# Chapter III

# Fundamentals concepts of thermodynamics

## Introduction:

Before we get into the first law of thermodynamics, we need to understand the relation between heat and work and the concept of internal energy. Just like mass, energy is always conserved, it can neither be created nor destroyed, but it can be transformed from one form to another.

## Definition of heat (Q):

Heat transfer is a thermodynamic process representing the transfer of energy in the form of thermal agitation of the constituent particles. In practice one needs heating elements to do the job

**Example**:

- When a container is placed over a fire, the temperature of the water rises. It is said that the heat source has given heat to the water.
- When water cools, it loses heat.

The amount of energy transferred to water is called 'heat'.

it is given by the relation:

$$Q = m.C.\,\Delta T$$

C: specific heat

### II-1- Specific heat (C):

Is the quantity of heat required to raise the temperature of one gram of a substance by one Celsius degree. The units of specific heat are usually calories or joules per gram per Celsius degree. For example, the specific heat of water is 1 calorie (or 4.186 joules) per gram per Celsius degree. Heat is frequently also measured in the calorie (cal), which is defined as "the amount of heat required to raise the temperature of one gram of water from 14.5 degrees Celsius to 15.5 degrees Celsius."

### II-2- Measuring the Heat:

A **calorimeter** is an object used for calorimetry, or the process of measuring the heat of chemical reactions or physical changes as well as heat capacity. It mainly consists of a metallic vessel made of materials which are good conductors of electricity such as copper and aluminium etc. There is also a facility for stirring the contents of the vessel. This metallic vessel with a stirrer is kept in an insulating jacket to prevent heat loss to the environment. There is just one opening through which a thermometer can be inserted to measure the change in thermal properties inside.

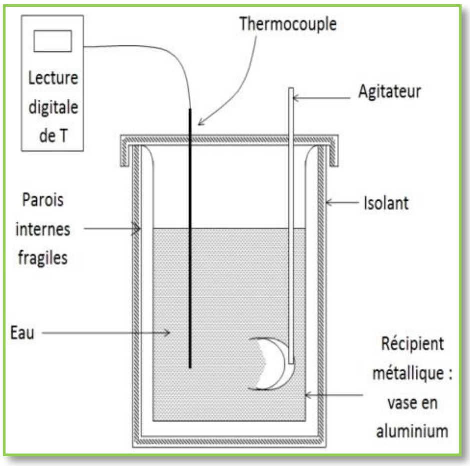
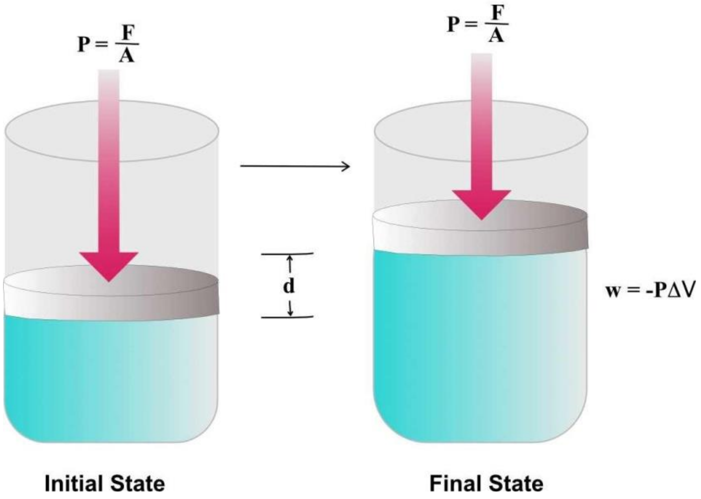


**Figure 1**

## II- Mechanical work (W) :

Mechanical work is defined as an energy transfer to the system through the change of an external parameter. Work is the only energy which is transferred to the system through external macroscopic forces.



$$\vec{F} = \vec{P} \times S$$

When an external operator exerts a force on the piston, it moves to the higher: the gas then exerts a force ‘F’; where: 'F' is in Newton (N); 'S' is in square meter ($m^2$).

Work is equal to the product of force (F) time’s displacement (dx) according to the equation:

$$\delta W = \vec{F} \times \overrightarrow{dx}$$

The volume (V) represents the surface by a distance (x):

$$V = S.x$$

$\delta W = F \times dx = P.S.dx$ and V= S.x dV=S.dx

$$W = P\,.\,S\,.\frac{dV}{S} \Longrightarrow \delta\, W = P\,.\,dV$$

### III-1- Expression of the work in case of reversible transformation:

**Example:**

When the gas expansion is reversible and this involves the external pressure being less than the internal pressure, by a small extent throughout the expansion process and in this case P = $P_{ext}$.

We have:

$$W = -\int_{V1}^{V2} \mathrm{Pext.\,dV}$$

By integrating the previous equation with gas being considered ideal and consisting of a number of moles, so the law can be used:

$$\text{Perfect gas} \Rightarrow P.V = n.R.T$$

If the transformation is isothermal:

$$w = -\int_{v1}^{v2} nRT\frac{dv}{v}$$

$$\Rightarrow W = -nRT\ln\frac{V_2}{V_1}$$

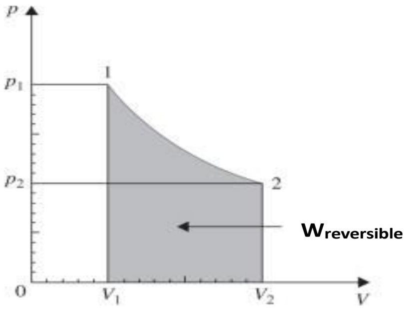
From ***Boyle's*** Law:

Becomes the previous equation

$$W = -nRT\ln\frac{P_1}{P_2}$$

- **Calculation of work graphically :**

The work is equal to the area calculated between the curve and the axis of the volumes and the two lines $1V_1$ and $2V_2$



### III-2- Expression of the work in case of irreversible transformation:

**Example:**

When the gas expansion is irreversible, this involves a sudden change of pressure, in which case: P = $P_2$ (final pressure).

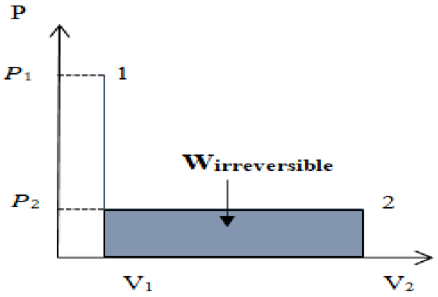
We have:

$$W = -\int_{V_1}^{V_2} P_2 . dV$$

By integrating the previous equation:

$$W = -P_2\,(V_2 - V_1)$$

- **Calculation of work graphically :**



## VI- First principle of thermodynamics:

Internal energy definition is given as:

The energy contained within the system associated with random motions of the particles along with the potential energies of the molecules due to their orientation.

The energy due to random motion includes translational, rotational, and vibrational energy. It is represented as U. *So* now we can say, since internal energy is a state function and in all the processes shown above the change in internal energy from state, ‘a’ to state ‘b’ will be the same.

### 1-Text of the first principle of the thermodynamic:

The first law of thermodynamics is based on the law of conservation of energy, which states that energy cannot be created or destroyed, but can be transferred from one form to another. Many power plants and engines operate by turning heat energy into work. The reason is that a heated gas can do work on mechanical turbines or pistons, causing them to move. The first law of thermodynamics applies the conservation of energy principle to systems where heat transfer and doing work are the methods of transferring energy into and out of the system. The first law of thermodynamics states that the change in internal energy of a system $\Delta U$ equals the net heat transfer into the system Q, plus the net work done on the system W. In equation form, the first law of thermodynamics is, $\Delta U=Q+W$.

Where,

- $\Delta U$ is the internal energy
- Q is the heat added to the system
- W is the work done by the system

**Note:**

- We have to be very careful with the first law. About half of textbooks, teachers, and professors write the first law of thermodynamics as $\Delta U=Q+W$ and the other half write it as $\Delta U = Q-W$.

Both equations are correct, and they say the same thing. The reason for the difference is that in the formula $\Delta U = Q + W_{\text{on gas}}$, we are assuming that W represents the **work done on the system**, and when we use $\Delta U=Q-W_{\text{by gas}}$, we are assuming that W represents the **work done by the system.**

The two different equations are equivalent since, $\mathbf{W_{\text{on gas}} = -W_{\text{by gas}}}$

When **work is done on a system**, the work done adds to the internal energy of the system (hence the plus sign in $\Delta U = Q + W_{\text{on gas}}$)

When **work is done by a system**, the work done takes away from the internal energy of the system (hence the minus sign in $\Delta U = Q-W_{\text{by gas}}$)

- It is a state function that depends only on the equilibrium state the system is in (it does not depend on the path followed by the system during the transformation);
- It is expressed in Joule (J) or calorie (cal);

**By convention**: if $\Delta U > 0$, energy is supplied to the system, if $\Delta U < 0$, energy is given up by the system

## 2- Application to transformations :

### a)-Isochore transformation (V = cte) :

At: V = Cte ; W = 0 ==> $\Delta U = Q_V + 0$ ==> $\mathbf{\Delta U = Q_V}$

$$\mathbf{\Delta U = Q_V = m.C_V.\,\Delta T\ ;\ \ \Delta U = Q_V = n.C_V.\,\Delta T}$$

### b)-Isobaric transformation (P= cte) :

According to the first principle:

So :

$$\Delta U = Q + W$$

**Enthalpy:** $$P = Cte \Rightarrow W = -\int_{V_1}^{V_2} P.dV = -P(V_2 - V_1)$$

$$\Delta U = P-(V_2 - V_1) + Q_P$$

During the transformation being made at constant pressure it can be written :

According to the first principle :

$$\Delta U = Q_P + W_P$$

$$= Q_P - P\Delta V \Rightarrow Q_P = \Delta U + P\Delta V = U_2 - U_1 + P\ (V_2 - V_1)$$

$$= (U_2 + P\ V_2) - (U_1 + P\ V_1)$$

And from it we know a new H function so that:

$$H = U + P\ V$$

The equation becomes:

$$Q_P = H_2 - H_1 = \Delta H \Rightarrow \mathbf{Q_P = \Delta H}$$

**Note:**

**U**: is a state function, **P.V**: is a state function, so **H** is a state function

### Heat capacity :

Mass or molar heat capacity or mass or molar specific heat is the heat required to raise the temperature of a unit mass or mole of a substance by one degree.

It is measured at constant pressure ($C_P$) or constant volume ($C_V$).

The heat capacities $C_p$ and $C_V$ of a pure body are respectively the derivatives of its enthalpy and internal energy with respect to temperature:

$$C_P = \left[\frac{\delta Q}{dT}\right]_P = \frac{\delta Q_p}{dT} = \frac{dH}{dT}$$
$$C_V = \left[\frac{\delta Q}{dT}\right]_V = \frac{\delta Q_V}{dT} = \frac{dU}{dT}$$

The amount of heat required to raise the temperature of 'n' moles of 1 pure substance from $T_1$ to $T_2$ is:

At: P = Cte: $\delta Q_P = dH = n.C_P.dT \Longrightarrow \Delta H = Q_P =$

$$\boldsymbol{\Delta H = n \int_{T_1}^{T_2} C_p.\, dT}$$

At : V = Cte : $\delta Q_V = dU = n.C_V.dT \Longrightarrow \Delta U = Q_V =$

$$\boldsymbol{\Delta \mathrm{U} = n \int_{T_1}^{T_2} C_V.\, dT}$$

The amount of heat required to raise the temperature of 'm' grammes of 1 pure substance from $T_1$ to $T_2$ is:

***At: P = Cte:*** $\Delta H = Q_P \ = m\int_{T_1}^{T_2} C_p.dT$

***At: V = Cte***: $\Delta U = QV = m \ \int_{T_1}^{T_2} C_v.dT$

**Note:**

Both $C_p$ and $C_V$ functions relate to temperature in shape: $aT^2 + bT + C$

In the case of $C_p$ and $C_V$ fixed numbers independent of temperature, it can be written:

$$\boldsymbol{\Delta \mathrm{U} = \mathrm{n}\, C_V.\Delta T, \Delta \mathrm{H} = \mathrm{n}\, C_p.\Delta T}$$

### Relation between $C_P$ and $C_V$ (MAYER relation):

We have: $dH = dU + d(P.V)$….(1)

$dH = n.C_P.\ dT$ ….(2)

$dU = n.C_V\ dT$ ….(3)

By exploiting equations: (1), (2) and (3) :

$dH = dU + d(PV) \Longrightarrow n.Cp.\ dT = n.Cv\ dT + d(PV)$ ; ( $P.V = n.\ R.T$)

$\Longrightarrow n.Cp.\ dT = n.Cv\ dT + d(n.R.T) = n.Cv\ dT + nRdT$ (ividing by 'n dT')

so we'll have: $Cp = Cv + R \Longrightarrow$ **Cp – Cv = R** **MAYER Relation**

- γ is the ratio between $C_p$ *and* $C_v$

$\boldsymbol{\gamma = \frac{C_p}{C_v}}$ ( γ is called the adiabatic constant).

## c)- Isothermal transformation (T = cte):

Characteristic equation

In Initial state: $P_1.V_1 = n.\ R.T$ ….. (1)

In the final state: $P_2.V_2 = n.\ R.T$….(2)

Expression of work

$$\mathrm{P} \ \neq \ \mathrm{Cte}\ and\ \mathrm{P.V} \ = \ \mathrm{n.R.T} \Rightarrow \mathrm{P} = \frac{nRT}{V} \dots\dots\dots\dots (2)$$

Replacing (2) in (1) gives:

$$W = -\int_1^2 \mathrm{n.R.T.}\frac{dV}{V} = -nRT\ ln\ \frac{V_2}{V_1} = -nRT\ ln\ \frac{P_1}{P_2}\ ;\ \left(Since\ \ \frac{P_1}{P_2} = \frac{V_2}{V_1}\right)$$

Expression of heat quantity:

$$W = -nRT\,ln\frac{V_2}{V_1}$$

$$W = -nRT\,ln\frac{P_1}{P_2}$$

Since U = f (T): so ΔU = 0 ⟹ Q +W = 0 ⟹ Q = − W

$$\boldsymbol{Q = nRT\,ln\frac{V_2}{V_1}}$$

$$\boldsymbol{Q = nRT\,ln\frac{P_1}{P_2}}$$

Expression of internal energy:

Since U = f (T): so **ΔU = 0**

Expression of enthalpy:

Since H = f (T): so **ΔH = 0**

**d)- Adiabatic transformation (Q = 0):**

An adiabatic transformation is one that takes place without any change in heat (**Q = 0**).

We have:

$$dU = \delta Q + \delta W = 0 + \delta W \Longrightarrow dU = \delta W = -PdV$$

$$\Delta U = W = \int nC_V dT = -\int PdV$$

This equation can be written:

$$nC_V dT = -PdV$$

According to the ideal gas relationship:

$$nC_V dT = -\frac{nRT}{V}dV$$

$$\frac{dT}{T} = -\frac{R}{C_V}.\frac{dV}{V}$$

According to Meyer's relationship

$$C_p - C_V = R$$

Dividing both sides of the equation by $C_V$:

$$\frac{C_P - C_V}{C_V} = \frac{R}{C_V} = \frac{C_P}{C_V} - 1 = \gamma - 1$$

So:

$$\frac{dT}{T} = -(\gamma - 1)\frac{dV}{V}$$

By integration we get:

$$\text{Ln T} + \ln \text{V}^{\gamma-1} = K \Longrightarrow T\ \text{V}^{\gamma-1} = K'$$

During reversible adiabatic transformation, $T\ \text{V}^{\gamma-1}$ the remains constant and writes the previous relationship:

$$\boldsymbol{T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}}$$

***It's the first equation of Laplace.***

The adiabatic equation of state can also be described:

- Temperature as a function of volume;
- Pressure as a function of volume.
- We have: P.V = n.R.T $\Longrightarrow V = \frac{nRT}{P}$

By replacing in the relation:

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

We get ***the second equation of Laplace:***

$$\boldsymbol{T_i^{\gamma} P_i^{1-\gamma} = T_f^{\gamma} P_f^{1-\gamma}}$$

- We have: P.V = n.R.T $\Longrightarrow T = \frac{PV}{nR}$

By replacing in the relation:

$$\boldsymbol{T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}}$$

We get ***the third equation of Laplace:***

$$\boldsymbol{P_i V_i^{\gamma} = P_f V_f^{\gamma}}$$

**Expression of adiabatic transformation work:** Based on the first principle of Thermodynamics:

$$\delta U = \delta Q + \delta W = \delta W$$

$As\ Q = 0$:

$$W = \Delta U = \int_{T_f}^{T_i} nC_V dT = nC_V(T_f - T_i)$$

With compensation we find: $$T_f = \frac{P_f V_f}{nR}, T_i = \frac{P_i V_i}{nR}$$

$$W = nC_V\left(\frac{P_f V_f}{nR} - \frac{P_i V_i}{nR}\right)$$

$$\frac{C_V}{R} = (\gamma - 1)^{-1}$$

$$\boldsymbol{W_{ad} = \frac{1}{\gamma - 1}(P_f V_f - P_i V_i)}$$

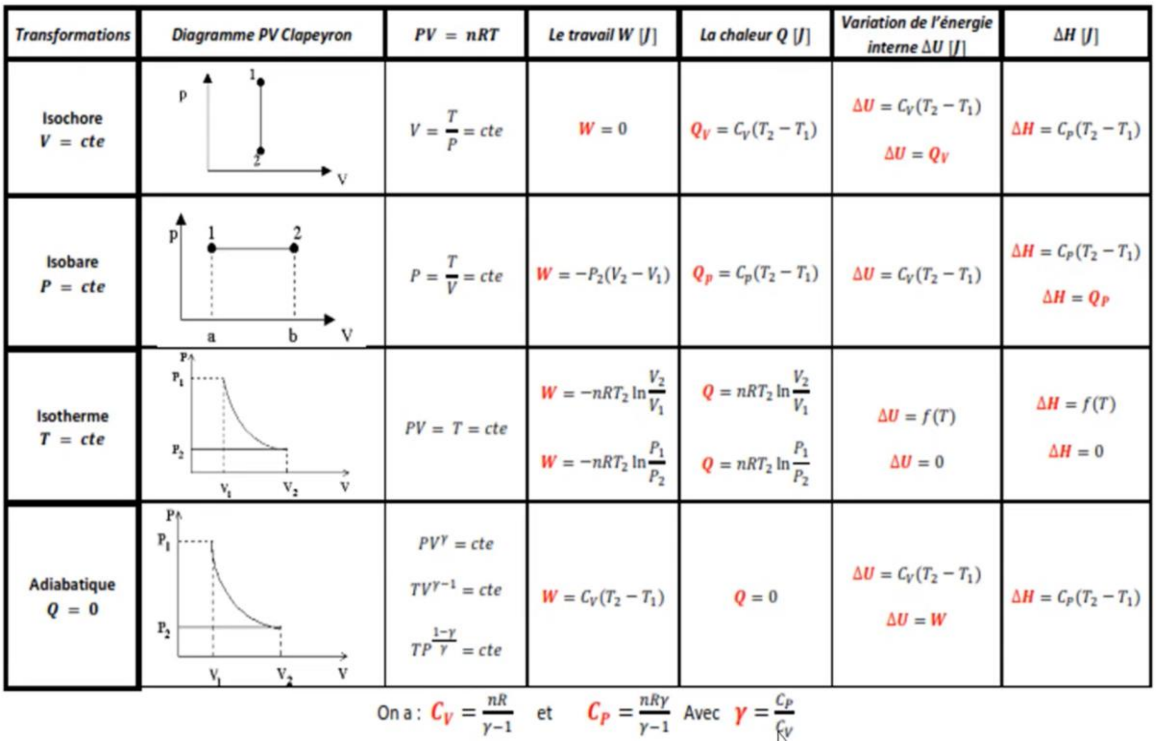
***Note:***

For diatomic gases: **γ = 7/5 = 1,4**

For monoatomic gases: **γ = 5/3 = 1,66**

The following table shows recipes for calculating *Q*, *W*, Δ*U*, and Δ*H* for an ideal gas undergoing a reversible change along the specified pathway.

***Table 1:*** Thermodynamics Properties for a Reversible Expansion or Compression.



| *Transformations* | *Diagramme PV Clapeyron* | $PV = nRT$ | *Le travail W [J]* | *La chaleur Q [J]* | *Variation de l'énergie interne ΔU [J]* | *ΔH [J]* |
|---|---|---|---|---|---|---|
| **Isochore**<br>$V = cte$ | p 1 2 V | $V = \frac{T}{P} = cte$ | $W = 0$ | $Q_V = C_V(T_2 - T_1)$ | $\Delta U = C_V(T_2 - T_1)$<br>$\Delta U = Q_V$ | $\Delta H = C_p(T_2 - T_1)$ |
| **Isobare**<br>$P = cte$ | p 1 2 a b V | $P = \frac{T}{V} = cte$ | $W = -P_2(V_2 - V_1)$ | $Q_p = C_p(T_2 - T_1)$ | $\Delta U = C_V(T_2 - T_1)$ | $\Delta H = C_P(T_2 - T_1)$<br>$\Delta H = Q_P$ |
| **Isotherme**<br>$T = cte$ | P P₁ P₂ V₁ V₂ V | $PV = T = cte$ | $W = -nRT_2 \ln\frac{V_2}{V_1}$<br>$W = -nRT_2 \ln\frac{P_1}{P_2}$ | $Q = nRT_2 \ln\frac{V_2}{V_1}$<br>$Q = nRT_2 \ln\frac{P_1}{P_2}$ | $\Delta U = f(T)$<br>$\Delta U = 0$ | $\Delta H = f(T)$<br>$\Delta H = 0$ |
| **Adiabatique**<br>$Q = 0$ | P P₁ P₂ V₁ V₂ V | $PV^\gamma = cte$<br>$TV^{\gamma-1} = cte$<br>$TP^{\frac{1-\gamma}{\gamma}} = cte$ | $W = C_V(T_2 - T_1)$ | $Q = 0$ | $\Delta U = C_V(T_2 - T_1)$<br>$\Delta U = W$ | $\Delta H = C_P(T_2 - T_1)$ |

On a : $C_V = \frac{nR}{\gamma - 1}$ et $C_P = \frac{nR\gamma}{\gamma - 1}$ Avec $\gamma = \frac{C_P}{C_V}$

For the ring:

$$\Delta U_{cycle} = \Delta H_{cycle} = 0$$

$$Q_{cycle} = \sum Q = -W_{cycle}$$

## Thermochemistry:

Thermochemistry is the study of the heat evolved (exothermic process) or heat absorbed (endothermic process) in chemical reactions. Thermochemistry, generally, is concerned with the heat exchange accompanying transformations, such as mixing, phase transitions, chemical reactions, etc., which include calculations of such quantities as the heat capacity, heat of combustion, heat of formation, etc.

## Changing State:

Changing state is the term used to describe the process of one state of matter (solid, liquid or gas) changing to another. An everyday example of this is ice melting. This is a solid (ice) changing state to become liquid (water). States of matter change when their particles either gain or lose energy; this can be due to a change in temperature. If it gets warmer, particles gain energy; if it gets colder, they lose energy. The important thing to remember is matter cannot be destroyed; it can only change. There are six changes of state possible between solids, liquids and gases:

- **Melting** is when a solid changes to a liquid.
- **Freezing** is when a liquid changes to a solid.
- **Evaporation** (or vaporization) is when a liquid changes to a gas.
- **Condensation** is when a gas changes to a liquid.
- **Sublimation** is when a solid changes to a gas.
- **Deposition** is when a gas changes to a solid.

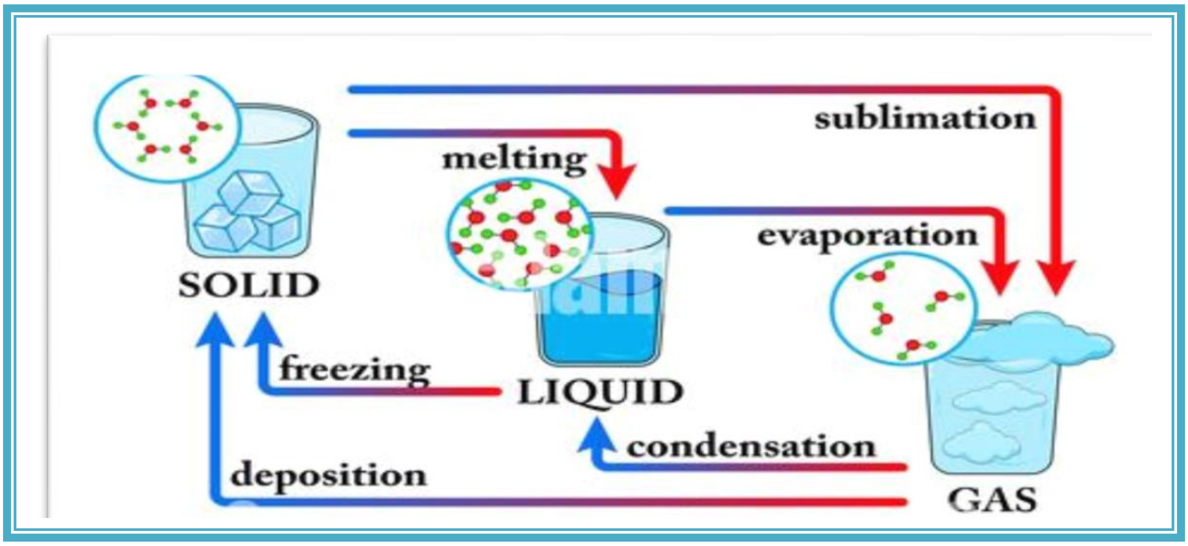


***Figure*: Changing state of matter**

## Types of enthalpy

### Enthalpy changes phase:

Enthalpy changes phase or latent heat, energy absorbed or released by a substance during a change in its physical state (phase) that occurs without changing its temperature. The latent heat associated with melting a solid or freezing a liquid is called the **heat of fusion**; that associated with vaporizing a liquid or a solid or condensing a vapor is called the **heat of vaporization**. The latent heat is normally expressed as the amount of heat (in units of joules or calories) per mole or unit mass of the substance undergoing a change of state.

Continuous heating of pure solid results in transformations represented in the following figure 2:

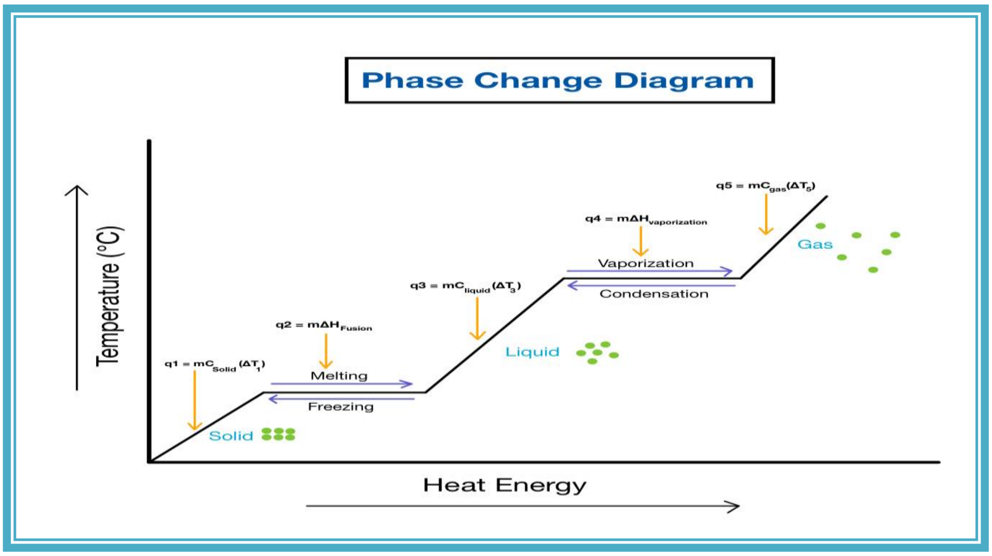


***Figure:*** ***Enthalpy changes phase***

- **Enthalpy of fusion ($\Delta H_{fus}$) (or Latent Heat of fusion):** change in enthalpy due to fusion (melting) of 1 mol of a substance.
- **Enthalpy of vaporization ($\Delta H_{vap}$) (or Latent Heat of vaporization):** change in enthalpy due to vaporizing (liquid to gas) of 1 mol of a substance.
- **Enthalpy of condensation ($\Delta H_{cond}$) (or Latent Heat of condensation):** change in enthalpy due to condensation of 1 mol of a substance, condensation is the polar opposite of evaporation.

$$\Delta H_{cond} = - \Delta H_{vap}$$

- **Enthalpy of solidification ($\Delta H_{solid}$) ( or Latent Heat of solidification):** change in enthalpy due to solidification (freezing) of 1 mol of a substance.

$$\Delta H_{solid} = - \Delta H_{fus}$$

### The standard enthalpy of formation $\Delta H^{\circ}_{f}$

The standard enthalpy of formation is the enthalpy change for the formation of 1 mol of a compound from its elements. These elements are in their standard state, which is the most stable form of the element at 1 atm and 298 K. Here is an example:

$$C + O2 \rightarrow CO2 \quad \Delta H^{\circ}_{f} = -393.5 \text{ kJ/mol}$$

Here is a table of some common standard enthalpies of formation:

| Compound | $\Delta H^{\circ}_{f}$ (kJ/mol) |
|---|---|
| $CO_{(g)}$ | -393.5 |
| $H_2O_{(g)}$ | -241.8 |
| $H_2O_{(l)}$ | -285.8 |
| $NaCl_{(s)}$ | -411.0 |
| $NH_{3\,(g)}$ | -46.2 |
| $NO_{2\,(g)}$ | 33.9 |

The standard enthalpy is dependent on the state (ex: solid/liquid/gas) of the molecule. As you'll see above, the standard enthalpy for water as a liquid and as a gas is different. In addition, The heat of formation ($\Delta H_f^{\circ}$) of an element in its standard state is zero. This is because it doesn't take any energy to form a naturally occurring compound (there is no reaction). A pure element in its standard state has a standard enthalpy of formation of zero.

$$\Delta H^{\circ}_{f}(H_2) = \Delta H^{\circ}_{f}(O_2) = \Delta H^{\circ}_{f}(N_2) = \Delta H^{\circ}_{f}(C) = 0$$

## Relation between internal energy enthalpy:

The following relation can be established between the standard enthalpy of a reaction and the variation in standard internal energy:

$$aA_{(g)} + bB_{(g)} \rightarrow cC_{(g)} + dD_{(g)}$$

$$P_1, V_1, T, n_1 = a + b \; P_2, V_2, T, n_2 = c + d$$

$$U_1,\; H_1 \; U_2,\; H_2$$

$$\Delta H = H_2 - H_1 = (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

$$\Delta H = \Delta U + (P_2V_2 - P_1V_1)$$

We have: $P_1V_1 = n_1RT$, $P_2V_2 = n_2RT$

Compensation in the previous equation we find:

$$\Delta H = \Delta U + (n_2RT - n_1RT)$$

$$\boxed{\Delta H = \Delta U + \Delta n_g RT}$$

***Important:*** $\Delta n_g$ calculated only for gaseous materials.

## Heat of a reaction:

We have the next chemical reaction:

$$\boldsymbol{aA + bB \rightarrow cC + dD}$$

Reactants products

Heat of a reaction is defined as the amount of heat absorbed or evolved at a given temperature when the reactants have combined to form the products is represented by balanced chemical equation.

When the reaction evolves energy in the form of heat, it called exothermic reaction and when the reactants absorb heat energy from the surroundings to form products, the reaction called endothermic reaction.

- If the reaction happens at constant volume, the heat of the reaction called constant volume heat $Q_V$.

$$Q_V = \Delta U_v$$

This quantity ($\Delta U_v$), called the change in internal energy of reaction, is the heat of reaction at constant volume.

- If the reaction occurs at constant pressure, the heat of the reaction called heat at constant pressure $Q_P$.

$$Q_P = \Delta H$$

This quantity ($\Delta H$), called the change in enthalpy of reaction, is the heat of reaction at constant pressure.

## Enthalpy of Reaction

### a. Definition:

The **enthalpy of reaction ($\Delta H_R$)** is the change in enthalpy due to a chemical reaction.

If $\Delta H_R > 0$, the reaction is **endothermic** (the system pulls in heat from its surroundings)

If $\Delta H_R < 0$, the reaction is **exothermic** (the system releases heat into its surroundings).

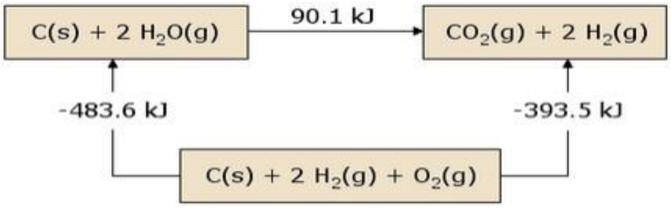
### b. Measurement of Enthalpy of chemical reaction:

#### a-direct method:

The experimental technique known as calorimetry is used to assess enthalpy and internal energy in most cases. Calorimetry is based on thermometric methods that are carried out in a calorimeter that is immersed in a known volume of liquid. The heat released during the process is typically computed using known heat capacities of the liquid and temperature changes measured by the calorimeter.

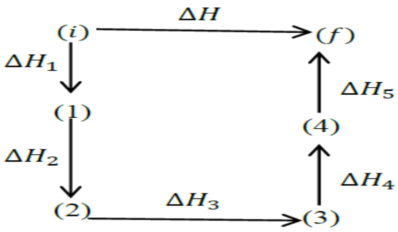
### b-Indirect method; Hess's law:

**Hess's law**, rule first enunciated by Germain Henri Hess, stating that the heat absorbed or evolved (or the change in enthalpy) in any chemical reaction is a fixed quantity and is independent of the path of the reaction or the number of steps taken to obtain the reaction. Hess's law can be written as $\Delta H° = \Sigma\Delta H_n$, where $\Delta H°$ is the heat absorbed or evolved and $\Sigma\Delta H_n$ is the sum of the heat absorbed or evolved in the individual *n* steps of the reaction. Hess's law is a consequence of the first law of thermodynamics and need not be considered a separate thermodynamic law; in thermochemistry, however, it retains its identity because of its importance as the basis for calculating heats of reactions. In figure 3, the reactants C(s) + 2 $H_2O$(g) are placed together in a box, representing the state of the materials involved in the reaction prior to the reaction. The products $CO_2$(g) + 2 $H_2$(g) are placed together in a second box representing the state of the materials involved after the reaction. The reaction arrow connecting these boxes is labeled with the heat of this reaction. Now we take these same materials and place them in a third box containing C(s), $O_2$(g), and 2 $H_2$(g). This box is connected to the reactant and product boxes with reaction arrows, labeled by the heats of reaction in equation [3] and equation [4].



***Equation 3***

## *In general*



$$\Delta H\}_i^f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$$

***Equation 4***

This includes, in general, all reactions: Enthalpy of chemical reaction is equal to the total standard enthalpy of formation of products minus the total standard enthalpy of formation of reactants.

$$\Delta H°_R = \sum n_p\,(\Delta H°_f)_p - \sum n_R\,(\Delta H°_f)_R$$

$$aA + bB \xrightarrow{\Delta H°_R} cC + dD$$

$$\Delta H°_R = [c\,\Delta H°_{f(C)} + d\,\Delta H°_{f(D)}] - [a\,\Delta H°_{f(A)} + b\,\Delta H°_{f(B)}]$$

**Example**: Calculate $\Delta H_R°$ for the following reaction:

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(S)}$$

We have:

$$\Delta H°_{(NH_{3(g)})} = -46{,}9\ KJ.mol^{-1},\ \Delta H°_{(HCl)} = -92{,}3\ KJ.mol^{-1}$$

$$\Delta H°_{(NH_4Cl_{(S)})} = -314{,}4\ KJ.mol^{-1}$$

According to the Hess law:

$$\begin{tikzcd}
NH_{3(g)} + HCl_{(g)} \arrow[rr, "\Delta H°_R"] & & NH_4Cl_{(S)} \\
& \frac{1}{2} N_{2(g)} + 2\,H_{2(g)} + \frac{1}{2} Cl_{2(g)} \arrow[ul, "\Delta H°_{(NH_{3(g)})} + \Delta H°_{f(HCl_{(g)})}"] \arrow[ur, "\Delta H°_{f\ NH_4Cl_{(S)}}"'] &
\end{tikzcd}$$

$$\Delta H°_R = \Delta H°_{(NH_4Cl_{(S)})} - [\Delta H°_{f(NH_{3(g)})} + \Delta H°_{f(HCl_{(g)})}]$$

$$\Delta H°_R = -314{,}4 - (-46{,}9 - 92{,}3) = -175{,}2\ \text{KJ}$$

This includes, in general, all reactions: enthalpy of chemical reaction is equal to the total standard enthalpy of formation of products minus the total standard enthalpy of formation of reactant

## Relation between enthalpy and bond energy:

Bond enthalpy and enthalpy of reaction help us understand how a chemical system uses energy during reactions. The bond enthalpy describes how much energy is needed to break or form a bond, and it is also a measure of bond strength. By combining the bond enthalpy values for all of the bonds broken and formed during a reaction, it's possible to estimate the total change in potential energy of the system, which is $\Delta H_R$ for a reaction at constant pressure. Depending on whether the enthalpy of reaction is positive or negative, we can determine whether a reaction will be endothermic or exothermic. $\mathbf{E_d = -E_l}$

$$\Delta H_f = \Delta H_1 + \Delta H_2 = \sum E_d + \sum E_l$$

$$= \sum -E_{l(\text{متفاعلات})} + \sum E_{l(\text{نواتج})}$$

$$= \sum E_{l(\text{نواتج})} - \sum E_{l(\text{متفاعلات})}$$

$$\Delta H_f = \sum E_{l(\text{نواتج})} - \sum E_{l(\text{متفاعلات})}$$

## Effect of Temperature on Heat of Reaction: (The Kirchhoff Equation)

***KIRCHHOFF's*** law involves determining the enthalpy of reaction at a temperature different from that of the standard state.

Kirchhoff's Equation is equality expressing the temperature dependence of the thermal quantities linked with a chemical reaction through the difference in heat capacities between the products and reactants. The same reaction, when carried at dissimilar temperatures, the enthalpies of reaction are also different.

We have the next chemical reaction:

$$aA + bB \rightarrow cC + dD$$

$$\Delta H_R = \sum n_p \left(\Delta H^\circ{}_f\right)_p - \sum n_R \left(\Delta H^\circ{}_f\right)_R$$

$$\Delta H_R = d\Delta H(D) + c\Delta H(C) - a\Delta H(A) - b\Delta H(B)$$

We know that:

$$C_P = \left(\frac{d\Delta H}{dT}\right)_p$$

By deriving the previous equation for T:

$$\frac{d\Delta H_R}{dT} = \frac{d}{dT}\left[\sum n_p \,(\Delta H)_p - \sum n_R \,(\Delta H)_R\right]$$

$$= \sum n_{P\,(produits)} - \sum n_{R\,(réactifs)}$$

$$\frac{d\Delta H_R}{dT} = \Delta nC_P \ldots\ldots\ldots..(1)$$

$$\Delta nC_P = dC_P(D) + cC_P(C) - aC_P(A) - bC_P(B)$$

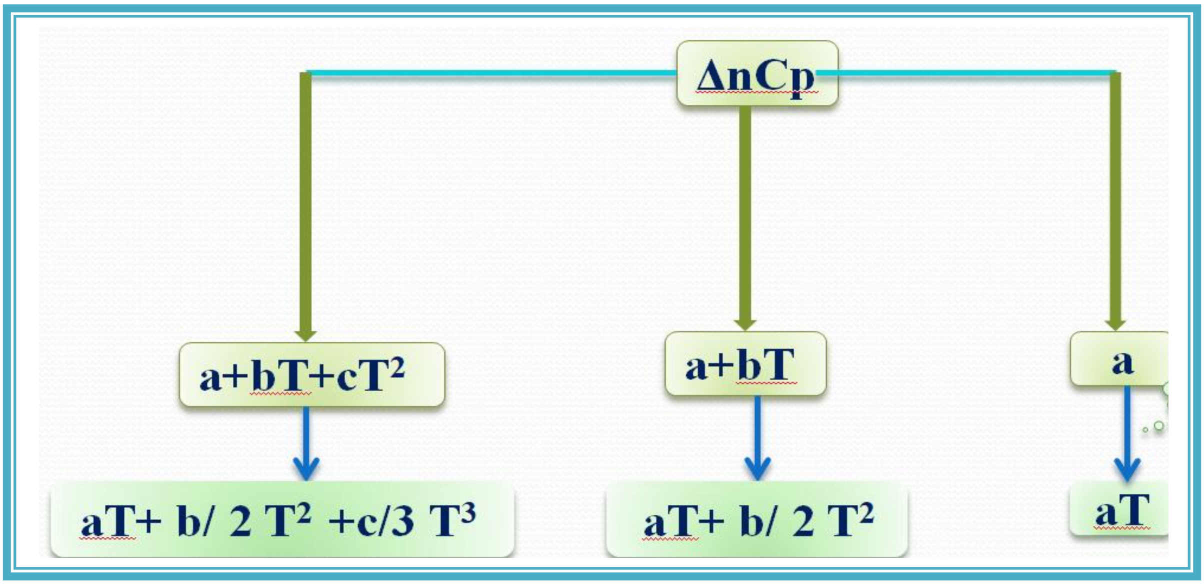
By integrating relationship (1) we find:

$$\int_{\Delta H_{T_0}}^{\Delta H_T} d\,(\Delta H_R) = \int_{T_0}^{T} \Delta nC_P \,dT$$

$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^{T} \Delta nC_P \,dT$$

Similarly, it may be shown that if the process is carried out at constant volume the relationship is:

$$\Delta U_T = \Delta U_{T_0} + \int_{T_0}^{T} \Delta nC_V \,dT$$



## Second principle of thermodynamics:

The first principle of thermodynamics, which states the conservation of energy, allows for the assessment of the energy balance of systems. If, for instance, an exchange of heat takes place between two systems of different temperature, the first principle demands that the quantity of heat given out by the one system shall be equal to that taken up by the other. Whether the flow of heat, however, takes place from the colder to the hotter system, or vice versa, cannot be answered by the first principle alone. Thus, we appeal to the second principle which is a principle of evolution that allows for predicting the direction in which a process takes place in nature.

A hot substance is brought into contact with a cold substance; after some time, it's observed that both temperatures equalize ($T_{eq}$). Heat is transferred spontaneously from the hotter substance to the colder substance until equilibrium is reached. A gas contained in one recipient is brought into contact with another empty recipient. It is observed that the gas spontaneously occupies the entire volume offered to it. When a piece of sugar is submerged in a glass of water, it spontaneously dissolves. These transformations are spontaneous (natural). The spontaneous transformation occurs in a well-defined direction; the reverse transformation is never observed (irreversible transformation).

The second principle introduces a new state function called "entropy" denoted by "**S**" which measures the degree of disorder of a system. Entropy is a scientific concept, as well as a measurable physical property and It is an extensive property of a thermodynamic system. Entropy is a measure of the randomness of the system, or it is the measure of energy or chaos within an isolated system, a highly ordered system has low entropy. It is expressed in units: **cal/K, J/K**. The entropy change of a system is given by:

$$dS = \partial S_e + \partial S_c = \frac{\partial Q}{\partial T} + \partial S_c$$

After integration:

$$\Delta S\text{system} = Se + Sc = \int_1^2 \frac{\partial Q}{\partial T} + Sc$$

**∂Q**: quantity of heat exchanged between the system and the surroundings.

**T**: temperature of the surroundings.

**Se**: entropy exchanged between the system and the surroundings.

**Sc**: entropy created within the system; $Sc \geq 0$.

**Sc = 0**; If the transformation is reversible.

**Sc** > **0**; If the transformation is irreversible.

The change in entropy **($\Delta S$)** is equal to the heat transfer **(Q)** divided by the temperature **(T).**

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

## Text of second law of thermodynamics:

The entropy of the universe increases in a spontaneous process and stays the same in an equilibrium process.

Mathematically, the second law of thermodynamics is represented as:

- ***For an non equilibrium process:*** $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$
- ***For an equilibrium process:*** $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0$

There is no possible process where the entropy of the universe decreases. It’s possible for the entropy of a system to decrease, but that results in greater corresponding entropy increase in the rest of the universe.

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

## Properties of Entropy:

**Thermodynamic function:** Entropy is a thermodynamic function, which means it is a property of the system's state and not a property of the process.

**State function:** Entropy is a state function, meaning it depends only on the system's current state and not on the path taken to reach that state. This property ensures that the second law of thermodynamics is obeyed.

***Monotonicity:*** Entropy is monotonic for adiabatic availability, meaning that it increases in a spontaneous process and decreases in a non-spontaneous process. This property is crucial for understanding the direction of change in a system.

***Additivity on composite systems:*** Entropy is additive on composite systems, meaning that a system's entropy of multiple parts is the sum of the entropies of its individual parts. This property helps analyze the behavior of complex systems.

***Extensivity:*** Entropy is extensive, meaning that it scales with the size or extent of a system. This property implies that the entropy of a large system is much larger than that of a small system.

Since, the state of a cyclic process does not change; the change in entropy is zero.

For an irreversible or spontaneous process, the change in total entropy is greater than 0.

## Change in entropy for Perfect Gas:

### *Entropy as a function of (V, T):*

According to the first principle: dU = δQ + δw; with, δW = - PdV

According to the second principle: dS = dQ/T

$$\Longrightarrow \ dQ = T\,dS$$

$$nCvdT = TdS - PdV$$

$$dS = \frac{nCvdT}{T} + \frac{PdV}{T}, \qquad \frac{P}{T} = \frac{nR}{V}$$

$$dS = n\,[Cv\frac{dT}{T} + R\frac{dV}{V}] \ldots\ldots\ldots\ldots\ldots.(\mathbf{1})$$

*If **$C_V$** is constant:*

$$\Delta S = n\,[C_v ln\frac{T_2}{T_1} + Rln\frac{V_2}{V_1}]$$

This relationship is generally valid for all transformations:

*If **T** is constant:*

$$\Delta S = nRln\frac{V_2}{V_1}$$

*If **V** is constant:*

$$\Delta S = nC_v ln\frac{T_2}{T_1}$$

### *Entropy as a function of (P, T):*

For a perfect gas: PV = n RT

d(PV) = d (nRT)

P dV + V dP = n R dT

dividing by PV we find:

$$\frac{dV}{V}+\frac{dP}{P}=\frac{nRdT}{nRT}=\frac{dT}{T}$$

$$\frac{dV}{V}=\frac{dT}{T}-\frac{dP}{P}$$

By replacing relation $\frac{dV}{V}$ in equation (1) we find:

$$\mathrm{dS}=n\,[Cv\frac{dT}{T}+R(\frac{dT}{T}-\frac{dP}{P})]$$

$$\mathrm{dS}=n\,[(Cv+R)\frac{dT}{T}-R\frac{dP}{P}]$$

*If **C<sub></sub>** is constant:*

$$\mathrm{dS}=n\,[C_P\frac{dT}{T}-R\frac{dP}{P}]\ \dots\dots\dots\dots\dots\dots..(\mathbf{2})$$

*If **T** is constant:*

$$\Delta\mathrm{S}=-nRln\frac{P_2}{P_1}$$

*If **P** is constant:*

$$\Delta\mathrm{S}=nC_Pln\frac{T_2}{T_1}$$

## Entropy as a function of (P, V):

By replacing relation $\frac{dT}{T}=\frac{dV}{V}+\frac{dP}{P}$ in equation (1) we find:

$$\mathrm{dS}=n\,[Cv(\frac{dV}{V}+\frac{dP}{P})+R\frac{dV}{V}]$$

$$\mathrm{dS}=n\,[(Cv+R)\frac{dV}{V}+Cv\frac{dP}{P}]$$

$$\mathrm{dS}=n\,[Cp\frac{dV}{V}+Cv\frac{dP}{P}]\ \dots\dots\dots\dots\dots\dots\dots\dots(\mathbf{3})$$

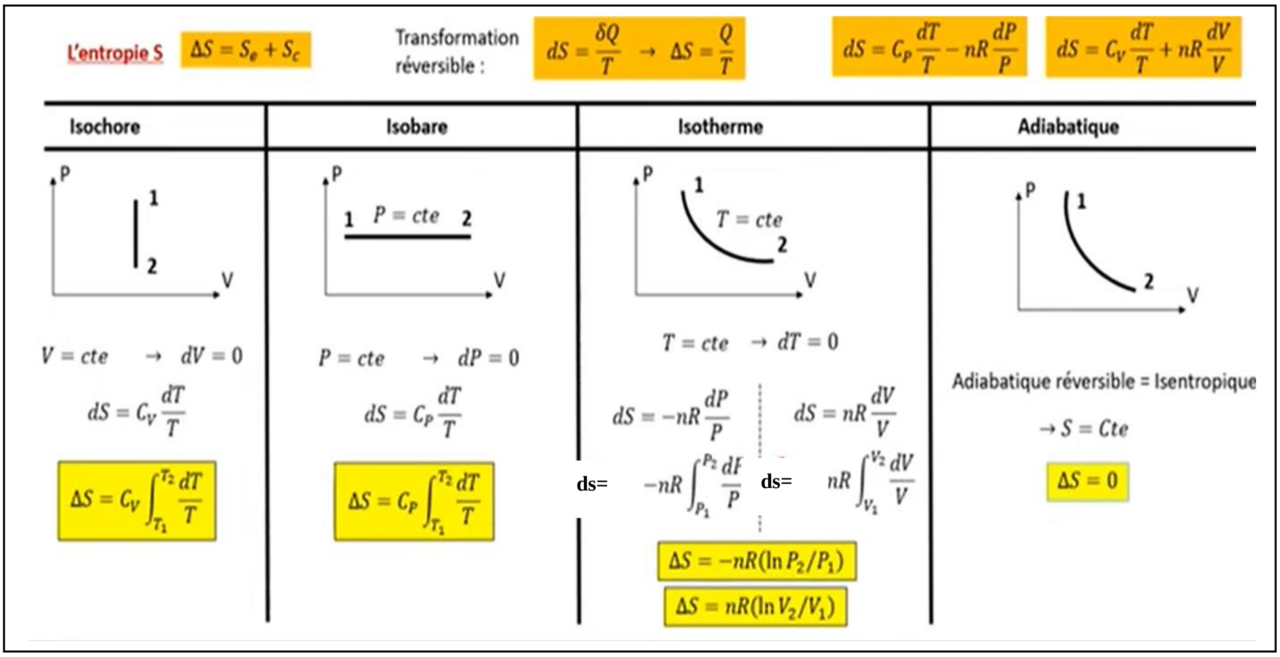
*If **P** is constant:*

$$\Delta\mathrm{S}=nC_Pln\frac{V_2}{V_1}$$

*If **V** is constant:*

$$\Delta S = nC_V ln\frac{P_2}{P_1}$$

***Table 2:***



L'entropie S $\Delta S = S_e + S_c$ Transformation réversible : $dS = \frac{\delta Q}{T} \rightarrow \Delta S = \frac{Q}{T}$ $dS = C_P\frac{dT}{T} - nR\frac{dP}{P}$ $dS = C_V\frac{dT}{T} + nR\frac{dV}{V}$

| Isochore | Isobare | Isotherme | Adiabatique |
|---|---|---|---|
| $V = cte \rightarrow dV = 0$ | $P = cte \rightarrow dP = 0$ | $T = cte \rightarrow dT = 0$ | Adiabatique réversible = Isentropique |
| $dS = C_V\frac{dT}{T}$ | $dS = C_P\frac{dT}{T}$ | $dS = -nR\frac{dP}{P}$ \| $dS = nR\frac{dV}{V}$ | $\rightarrow S = Cte$ |
| $\Delta S = C_V\int_{T_1}^{T_2}\frac{dT}{T}$ | $\Delta S = C_P\int_{T_1}^{T_2}\frac{dT}{T}$ | ds= $-nR\int_{P_1}^{P_2}\frac{dP}{P}$ ds= $nR\int_{V_1}^{V_2}\frac{dV}{V}$<br>$\Delta S = -nR(\ln P_2/P_1)$<br>$\Delta S = nR(\ln V_2/V_1)$ | $\Delta S = 0$ |

## Entropy Changes during a change of state

### Entropy of Fusion:

It is the increase in entropy when a solid melt into liquid. The entropy increases as the freedom of movement of molecules increases with phase change.

The entropy of fusion is equal to the enthalpy of fusion divided by the melting point (fusion temperature): $\Delta \boldsymbol{S}_{fus} = \frac{\Delta \boldsymbol{H}_{fus}}{\boldsymbol{T}_f}$.

A natural process such as a phase transition (for example, fusion) will occur when the associated change in the Gibbs free energy is negative. Most of the time, $\Delta S_{fus}$ is positive.

***Exception:***

Helium-3 has a negative entropy of fusion at temperatures below 0.3 K. Helium-4 also has a very slightly negative entropy of fusion below 0.8 K.

### Entropy of Vaporization:

The entropy of vaporization is a state when there is an increase in entropy as liquid changes into a vapor. This is due to an increase in molecular movement which creates a randomness of motion.

The entropy of vaporization is equal to the enthalpy of vaporization divided by boiling point. It can be represented as: $\Delta \boldsymbol{S}_{vap} = \frac{\Delta \boldsymbol{H}_{vap}}{\boldsymbol{T}_b}$

**Note:**

We can conclude that the **entropy of different states of matter increases as you move from solid to liquid to gas**. The increase in entropy is due to the **increasing disorder** between the molecules in the different states:

- **Solids** have the lowest entropy because their particles are held in an ordered arrangement.
- **Liquids** typically have higher entropy because their particles can move about more randomly.
- **Gases** have the highest entropy out of all three by a significant margin because their particles are free to move about however they like, in a totally disordered way.

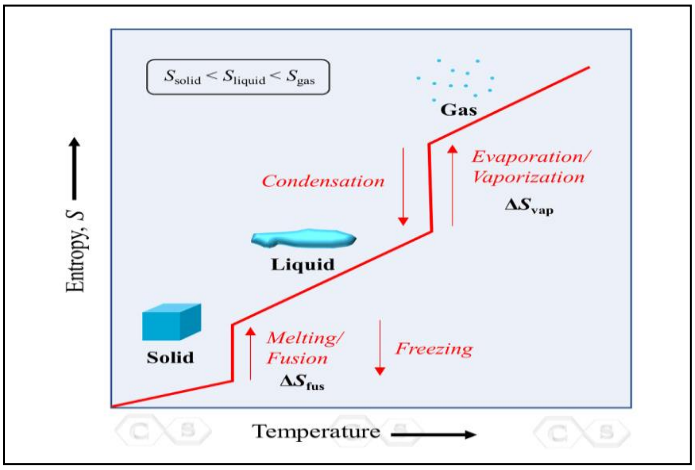


*Figure: Entropy Changes during a change of state*

All the **physical changes of states** are characterized by positive (an *increase* in entropy) or negative (a *decrease* in entropy) entropy changes. You can see the entropy changes of physical processes in the table below:

| **Physical process** | **Entropy change** |
|---|---|
| Melting (solid to liquid) | Positive |
| Boiling (solid to gas) | Positive |
| Freezing (liquid to solid) | Negative |
| Sublimation (solid to gas) | Positive |
| Condensing (gas to liquid) | Negative |

*Table: the entropy changes of physical processes*

**In general:** reactions that feature melting, boiling, or sublimation typically have a positive entropy change, whilst reactions that feature freezing or condensing have a negative entropy change.

## Third Law of Thermodynamics:

You might ask, what is the Third Law of Thermodynamics? In a simple and straight-forward explanation, it states that the entropy of a perfect crystal of a pure substance approaches zero as the temperature approaches absolute zero.

## The Basic Concept of Third Law of Thermodynamics:

The third law of thermodynamics states that the entropy of a pure substance in a perfect crystalline state at zero temperature is zero. The third law of thermodynamics defines that the temperature of a system proceeds towards absolute zero, but its entropy becomes constant, or the change in entropy is zero. The third law of thermodynamics forecasts the behavior of entropy and the properties of a system in a unique environment, known as absolute temperature. This law assists in computing the absolute entropy of a substance at any given temperature. This resoluteness is traditionally based on heat capacity measurements.

## Explanation of Third Law of Thermodynamics:

As the temperature of any system decreases, the atom and molecules in the system lose their energy and approach their lowest energy points, by doing so atom & molecule’s kinetic energy decreases and hence their random motion.

In simple terms, the third law states that the entropy of a perfect crystal of a pure substance approaches zero as the temperature approaches zero. The alignment of a perfect crystal leaves no ambiguity as to the location and orientation of each part of the crystal. As the energy of the crystal is reduced, the vibrations of the individual atoms are reduced to nothing, and the crystal becomes the same everywhere.

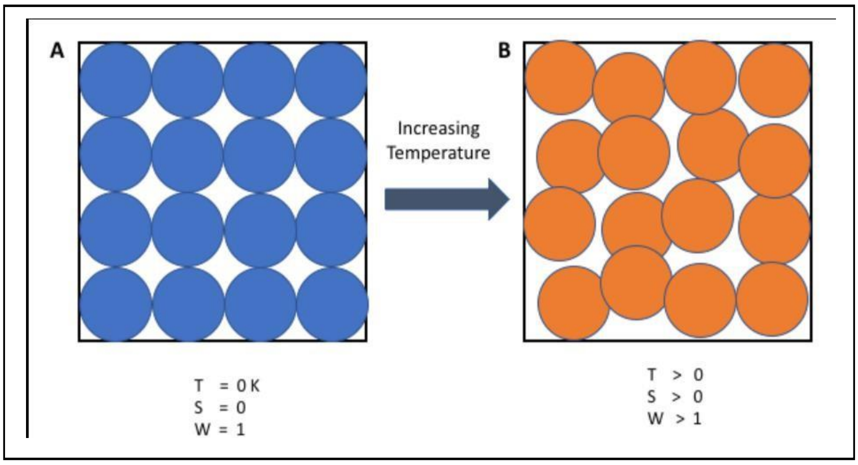


***Figure:***

The third law provides an absolute reference point for the determination of entropy at any other temperature. The entropy of a closed system, determined relative to this zero point, is then the absolute entropy of that system. Mathematically, the absolute entropy of any system at zero temperature is the natural log of the number of ground states times the ***Boltzmann constant*** $k_B = 1.38\times10^{-23}$ J $K^{-1}$.

## Mathematical Application:

Let for any solid $S_{0\,0}$i s entropy at zero kelvin and S is entropy at T kelvin.
So, $\Delta S = S - S_0$

$$\Delta S = \int_0^T \frac{C_p}{T} dt$$

Also, we know Since $S_0 = 0$ at by third law.

$$\boxed{\Delta S = \int_0^T \frac{C_p}{T} dt}$$

So, by this we can calculate the absolute entropy of any solid at temperature T.

## Entropy change in chemical reaction ($\Delta S_R$):

Consider the following chemical reaction:

$$aA + bB \rightarrow cC + dD$$

You should now be able to look at a chemical reaction and predict the entropy change that takes place within the system. In this next section, we will explore one formula, which you can use to calculate this entropy change quantitively. Formed from the elements in the standard state.

The change in entropy of the chemical reaction is equal to the total absolute entropy of all the products, minus the total absolute entropy of all the reactants.
The formula given by the following equation:

$$\boxed{\Delta S^\circ_R = \sum n_p\, S_{porducts} - \sum n_R\, S_{reactants}}$$

The entropy variation of a chemical reaction at a new temperature is given by **KIRCHHOFF's** relation:

$$\boxed{\Delta S_{T_2} = \Delta S_{T_1} + \int_{T_1}^{T_2} \Delta n C_P \frac{dT}{T}}$$

With:

$$\Delta n C_P = \sum n_p \, C_{P_{porducts}} - \sum n_R \, C_{P_{reactants}}$$

## Application of the Third Law of Thermodynamics:

Applying the third law of thermodynamics helps calculate the absolute entropy at any temperature ‘T’ these calculations are based on the heat capacity measurements of the substance.

There are two major applications of the third law of thermodynamics, which are given below.

1. The third law of thermodynamics is used. It helps to find if substances are pure crystalline or not?
2. It helps find the absolute entropy related to substances at a specific temperature.

The third law of thermodynamics refers to perfectly crystalline substances to find whether the substance is pure crystalline or not. It defines the entropy of a perfectly Crystalline substance that might be zero at Kelvin temperature. If the substance is not perfectly crystalline, its entropy will not be zero at 0 Kelvin temperature.

Such substances will not be purely crystalline substances. The substances will be imperfect within their crystal structure and show some disorders. Thus, whether the substances are purely crystalline or not could be found.

To find the absolute entropies of substances at a given temperature, utilizing the third law of thermodynamics. The comparison over entropies of a given substance at T temperature with the entropy of that substance at zero Kelvin temperature. We should estimate the changes within entropies between the temperatures.

## Contradiction with the other laws of Thermodynamics:

The third law of thermodynamics defines absolute zero as a state, whereas the second Law of Thermodynamics denotes that the temperature can never become zero. Based on the second law, the heat cannot spontaneously be moved from a colder body to a hotter body. If a system tries to reach absolute zero, its actual tendency is to draw heat from an external environment, and if it happens. As a result, it will never reach absolute zero.

On the other hand, the first law defines that energy can neither be created nor be destroyed. In that case, the heat energy has to be drawn from outside the system, which ends the chances of the system reaching absolute zero.

## Characteristics of free energy and thermodynamic equilibrium:

We can determine the reversibility of the process by looking at the total entropy change. However, total entropy change is not the system property. We need information on the surrounding and that's not very convenient thermodynamically. We need some system properties that can determine the reversibility. The free energy, such as Gibbs free energy and Helmholtz free energy, is the system property. Under a certain limited condition, their sign can be the criteria for the reversibility equivalent to the total entropy change. We derive at two important free energy functions, the Helmholtz free energy (*F*, *work function*) and the Gibbs free energy (*G*).

### Helmholtz Energy:

In thermodynamics, the Helmholtz free energy (or Helmholtz energy) is a thermodynamic potential that measures the useful work obtainable from a closed thermodynamic system at a constant temperature (isothermal). The change in the Helmholtz energy during a process is equal to the maximum amount of work that the system can perform in a thermodynamic process in which temperature is held constant. At constant temperature, the Helmholtz free energy is minimized at equilibrium.

### *Reversible process:*

According to the first law of thermodynamics:

$$dU = \delta w + \delta Q$$

Where U is the internal energy, $\delta Q$ is the energy added as heat, and $\delta W$ is the work done on the system. The second law of thermodynamics for a reversible process yields: $\delta Qrev = TdS$.

$$V = Cte \;\Rightarrow \delta W = 0\,;\; dU = \delta Q;\;\; \delta Q = TdS \;\Rightarrow\; dU - TdS = 0$$

$$T = Cte \Rightarrow\; dU - Tds = 0 \Rightarrow (U{-}TS){=}0$$

U and S: state functions

$$\boxed{\Delta F = \Delta U - T\Delta S}$$

**If T and V constant**:

$$\boxed{dF = 0 \Rightarrow F_1 = F_2}$$

### *Irreversible process:*

$$\delta Q_{rev} = TdS$$

$V = Cte \;\Rightarrow \delta W = 0\,;\; dU = \delta Q;\;\; \delta Q < TdS \;\Rightarrow\; dU - TdS < 0$

$d(U - TS) < 0 \Rightarrow\; \Delta F < 0 \Rightarrow \boldsymbol{F_1} < \boldsymbol{F_2}$

We define a new state function:

$$F = U - TS \text{ such that } dF \leq 0.$$

We call **F** the ***Helmholtz free energy***.

- At constant T and V the Helmholtz free energy will **decrease** until all possible spontaneous processes have occurred.
- At that point the system will be in equilibrium. The condition for equilibrium is dF = 0.

## Gibbs free energy (Free Energy at Constant T and P):

In thermodynamics, the Gibbs free energy (or Gibbs energy as the recommended name; symbol G is a thermodynamic potential that can be used to calculate the maximum amount of work, other than pressure-volume work, that may be performed by a thermodynamically closed system at constant temperature and pressure. It also provides a necessary condition for processes such as chemical reactions that may occur under these conditions.

### *Reversible process*

According to the first law of thermodynamics:

$$dU = \delta w + \delta Q$$

$$\delta Q_{rev} = TdS$$

$$dU = \delta Q - PdV => \delta Q = dU + PdV = TdS => dU + PdV - TdS = 0$$

$$d(U + PV - TS) = 0 => U + PV = H => d(H - TS) = 0$$

S and H: state functions

$$G = H - TS => \Delta G = \Delta H - T\Delta S = 0,$$

$$\Delta \boldsymbol{G} = \Delta \boldsymbol{H} - \boldsymbol{T}\Delta S$$

**If T and P constant**: $\boldsymbol{dG = 0 => G_1 = G_2}$

### *Irreversible process:*

$$\delta Q_{rev} = TdS$$

$$dU = \delta Q - PdV => \delta Q = dU + PdV < TdS => dU + PdV - TdS < 0$$

$$d(U + PV - TS) < 0 => U + PV = H => d(H - TS) < 0$$

$$\Delta \boldsymbol{G} = \Delta \boldsymbol{H} - \boldsymbol{T}\Delta \boldsymbol{S} < 0$$

**If T and P constant**: $\boldsymbol{dG < 0 => G_1 < G_2}$

Based on the equation $\Delta \boldsymbol{G} = \Delta \boldsymbol{H} - \boldsymbol{T}\Delta \boldsymbol{S}$, we can be predicted if the reaction is spontaneous or not:

|  | **Sign of $\Delta H$** | **Sign of $\Delta S$** | **Sign of $\Delta G$** | **remark** |
|---|---|---|---|---|
| **1** | Negative (-)<br>Exothermic | Positive (+)<br>Endothermic | Always<br>Negative (-) | Reaction is spontaneous at all temperatures |
| **2** | Positive (+)<br>Endothermic | Negative (-)<br>Decrease in entropy | Always<br>Positive (+) | Reaction is non-spontaneous at all temperatures |
| **3** | Negative (-)<br>Exothermic | Positive (+)<br>Decrease in entropy | Depends upon temperature:<br>1) At low temperature $T\Delta S < \Delta H$<br>2) At high temperature at $T > T_i$<br>where, $T_i = \frac{\Delta H}{\Delta S}$ | Reaction is spontaneous at low temperature.<br>Reaction is non-spontaneous at high temperature. |
| **4** | Positive (+)<br>Endothermic | Negative (-)<br>Decrease in entropy | Depends upon temperature:<br>1) At low temperature $T\Delta S < \Delta H$<br>2) At high temperature $T\Delta S > \Delta H$ | Reaction is non-spontaneous at low temperatures<br>Reaction is spontaneous at high temperature |

## Variation of Gibbs free energy:

Starting with Gibb's function:

$$G = H - TS$$

$$dG = dH - TdS - SdT, \quad H = U + PV$$

$$dG = (dU + PdV + VdP) - TdS - SdT$$

$$dU = \delta Q + \delta W = TdS - PdV$$

$$dG = TdS - PdV + PdV + VdP - TdS - SdT$$

$$\Rightarrow \boxed{\mathbf{dG = VdP - SdT}} \quad \ldots\ldots\ldots\ldots\ldots.(1)$$

*If **T** is constant:* $\boxed{dG = VdP}$

*If **P** is constant*: $\boxed{dG = -SdT}$

## Variation Helmholtz free energy:

Starting with free enthalpy function:

$$F = U - TS$$

$$dF = dU - TdS - SdT$$

$$dU = \delta Q + \delta W = TdS - PdV$$

$$dF = TdS - PdV - TdS - SdT$$

$$\Rightarrow \boxed{dF = -PdV - SdT} \dots\dots\dots\dots\dots.(2)$$

*If **T** is constant*: $\boxed{dF = -PdV}$

*If **V** is constant*: $\boxed{dF = -SdT}$

## The change in Gibbs free energy (ΔG) for a chemical reaction:

The change in Gibbs free energy ($\Delta G$) for a chemical reaction at constant temperature (T) and pressure can be calculated:

**Using $\Delta G = \Delta H - T\Delta S$ formula:**

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

**$\Delta G$**: change in Gibbs free energy for the reaction (kJ $mol^{-1}$)

**$\Delta H$**: enthalpy change for the reaction (kJ $mol^{-1}$)

**T**: temperature of the reaction (K)

**$\Delta S$**: change in entropy for the reaction (kJ $K^{-1}$ $mol^{-1}$)

- For a reaction in which the reactants and products are present in their standard states (state at 298.15 K and atmospheric pressure):

$$\boxed{\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}}$$

Where:

**$\Delta G°$:** change in standard Gibbs free energy for the reaction (kJ $mol^{-1}$)

**$\Delta H°$:** standard enthalpy change for the reaction (kJ $mol^{-1}$)

**T:** temperature of the reaction (K)

**$\Delta S°$:** change in standard absolute entropy for the reaction (kJ $K^{-1}$ $mol^{-1}$)

### Using $\Delta G^{\circ}_{f}$ :

The standard free energy of formation $(\Delta G_f^{\circ})$of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K, for example one mole of $Cl_2$ gas at 298.15 K has $\Delta G_f^{\circ} = 0$.

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard enthalpy changes from standard enthalpies of formation using the familiar "products minus reactants" rule:

$$\boxed{\Delta G°_R = \sum n_p\, (\Delta G°f)_{products} - \sum n_R\, (\Delta G°f)_{Reactants}}$$

Where: $n_p$ and $n_R$ are the stoichiometric coefficients of each product and reactant in the balanced chemical equation.

A very large negative ΔG° indicates a strong tendency for products to form spontaneously from reactants; it does not, however, necessarily indicate that the reaction will occur rapidly. To make this determination, we need to evaluate the kinetics of the reaction.

### The Relationship between ΔH and ΔS:

There is a relationship between ΔH and ΔS for a system at one of its phase change temperatures, (melting/freezing or boiling point) students are often required to know. Take for example boiling water at 100°C. At the boiling temperature you actually have liquid and gaseous water in equilibrium with each other. As for any system at equilibrium ΔG = 0 leading to the following derivation:

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

$$\Delta H - T\Delta S$$

$$\Rightarrow T\Delta S = \Delta H$$

$$\boxed{\Delta S = \frac{\Delta H}{T}}$$

It is from this last expression that undergraduate students are presented with equations that relate the freezing temperature to the ΔH and ΔS of fusion and the boiling temperature to the ΔH and ΔS of vaporization:

$$\boxed{\Delta S^{\circ}_{fus} = \frac{\Delta H^{\circ}_{fus}}{T_{fus}}} \qquad \boxed{\Delta S^{\circ}_{vap} = \frac{\Delta H^{\circ}_{vap}}{T_{b}}}$$