4.1. Introduction :

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.

4.2. Natural evolutions "irreversible transformations" :

Examples :

-A hot substance is brought into contact with a cold substance; after some time, it's observed that both temperatures equalize (Teq). 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).

4.3. Statement of the second principle of thermodynamics:

The second principle introduces a new state function called "*entropy*" denoted by "*S*" which measures *the degree of disorder* of a system. It is expressed in units : **cal/K**, **J/K**.

The entropy change of a system is given by:

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

After integration :

$$\Delta S_{sys} = S_e + S_c = \int_1^2 \frac{\partial Q}{T} + S_c$$

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

T: temperature of the surroundings.

S_e: entropy exchanged between the system and the surroundings.

S_c: entropy created within the system.

$S_c \geq 0 \rightarrow$ $\begin{cases} S_c = 0 \text{ ; If the transformation is } \textbf{reversible}. \\ S_c > 0 \text{ ; If the transformation is } \textbf{irreversible}. \end{cases}$

*For a reversible transformation :

$$\Delta S_{sys} = S_e = \int_1^2 \frac{\partial Q_{rev}}{T}$$

*For an irreversible transformation :

$$\Delta S_{sys} = S_e + S_c = \int_1^2 \frac{\partial Q_{irrev}}{T} + S_c$$

4.4. General expression of the second principle of thermodynamics:

The second principle of thermodynamics, in its most general formulation, states that during a spontaneous transformation, the entropy of the universe (system + surroundings) can only increase.

$\Delta S_{tot} = \Delta S_{universe} = \Delta S_{syst} + \Delta S_{surr}$

$\Delta S_{universe} = 0 \implies$ **reversible transformation.**

$\Delta S_{universe} > 0 \implies$ **irreversible transformation.**

4.5. Calculation of the entropy change :

In the case of reversible transformation: $\Delta S = \int_1^2 \frac{\partial Q}{T}$

4.5.1. Entropy of solids and liquids :

In the case of solids and liquids : $\partial Q = n.c.dT$

$\Delta S = \int_1^2 \frac{\partial Q}{T} = \int_{T1}^{T2} \frac{n.c.dT}{T} = n.c \int_{T1}^{T2} \frac{dT}{T} = n.c.Ln\left(\frac{T_2}{T_1}\right)$ $\boxed{\Delta S = n.c.Ln\left(\frac{T_2}{T_1}\right)}$

4.5.2. Entropy of ideal gases :

a) Isochoric transformation:

$\partial Q = n.c_V.dT$

$\Delta S = \int_1^2 \frac{\partial Q}{T} = \int_{T1}^{T2} \frac{n.c_V.dT}{T} = n.c_V \int_{T1}^{T2} \frac{dT}{T} = n.c_V.Ln\left(\frac{T_2}{T_1}\right)$ $\boxed{\Delta S = n.c_V.Ln\left(\frac{T_2}{T_1}\right)}$

b) Isothermal transformation:

$\partial Q = -\partial W = P\,dV = nRT\frac{dV}{V}$

$\Delta S = \int_1^2 \frac{\partial Q}{T} = n.R \int_{V1}^{V2} \frac{dV}{V} = n.R.Ln\left(\frac{V_2}{V_1}\right) = n.R.Ln\left(\frac{P_1}{P_2}\right)$

$\boxed{\Delta S = n\,R\,Ln\left(\frac{V_2}{V_1}\right) = n\,R\,Ln\left(\frac{P_1}{P_2}\right)}$

c) Isobaric transformation:

$\partial Q = n.c_P.dT$

$\Delta S = \int_1^2 \frac{\partial Q}{T} = \int_{T1}^{T2} \frac{n.c_P.dT}{T} = n.c_P \int_{T1}^{T2} \frac{dT}{T} = n.c_P.Ln\left(\frac{T_2}{T_1}\right)$

$\boxed{\Delta S = n.c_P.Ln\left(\frac{T_2}{T_1}\right)}$

d) Adiabatic transformation:

$\partial Q = 0 \rightarrow$ $\boxed{\Delta S = 0}$ (Isentropic)

4.6. Expressions of entropy as a function of (V, T); (P, T) and (P, V):

a) Expression of entropy as a function of V and T:

$dU = \partial Q + \partial W$ with : $\partial Q = T.dS$; and; $\partial W = -P.dV$

Therefore: $dU = T.dS - P.dV \rightarrow dS = \frac{dU}{T} + P\frac{dV}{T}$

We have : $dU = n.c_V.dT$, and, $p = \frac{n.R.T}{V}$

Therefore : $dS = n.c_v.\frac{dT}{T} + n.R\frac{dV}{V}$ $\rightarrow$ $\int_{S1}^{S2} dS = n.c_v.\int_{T1}^{T2}\frac{dT}{T} + n.R.\int_{V1}^{V2}\frac{dV}{V}$

$$\Delta S = S_2 - S_1 = n.c_v \, Ln \left(\frac{T_2}{T_1}\right) + n.R.Ln \left(\frac{V_2}{V_1}\right)$$

b) Expression of entropy as a function of T and P:

$$H = U + P.V \rightarrow dH = dU + d(P.V)$$

$$dH = dU + P.dV + V.dP$$

$$= T.dS - P.dV + P.dV + V.dP$$

$$dH = T.dS + V.dP \rightarrow dS = \frac{dH}{T} - V\frac{dP}{T}$$

We have : $dH = n.c_P.dT$, and, $V = \frac{n.R.T}{P}$

Therefore : $dS = n.c_p.\frac{dT}{T} - n.R\frac{dP}{P}$ $\rightarrow$ $\int_{S1}^{S2} dS = n.c_p.\int_{T1}^{T2}\frac{dT}{T} - n.R.\int_{P1}^{P2}\frac{dP}{P}$

$$\Delta S = S_2 - S_1 = n.c_p \, Ln \left(\frac{T_2}{T_1}\right) - n.R.Ln \left(\frac{p_2}{p_1}\right)$$

c) Expression of entropy as a function of V and P:

$$dS = n.c_v.\frac{dT}{T} + n.R\frac{dV}{V} = n.c_p.\frac{dT}{T} - n.R\frac{dP}{p}$$

$$(c_p - c_v).\frac{dT}{T} = R.\left(\frac{dV}{V} + \frac{dp}{p}\right) \quad ; \text{and} ; c_p - c_V = R \quad ; \text{therefore} : \quad \frac{dT}{T} = \frac{dV}{V} + \frac{dp}{p}$$

$$dS = n.c_p.\frac{dT}{T} - n.R\frac{dp}{p} = n.c_p.\left(\frac{dV}{V} + \frac{dp}{p}\right) - n.R\frac{dp}{p}$$

$$dS = n.c_p.\left(\frac{dV}{V}\right) + n.(c_p - R)\frac{dp}{p} \rightarrow dS = n.c_p.\frac{dv}{v} + n.c_v\frac{dp}{p}$$

$$S = n.c_v.LnP + n.c_p.LnV \quad ; \text{and}: c_p = \gamma.c_V$$

Therefore : $S = n.c_v.LnP + n.\gamma.c_v.LnV \rightarrow S = n.c_v.(LnP + \gamma.LnV)$

$$S = n.c_v.(LnP + LnV^\gamma)$$

$$S = n.c_v.Ln \, (P.V^\gamma)$$

4.7. Entropy of state change:

We know that a state change of a pure substance occurs at constant temperature, hence:

$$\Delta S = \int_1^2 \frac{\partial Q}{T} = \frac{1}{T}\int_1^2 \partial Q = \frac{Q}{T}$$

$$\Delta S = \frac{Q}{T} = \frac{n.L}{T}$$
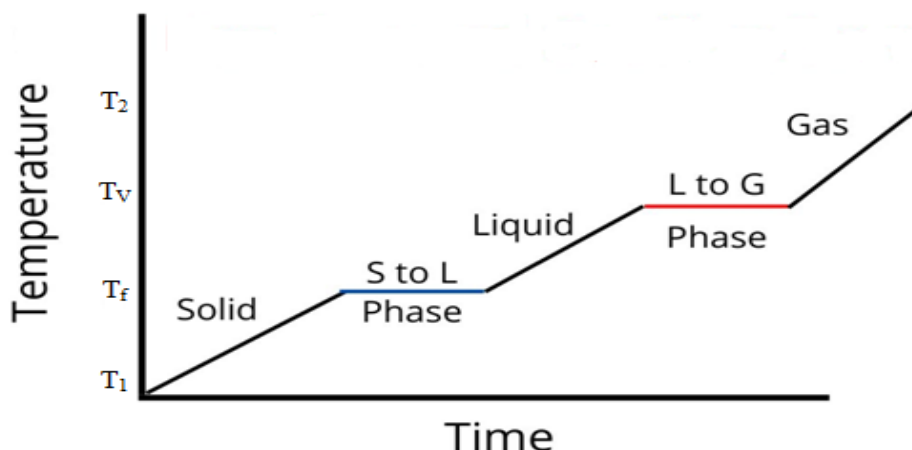
With:

Q: Quantity of heat of state change.

T: Temperature of state change.

Example :

$$\Delta S_{fusion} = \frac{Q_{fusion}}{T_{fusion}} = \frac{n.L_{fusion}}{T_{fusion}}$$

$$\Delta S_{vaporization} = \frac{Q_{vaporization}}{T_{vaporization}} = \frac{n.L_{vaporization}}{T_{vaporization}}$$

*Calculating ΔS during the heating of a pure substance:

Let's consider a pure substance in the solid state characterized by an initial temperature (T_1). It is heated at constant pressure until it reaches the gaseous state characterized by a final temperature (T_2). The entropy change (ΔS) is expressed as:

$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5$

$\Delta S = n.\, c_{P(solid)} Ln\left(\frac{T_{fusion}}{T_1}\right) + \frac{n.L_{fusion}}{T_{fusion}} + n.\, c_{P(liquid)} Ln\left(\frac{T_{vaporization}}{T_{fusion}}\right) + \frac{n.L_{vaporization}}{T_{vaporization}} +$

$n.\, c_{P(gas)} Ln\left(\frac{T_2}{T_{vaporization}}\right)$

4.8. Entropy change of a chemical reaction (Hess's Law):

Consider the following reaction: $a\, A_{(*)} + b\, B_{(*)} \rightarrow c\, C_{(*)} + d\, D_{(*)}$ at standard temperature (T = 298K), the entropy change of the reaction is given by Hess's law:

$\Delta S°_{R,298} = (c.\, S°_{298,C} + d.\, S°_{298,D}) - (a.\, S°_{298,A} + b.\, S°_{298,B})$

In the general case :

$\Delta S°_{R,298} = \Sigma\, (v_j.\, S°_{298,j})\,_{products} - \Sigma\, (v_i.\, S°_{298,i})\,_{reactants}$

v_j: Stoichiometric coefficients of the products.

v_i: Stoichiometric coefficients of the reactants.

$S°_{298}$: Standard molar entropy of the chemical species (cal/K.mol).

4.9. Entropy change of a chemical reaction at temperature T (Kirchhoff's Law):
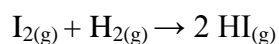
Knowing the standard entropy of the reaction ($\Delta S°_{R,298}$), we can determine the entropy of this reaction at temperature T ($\Delta S°_{R,T}$) using Kirchhoff's law:

$\Delta S°_{R,T} = \Delta S°_{R,298} + \int_{298}^{T} \Delta c_P.\frac{dT}{T}$

<u>With :</u> $\Delta c_P = \Sigma\left(\gamma_j.\, c_{P(j)}\right)_{products} - \Sigma\left(\gamma_i.\, c_{P(i)}\right)_{reactants}$

Exercise :

Consider the following reaction at 298K:

$I_{2(g)} + H_{2(g)} \rightarrow 2\, HI_{(g)}$

Calculate the entropy change during this reaction at 298K and 700K.

Data : at 298K

substance	$I_{2(g)}$	$H_{2(g)}$	$HI_{(g)}$
S° (J/K.mol)	260	130	206
c_p (J/K.mol)	36,86	28,48	29,16

1) According to the Hess's law : $\Delta S°_{R, 298} = \Sigma\ (v_j.\ S°_{298,j})\ _{products} - \Sigma\ (v_i.\ S°_{298,i})\ _{reactants}$

$\Delta S°_{R, 298} = 2.\ S°_{HI} - S°_{I2} - S°_{H2} = 2*206 - 260 - 130 = \textbf{22 J/K}$

2) According to the Kirchhoff's law : $\Delta S°_{R,T} = \Delta S°_{R,298} + \int_{298}^{T} \Delta c_P . \frac{dT}{T}$

$\Delta S°_{R,700} = \Delta S°_{R,298} + \int_{298}^{700} \Delta c_P . \frac{dT}{T} = \Delta S°_{R,298} + \Delta c_P . Ln\left(\frac{700}{298}\right)$

$\Delta c_p = 2.\ c_{p\ (HI)} - c_{p\ (I2)} - c_{p\ (H2)} = 2*29.16 - 36.86 - 28.48 = \textbf{-7,02 J/K}$

$\Delta S°_{R,700} = 22 - 7.02\ Ln\left(\frac{700}{298}\right) = \textbf{16.005 J/K}$

4.10. Statement of the third principle of thermodynamics:

The third principle of thermodynamics states that : **« The entropy of a perfect crystal at a temperature of zero Kelvin (absolute zero) is equal to zero »**

4.11. Absolute molar entropy:

The third principle allows assigning an absolute entropy to any pure substance brought to temperature T. At standard conditions, the absolute molar entropy is denoted as $S°_T$.

$$A \xrightarrow{\ \ \Delta S°\ \ } A$$

Initial state   final state

$T_{initial} = 0K$ $T_{final} = T\ (K)$

$\Delta S° = S°_{final} - S°_{initial} = S°_T\ (A) - S°_0\ (A) = S°_T\ (A) - 0 = S°_T\ (A)$

$S°_T(A)$: Absolute molar entropy at temperature T.

$S°_0(A)$: Absolute molar entropy at temperature T = 0K.

The absolute entropy of a pure substance A at temperature T is the change in its entropy between zero Kelvin and temperature T.