}(V_2 - V_1)$$



Here the negative sign is to make the work done positive, since
$(V_2 - V_1)$ is negative.
If the pressure is not constant, but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV.
Then we can calculate the work done on the gas, $w = -\int_{V1}^{V2}(p_{ex}.dV)$
Here, p_{ex} at each stage is equal to $(p_{in} + dp)$ in case of compression and $(p_{in} - dp)$ in case of expansion.
Generally, $p_{ex} = (p_{in} \pm dp)$. Such processes are called reversible processes.
Therefore, $w_{rev} = -\int_{V1}^{V2}(p_{in} \pm dp).dV$
Since dp × dV is very small, we can write $w_{rev} = -\int_{V1}^{V2} p_{in}.dV$
But $p_{in} = p$, the pressure of the gas inside the cylinder.
$w_{rev} = -\int_{V1}^{V2} p.dV$
For n mol of an ideal gas i.e., $pV = nRT$. So $p = \frac{nRT}{V}$
Thus $w_{rev} = -\int_{V1}^{V2} \frac{nRT}{V}. dV$
On integrating this equation, we get, $w_{rev} = -nRT \ln \frac{V_2}{V_1}$ $\left[since \int \frac{1}{V}. dV = \ln V\right]$
On changing the base of logarithm, we can write: $\mathbf{w_{rev} = -2.303\ nRT \log \frac{V_2}{V_1}}$
Where n – no. of moles of the gas, R – Universal gas constant ($R = 8.314\ J\ K^{-1}\ mol^{-1}$), T – Absolute temperature, V_1 – initial volume of the gas and V_2 – the final volume)
{Note: Here ln is the natural logarithm. To convert natural logarithm (base e) to common logarithm (base 10), multiply by 2.303}.

Free expansion: Expansion of a gas into vacuum (external pressure = 0) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible.

Internal Energy (U)

Every body is associated with a definite amount of energy. This energy is called internal or intrinsic energy. It is the energy possessed by a body. It is the sum of different types of molecular energies like translational kinetic energy, rotational kinetic energy, vibrational kinetic energy, electronic energy, nuclear energy etc.

Internal energy of a body is an extensive property and state function. We cannot calculate the exact value of internal energy, but we can calculate the change in internal energy (ΔU) during a process by using an apparatus called *Bomb Calorimeter*.

The change in internal energy $(\Delta U) = U_2 - U_1$, where U_1 and U_2 are the initial and final internal energies respectively. The unit of internal energy is kJ/mol.
The internal energy of a system can be changed in the following ways:

1. by the transfer of heat into or out of the system
2. by work done on or by the system
3. by the transfer of matter into or out of the system.

First law of thermodynamics:

It is same as law of conservation of energy. It states that energy can neither be created nor be destroyed. Or, the total energy in the universe is always a constant. Or, the total energy of an isolated system is always a constant.

Mathematically, $\Delta U = q + w$ ……………… (1)

Where q is the amount of heat absorbed by the system and w is the amount of work done on the system.

If there is only expansion work, the above equation becomes $\Delta U = q - p\Delta V$ ………………(2)

(since, $W_{exp} = - p\Delta V$)

Special cases:

- 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, $\Delta U = 0$.
- For a system containing only solids or liquids, $\Delta V = 0$. So, $\Delta U = q$
- For an isothermal reversible process, $\Delta U = 0$. So $q = - w = 2.303nRT \log(V_2/V_1)$
- For an adiabatic process, q = 0, so $\Delta U = w$.

Significance of ΔU

We know that $\Delta U = q - p\Delta V$

For a process taking place at constant volume, $\Delta V = 0$. So $\Delta U = q_v$

i.e., ΔU gives the amount of heat absorbed or evolved by a system at constant volume. It can be measured by using a bomb calorimeter.

Enthalpy (H)

It is the total heat content of a system. It is the sum of internal energy and pressure-volume energy of a system.

i.e. $H = U + pV$

It is a state function and an extensive property. i.e, whenever there is a change in enthalpy, it depends only on the initial and final values and not on the path followed.

If H_1 is the enthalpy of a system in the initial state and H_2 is that in the final state, then the change in enthalpy, $\Delta H = H_2 - H_1$.

The unit of enthalpy is kJ/mol. ΔH is determined by using an apparatus called calorimeter.

For a chemical reaction, if H_P is the enthalpy of products and H_R is that of reactants, then

$\Delta H = H_P - H_R$.

If $H_P > H_R$, ΔH is positive and heat is absorbed during the process. Such a process is called endothermic process.

If $H_P < H_R$, ΔH is negative and heat is evolved during the process. Such a process is called exothermic process.

Relation between ΔH and ΔU

Consider a gaseous reaction taking place at constant pressure (P) and temperature (T). Let H_1, U_1 and V_1 be the initial enthalpy, internal energy and volume respectively. Let these values changes to H_2, U_2 and V_2 respectively. Then,

$H_1 = U_1 + pV_1$ ……………… (1)

And $H_2 = U_2 + pV_2$ ……………… (2)

(2) – (1) gives: $H_2 - H_1 = (U_2 + pV_2) - (U_1 + pV_1)$

Or, $\Delta H = (U_2 - U_1) + (pV_2 - pV_1)$

Or, $\Delta H = \Delta U + p(V_2 - V_1)$

Or, $\boldsymbol{\Delta H = \Delta U + p\Delta V}$ …… (3)

From ideal gas equation, $pV = nRT$ [where R is the universal gas constant, $R = 8.314\ J\ K^{-1}\ mol^{-1}$]

If n_1 and n_2 are the total no. of moles of reactants and products respectively, then

$pV_1 = n_1RT$ and $pV_2 = n_2RT$

$pV_2 - pV_1 = n_2RT - n_1RT$

Or, $p(V_2 - V_1) = (n_2 - n_1)RT$

Or, $p\Delta V = \Delta nRT$

So equation (3) becomes, **$\Delta H = \Delta U + \Delta nRT$**

where $\Delta n = n_{p(g)} - n_{R(g)}$

i.e., Δn = no. of moles of gaseous products – no. of moles of gaseous reactants

If $\Delta n = 0$, then $\Delta H = \Delta U$

If $\Delta n > 0$, then $\Delta H > \Delta U$

and if $\Delta n < 0$, then $\Delta H < \Delta U$.

Significance of ΔH

We know that $\Delta H = \Delta U + P\Delta V$ (at constant pressure)

From first law of thermodynamics, $\Delta U = q - P\Delta V$

So, $q = \Delta U + P\Delta V$

From the above equations, we can write, $\Delta H = q_p$

i.e. enthalpy change in a chemical reaction is equal to the amount of heat evolved or absorbed at constant pressure. This is the significance of ΔH.

Heat capacity (C)

It is the amount of heat required to raise the temperature of a body through 1^0C or 1K. if q amount of heat is required to raise the temperature of a body through ΔT, then heat capacity (C) = $\frac{q}{\Delta T}$.

Specific heat capacity is the amount of heat required to raise the temperature of unit mass of a body through 1^0C or 1K.

Molar heat capacity is the amount of heat required to raise the temperature of 1 mole of a substance through 1^0C or 1K.

Relation between C_p and C_v

At constant volume, the heat capacity, *C* is denoted by C_v and at constant pressure, it is denoted by C_p .

We know that heat, $q = C\,\Delta T$

At constant volume, the heat $q_V = \Delta U = C_v.\Delta T$

At constant pressure, $q_p = \Delta H = C_p.\Delta T$

We know that $H = U + pV$

For 1 mole of an ideal gas, $\Delta H = \Delta U + \Delta(pV)$

From ideal gas equation $pV = nRT$, for 1 mol of an ideal gas, $pV = RT$

So, $\Delta H = \Delta U + \Delta(RT)$

Or, $\Delta H = \Delta U + R\Delta T$

On putting the values of ΔH and ΔU, we get

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

Or, $C_p = C_v + R$

Or, **$C_p - C_v = R$** *[This is known as Meyer's relation]*

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 a liquid.

Measurement of ΔU

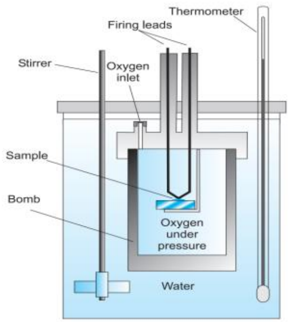
ΔU is measured in a bomb calorimeter. Here, a steel vessel (the bomb) is immersed in a water bath. A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb. The increase in temperature is measured by using a thermometer.

Since the bomb calorimeter is sealed, its volume does not change.

i.e., the energy changes associated with the reaction is measured at constant volume.

Under these conditions, no work is done as the reaction is carried out at constant volume (i.e. $\Delta V = 0$) in the bomb calorimeter. By knowing the heat capacity of the calorimeter and the temperature change during the reaction, we can calculate ΔU by the equation:

$\Delta U = q_v = C_v.\Delta T$



Bomb calorimeter

Measurement of ΔH

Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a calorimeter. Here the reaction is carried out at normal pressure and the temperature change is measured by using a thermometer. By knowing the heat capacity of the calorimeter, we can calculate ΔH by the equation:

$\Delta H = q_p = C_p.\Delta T$

ΔH obtained here is also called the heat of reaction or enthalpy of reaction, $\Delta_r H$.

ENTHALPY CHANGE OF A REACTION – REACTION ENTHALPY ($\Delta_r H$)

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

Reactants ⟶ Products Or, R ⟶ P

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

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

i.e. $\Delta_r H = \sum H_P - \sum H_R$

Standard enthalpy of reactions ($\Delta_r H^\Theta$)

The standard enthalpy of reaction is the enthalpy change for a reaction when all the substances are in their standard states. In thermodynamics, the standard state refers to the existence of a substance in its pure form at 1 bar pressure and 298 K temperature.

Standard enthalpy of formation ($\Delta_f H^\Theta$)

It is the standard enthalpy change for the formation of one mole of a compound from its elements in their most stable state of aggregation (or, reference state). It is denoted by the symbol $\Delta_f H^\Theta$. For e.g. the std. enthalpy of formation of CO_2 is the enthalpy change when 1 mole of CO_2 is formed from C and O_2 at 298K temperature, 1 bar pressure and all the substances are in their stable state.

The reference state of an element is its most stable state at 25°C and 1 bar pressure. The reference state of dihydrogen is H_2 gas and those of dioxygen, carbon and sulphur are O_2 gas, $C_{graphite}$ and $S_{Rhombic}$ respectively. The enthalpy of formation may be positive or negative.

By convention, standard enthalpy of formation ($\Delta_f H^\Theta$) of an element in reference state (i.e., its most stable state of aggregation) is taken as zero.

By knowing the std. enthalpies of formation of reactants and products, we can determine the std. enthalpy of reaction by the equation: $\Delta_r H^\Theta = \sum \Delta_f H^\Theta_{(P)} - \sum \Delta_f H^\Theta_{(R)}$

i.e. std. enthalpy of reaction = sum of the standard enthalpies of formation of products – sum of the std. enthalpies of formation of reactants.

Enthalpies of phase transition

It is the enthalpy change when one mole of a substance changes from one phase to another phase at a particular temperature. The important types of Enthalpies of phase transition are:

1) **Molar Enthalpy of fusion ($\Delta_{fus}H^{\ominus}$)**: It is the enthalpy change when one mole of a solid substance changes to liquid state at its melting point.

2) **Molar Enthalpy of vaporization** ($\Delta_{vap}H^{\ominus}$): It is the enthalpy change when one mole of a liquid substance changes to its vapour state at its boiling point.

3) **Molar Enthalpy of sublimation ($\Delta_{sub}H^{\ominus}$)**: It is the enthalpy change when one mole of a solid substance is directly converted to gaseous state at a particular temperature below its m.p.

Enthalpies of fusion, vaporization and sublimation are positive, since heat is absorbed during these process. The magnitude of the enthalpy change depends on the strength of the intermolecular forces in the substance.

Thermochemical equations

A balanced chemical equation together with the value of enthalpy of reaction is called a thermochemical equation. Here the physical state of the each of the reactants and products is also shown in bracket.

e.g. $H_{2(g)} + ½ O_{2(g)} \rightarrow H_2O_{(g)}$, $\Delta_rH^{\ominus} = -285.83$ kJ/mol

or, $H_{2(g)} + ½ O_{2(g)} \rightarrow H_2O_{(g)} + 285.83$ kJ/mol

When we multiply or divide a thermochemical equation with a number, then $\Delta_rH^{\ominus}$ is also multiplied or divided with the same number.

For e.g. $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3\ (g)}$; $\Delta_rH^{\ominus} = -91.8$ kJ/mol

Then, $½ N_{2(g)} + {}^3/_2 H_{2(g)} \rightarrow NH_{3(g)}$; $\Delta_rH^{\ominus} = -45.9$ kJ/mol

When a chemical equation is reversed, the value of $\Delta_rH^{\ominus}$ is reversed in sign.

For e.g. $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3\ (g)}$; $\Delta_rH^{\ominus} = -91.8$ kJ/mol

Then, $2NH_{3(g)} \rightarrow N_{2(g)} + 3H_{2(g)}$; $\Delta_rH^{\ominus} = +91.8$ kJ/mol

Hess's Law of Constant Heat Summation

The law states that the total enthalpy change for a physical or chemical process is the same whether the reaction taking place in a single step or in several steps.

Or, the total enthalpy change for a process is independent of the path followed.

Thus according to Hess's law, if a reaction takes place in several steps, then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions.

Illustration:

Consider a process in which the reactant A is converted to product B in a single step by involving heat change ΔH. Let the same reactant A is first converted to C, then to D and finally to B involving heat changes ΔH_1, ΔH_2 and ΔH_3 respectively.

$$\begin{tikzcd} A \arrow[r, "\Delta H"] \arrow[d, "\Delta H_1"] & B \\ C \arrow[r, "\Delta H_2"] & D \arrow[u, "\Delta H_3"'] \end{tikzcd}$$

Then according to Hess's law: $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

Standard enthalpy of combustion ($\Delta_cH^{\ominus}$)

It is defined as the enthalpy change when 1mole of a substance is completely burnt in presence of excess of air or oxygen and all the reactants and products being in their standard states. It is always negative since heat is always evolved during combustion.

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

Enthalpy of atomization ($\Delta_aH^{\ominus}$)

It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase. In the case of diatomic molecules the enthalpy of atomization is same as the bond dissociation enthalpy.

E.g. $H_2(g) \rightarrow 2H(g)$; $\Delta_aH^{\ominus} = 435.0$ kJ mol^{-1}

Bond Enthalpy ($\Delta_{bond}H^{\ominus}$)

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. So enthalpy of bond dissociation is positive and enthalpy of bond formation is negative.

The amount of heat required to break one mole of covalent bonds to form products in the gas phase is called the **bond dissociation enthalpy**. For diatomic molecules, bond dissociation enthalpy and bond enthalpy are same.

e.g. $H_2(g) \rightarrow 2H(g)$; $\Delta_{bond}H^{\ominus} = 435.0 \text{ kJ mol}^{-1}$

In the case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule. So here **bond enthalpy is the average of bond dissociation enthalpies of various similar bonds**.

For e.g. for water, the bond enthalpy is calculated as follows:

$H_2O_{(g)} \rightarrow H_{(g)} + OH_{(g)}$; $\Delta_a H^{\ominus} = 502$ kJ/mol

$OH_{(g)} \rightarrow O_{(g)} + H_{(g)}$; $\Delta_a H^{\ominus} = 427$ kJ/mol

Here the bond enthalpy of O-H bond is taken as the average of the two bond dissociation enthalpies.

i.e. bond enthalpy of O-H bond = $\frac{502+427}{2}$ = 464.5kJ/mol

The standard enthalpy of reaction, $\Delta_r H^0$ is related to bond enthalpies of the reactants and products in gas phase reactions as:

$\Delta_r H^{\ominus} = \sum$ bond enthalpies of reactants - $\sum$ bond enthalpies of products

This equation is valid when all the reactants and products in the reaction are in gaseous state.

Enthalpy of Solution ($\Delta_{sol}H^{\ominus}$)

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

The enthalpy of solution in water is determined by the values of the lattice enthalpy, $\Delta_{lattice}H^{\ominus}$ and enthalpy of hydration of ions, $\Delta_{hyd}H^{\ominus}$.

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

For most of the ionic compounds, $\Delta_{sol}H^{\ominus}$ is positive and the dissolution process is endothermic. Therefore the solubility of most salts in water increases with rise of temperature.

If the lattice enthalpy is very high, the dissolution of the compound may not take place at all. Fluorides of many metals are less soluble than the corresponding chlorides, because of their higher lattice enthalpies.

Lattice Enthalpy ($\Delta_{lattice}H^{\ominus}$)

The lattice enthalpy of an ionic compound is the enthalpy change when one mole of an ionic compound dissociates into gaseous ions.

We cannot determine lattice enthalpies directly by experiment. So an indirect method called **Born-Haber Cycle** is used to calculate lattice enthalpy of a compound.

This can be explained by consider the formation of NaCl.

$Na(s) + \frac{1}{2} Cl_2(g) \rightarrow NaCl(s)$

This involves the following steps:

1. Conversion of solid sodium atom to gaseous sodium atom. The energy change involved in this process is called sublimation energy.

   $Na(s) \rightarrow Na(g)$; $\Delta_{sub}H^{\ominus}$

2. Conversion gaseous sodium atom to gaseous sodium ion. The energy change in this process is called ionisation enthalpy.

   $Na_{(g)} \rightarrow Na^+_{(g)}$; $\Delta_i H^{\ominus}$

3. Conversion of gaseous chlorine molecule to gaseous chlorine atom. The energy change during this process is called bond dissociation enthalpy.

$Cl_{2(g)} \rightarrow 2Cl_{(g)}$; $\Delta_{bond}H^{\ominus}$

$\frac{1}{2} Cl_{2(g)} \rightarrow Cl_{(g)}$; $\frac{1}{2} \Delta_{bond}H^{\ominus}$

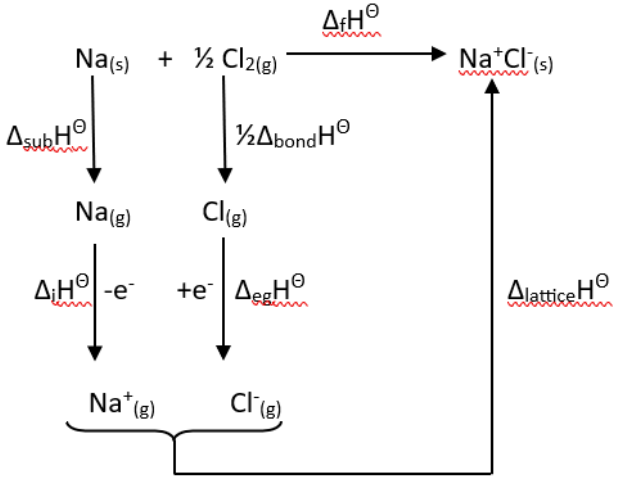
4. Conversion of chlorine atom to chloride ion. The energy change involved in this process is called electron gain enthalpy ($\Delta_{eg}H^{\ominus}$).

$Cl_{(g)} \rightarrow Cl^{-}_{(g)}$; $\Delta_{eg}H^{\ominus}$

5. Packing of $Na^{+}_{(g)}$and $Cl^{-}_{(g)}$ to form NaCl(s). the energy change in this process is called lattice enthalpy ($\Delta_{lattice}H^{\ominus}$)

$Na^{+}_{(g)} + Cl^{-}_{(g)} \rightarrow NaCl_{(s)}$; $\Delta_{lattice}H^{\ominus}$

The different steps can be represented in a cyclic for as follows:



By applying Hess's law we can write: $\Delta_fH^{\ominus} = \Delta_{sub}H^{\ominus} + \Delta_iH^{\ominus} + \frac{1}{2}\Delta_{bond}H^{\ominus} + \Delta_{eg}H^{\ominus} + \Delta_{lattice}H^{\ominus}$

Form this lattice enthalpy can be determined as:

$\Delta_{lattice}H^{\ominus} = \Delta_fH^{\ominus} - [\Delta_{sub}H^{\ominus} + \Delta_iH^{\ominus} + \frac{1}{2}\Delta_{bond}H^{\ominus} + \Delta_{eg}H^{\ominus}]$

Enthalpy of Dilution ($\Delta_{dil}H^{\ominus}$):

It is the enthalpy change when a solution is diluted (i.e. more solvent is added to the solution. It depends on the original concentration of the solution and the amount of solvent added.

Spontaneous Process

It is a process that takes place without the help of any external agency. All natural processes are spontaneous. E.g. flow of water from high level to low level, flow of heat from hot body to cold body, inter mixing of gases, burning of fuels, melting of ice, evaporation of water etc. A spontaneous process cannot reverse its direction by its own.

Spontaneous chemical reactions are also called *feasible or probable or irreversible reactions*.

e.g. $N_2 + 3H_2 \longrightarrow 2NH_3$; $\Delta_rH^{\ominus}$ = - 91.8 kJ/mol

$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$; $\Delta_rH^{\ominus}$ = - 285.8 kJ/mol

A process that takes place with the help of an external agency is called *non-spontaneous process*. E.g. flow of water from low level to high level.

Criteria for spontaneity

During spontaneous processes like burning of fuels, flow of heat from hot body to cold body, flow of water from high level to low level etc, energy of the system decreases. So one of the criteria for spontaneity is decrease in energy.

But for some spontaneous processes like melting of ice, evaporation of water etc, heat is absorbed. i.e. the energy of the system increases during the process. The above processes are accompanied with increase in disorder (entropy) of the system. Thus another criterion for spontaneity is increase in disorderness or randomness of the system.

Entropy (S)

It is ***a measure of degree of disorderness or randomness of a system***. As the disorderness increases, entropy also increases. It is an extensive property and state function.

If S_1 is the initial entropy of a system and S_2 is its final value, then the change in entropy $\Delta S = S_2 - S_1$.

For a given substance, the solid state has the least entropy and the gaseous state has the most. *When temperature increases entropy also increases*. The unit of entropy and entropy change is J/K/mol.

If a system absorbs 'q' amount of heat reversibly at a temperature T, then the change in entropy, $\Delta S = \frac{q_{rev}}{T}$, where $q_{rev.}$ is the amount of heat absorbed reversibly.

Entropy and spontaneity

During a spontaneous process, disorderness of the system increases. Thus entropy increases and hence ΔS becomes positive.

The total entropy change for the system and surroundings is given by $\Delta S_{Total} = \Delta S_{syst.} + \Delta S_{surr.}$

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

When a system attains *equilibrium*, the entropy becomes maximum and there is no further change in entropy. So $\Delta S_{Total} = 0$

If $\Delta S_{Total} < 0$, the process is non-spontaneous.

Second Law of Thermodynamics:

It can be stated as the entropy of the universe always increases during every spontaneous process.

Third law of Thermodynamics:

It states that the entropy of any perfectly crystalline substance is zero at absolute zero of temperature. By using this law, we can calculate the absolute value of entropy of pure substances from their thermodynamic data.

Gibb's energy (G)

It is defined as *the maximum amount of available energy that can be converted to useful work*. It is given by the equation, $G = H - TS$

It is an extensive property and a state function.

If G_1 is the initial Gibb's energy and G_2 is its final value, then the change in Gibb's energy $(\Delta G) = G_2 - G_1$

The unit of Gibb's energy is kJ/mol.

Relation between ΔG, ΔH and ΔS (Gibb's Equation)

We know that $G = H - TS$

So, $\Delta G = \Delta H - \Delta(TS)$

$= \Delta H - (T\Delta S + S\Delta T)$

At constant temperature, $\Delta T = 0$.

So, $\Delta G = \Delta H - T\Delta S$. This equation is known as *Gibb's equation.*

At standard state, $\Delta G^\Theta = \Delta H^\Theta - T\Delta S^\Theta$

The change in Gibb's energy for a system can be written as

$\Delta G_{syst.} = \Delta H_{syst.} - T\Delta S_{syst.}$

Gibb's energy and Spontaneity

We know that $\Delta S_{Total} = \Delta S_{syst.} + \Delta S_{surr.}$ .... (1)

Consider a system which absorbs 'q' amount of heat reversibly at a constant temperature T and constant pressure p.

Then, $\Delta S_{surr.} = \frac{q_p}{T}$

But $q_p = \Delta H_{surr.}$ and $\Delta H_{surr.} = -\Delta H_{syst.}$

So, $\Delta S_{surr.} = \frac{-\Delta H_{syst}}{T}$

So equation (1) becomes, $\Delta S_{Total} = \Delta S_{syst.} - \frac{\Delta H_{syst}}{T}$

On multiplying by –T, we get

$-T\Delta S_{Total} = -T\Delta S_{syst.} + \Delta H_{syst.}$

Or, $-T\Delta S_{Total} = \Delta G_{syst.}$ (Since, $\Delta H_{syst.} - T\Delta S_{syst.} = \Delta G_{syst.}$)

For a spontaneous process, ΔS_{Total} is positive. So $\Delta G_{syst.}$ is negative. (or, $\Delta G_{syst.} < 0$)

For a non-spontaneous process, ΔS_{Total} is negative, so *$\Delta G_{syst.}$ is positive.* (or, $\Delta G_{syst.} > 0$)

For a process at equilibrium, $\Delta S_{Total} = 0$. So *$\Delta G_{syst.} = 0$*

Conditions for ΔG to be negative

We know that for a spontaneous process, $\Delta G_{syst.}$ is negative. Also $\Delta G = \Delta H - T\Delta S$.

1) If ΔH is negative and ΔS is +ve, ΔG is always –ve and the process is always spontaneous.
2) If both ΔH and ΔS are positive, ΔG will be –ve when $T\Delta S > \Delta H$. This is possible at high temperature. i.e. the process will be spontaneous at higher temperature. E.g. melting of ice.
3) If both ΔH and ΔS are negative, ΔG will be –ve when $T\Delta S < \Delta H$. This is possible at low temperature. i.e. the process will be spontaneous at lower temperature. E.g. Condensation of water-vapour.

Note: If ΔH is +ve and ΔS – ve, then ΔG will be always +ve and the process will be always non-spontaneous.

Gibb's energy change (ΔG) and Equilibrium constant (K)

Consider a reversible reaction: $A + B \rightleftharpoons C + D$

The Gibb's energy change of this reaction is $\Delta_r G = \Delta_r G^{\ominus} + RT \ln K$

At equilibrium, $\Delta_r G = 0$

So, $0 = \Delta_r G^{\ominus} + RT \ln K$

Or, $\Delta_r G^{\ominus} = -RT \ln K$

Or, $\Delta_r G^{\ominus} = -2.303RT \log K$

Where R is the universal gas constant and T is the absolute temperature. [$R = 8.314\ J\ K^{-1} mol^{-1}$]

So *for a spontaneous process, the value of K should be positive*.

Q1) The equilibrium constant for a reaction is 5. What will be the value of ΔG^o? Given that $R = 8.314\ J\ K^{-1} mol^{-1}$ and $T = 300K$.

Ans: $\Delta G^0 = -2.303RT\log K$

$= -2.303 \times 8.314 \times 300 \times \log 5 =$ **$-4014.58\ J\ mol^{-1}$**

Q2) For the reaction, $4Fe(s) + 3O_2(g) \rightarrow 2\ Fe_2O_3\ (s)$, the entropy change is $-549.4\ J\ K^{-1}\ mol^{-1}$ at 298 K. Inspite of the negative entropy change, why is the reaction spontaneous? Given $\Delta H^o = -1648\ kJ\ mol^{-1}$.

Ans: We know that $\Delta G^0 = \Delta H^0 - T\Delta S^0$

Here $\Delta H^o = - 1648$ kJ mol^{-1} = -1648×10^3 J/mol. $\Delta S^o = - 549.4$ J K mol^{-1} and T = 298 K

So, $\Delta G^0 = -1648 \times 10^3 - 298 \times -549.4 = =$ **-1484.28×10^3 J mol^{-1} = -1484.28 kJ mol^{-1}**

Q3) Calculate the work done for the reversible isothermal expansion of 1 mole of an ideal gas at 27°C, from a volume of 10 dm^3 to a volume of 20 dm^3.

Ans: *Here n = 1 mol, R = 8.314 J/K/mol, $V_1 = 10$ dm^3, $V_2 = 20$ dm^3 and T = 25 + 273 = 298 K*

For isothermal reversible expansion, work done, $w_{exp} = -2.303nRT \log\frac{V_2}{V_1}$

$= -2.303 \times 1 \times 8.314 \times 298 \times \log\frac{20}{10}$

$=$ ***-1717.46 J***

Q4) Find the temperature above which the reaction $MgO_{(s)} + C_{(s)} \rightarrow Mg_{(s)} + CO_{(g)}$ becomes spontaneous. (Given $\Delta_r H^o = 490$ kJ mol^{-1} and $\Delta_r S^o = 198$ JKmol^{-1}).

Ans: *At equilibrium,* $\Delta_r G^0 = 0$

So the Gibb's equation, $\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0$ *becomes:*

$0 = \Delta_r H^0 - T\Delta_r S^0$

Or, $\Delta_r H^0 = T\Delta_r S^0$

So, $T = \Delta_r H^0/\Delta_r S^0 = 490 \times 10^3/198 =$ ***2474.74K.***

So at 2474.74K, the reaction is at equilibrium.

Above this temperature, the reaction becomes spontaneous. [Here both $\Delta_r H^0$ *and* $\Delta_r S^0$ *are +ve. So* $\Delta_r G^0$ *becomes –ve only when* $T\Delta_r S^0 > \Delta_r H^0$*. This is possible at high temperature.]*

Q5) The enthalpy of combustion of $CH_{4(g)}$, $C_{(graphite)}$ and $H_{2(g)}$ at 298K are -890.3 kJ mol^{-1}, -393.5 kJ mol^{-1} and -285.8 kJ mol^{-1} respectively. Calculate the enthalpy of formation of $CH_{4(g)}$.

Ans: *The required equation is:* $C_{(graphite)} + 2H_{2(g)} \rightarrow CH_{4(g)}$

The given data are: $CH_{4(g)} + 2\,O_{2(g)} \rightarrow CO_{2(g)} + 2\,H_2O_{(l)}$; $\Delta H = -890.3$ kJ/mol ………… (i)

$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H = -393.5$ kJ/mol …………………….. (ii)

$H_{2(g)} + ½\,O_{2(g)} \rightarrow H_2O_{(l)}$; $\Delta H = -285.8$ kJ/mol ……………………….. (iii)

Multiply equation (iii) x 2: $2H_{2(g)} + O_{2(g)} \rightarrow 2\,H_2O_{(l)}$; $\Delta H = -285.8 \times 2 = -571.6$ kJ/mol …… (iv)

Reverse equation (i): $CO_{2(g)} + 2H_2O_{(l)} \rightarrow CH_{4(g)} + 2\,O_{2(g)}$; $\Delta H = 890.3$ kJ/mol ……….. (v)

Now add the equations (ii) + (iv) + (v) we get $C_{(graphite)} + 2H_{2(g)} \rightarrow CH_{4(g)}$; $\Delta H = -393.5 + -571.6 + 890.3 =$ ***-74.8 kJ/mol***

yyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyyy