4.1. Irreversibility and evolution of natural phenomena:

The first principle of thermodynamics is a principle of energy conservation, stating that energy cannot be created or destroyed, but only transformed into different forms.

The first principle allows us to assert that the following transformations are possible between two states, A and B.

$A \longrightarrow B \quad \Delta H = H_B - H_A$

$B \longrightarrow A \quad \Delta H = H_A - H_B$

However, experimentation shows that when a transformation is spontaneous (the final state is more stable than the initial state), the reverse transformation does not occur spontaneously.

The first principle does not provide information about the direction of the transformation's evolution; it only allows for the determination of ΔU and ΔH.

Therefore, spontaneous (or natural) transformations are not reversible under the conditions in which they occur.

Example : When a hot body comes into contact with a cold body, heat transfers from the hot body to the cold body until thermal equilibrium is reached. The reverse transformation never occurs spontaneously. However, the first principle of thermodynamics does not prohibit this transformation; it only requires the conservation of energy. In chemistry, it is important to determine the direction of the reaction's evolution. The second principle of thermodynamics is a principle of evolution based on the concept of **entropy.**

4.2. Concept of entropy:

4.2.1. Thermodynamic definition:

Let's consider a closed system that undergoes a transformation from an initial state (A) to a final state (B) while exchanging heat with the external environment at temperature T. We define a new state function called "Entropy," denoted as S, and its variation $\Delta S = S_B - S_A$ is given by the following expressions:

a. **For a reversible transformation:**

$$\Delta S_{syst} = S_B - S_A = \int_A^B \frac{\delta Q_{rev}}{T}$$

b. **For an irreversible transformation:**

$$\Delta S_{syst} > \int_A^B \frac{\delta Q_{irré}}{T}$$

This inequality is called the Clausius inequality.

$$\Delta S_{syst} = S_c + \int_A^B \frac{\delta Q_{irré}}{T}$$

$$\Delta S_{syst} = S_c + S_e$$

$\mathbf{S_c}$: Entropy generated during the evolution

$\mathbf{S_e}$ **:** Entropy accompanying thermal exchanges with the external environment

Note :

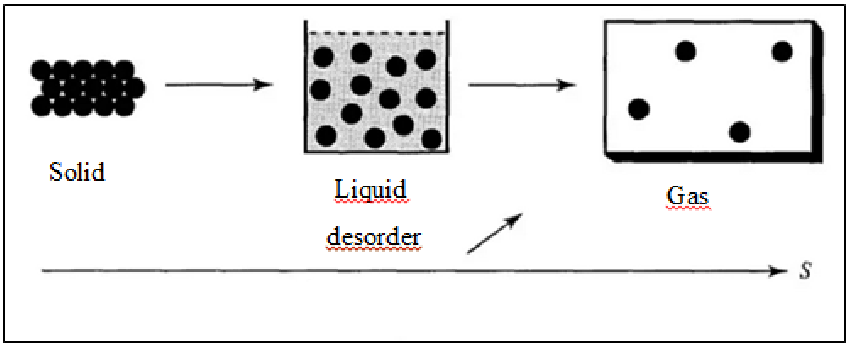
- $\mathbf{S_c = 0}$ for a reversible transformation.
- $\mathbf{S_c > 0}$ for an irreversible transformation
- For an isolated system (Q = 0), $\mathbf{S_e = 0}$ and thus, it follows $\mathbf{\Delta S_{syst} = S_c}$, the entropy variation is maximum.

- S is an extensive quantity, expressed in J.K-1.J.K^{-1}.

4.2.2. Physical meaning of entropy:

The concept of entropy is related to the possibilities of movements existing at the microscopic scale (vibration, rotation and translation movements). Entropy constitutes a sort of measure of the disorder reigning at the molecular scale.

Entropy = disorder



If ΔS>0 ⟶ increase in disorder at the microscopic scale.

4.2.3. Statement of the second principle:

The second principle of thermodynamics, in its most general formulation, states that during a transformation of a system, the total entropy cannot decrease.

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{ext} \geq 0$$

"During a spontaneous transformation, the entropy of the universe (system + surroundings) can only increase. Its variation is zero for a reversible transformation and positive for an irreversible transformation."

<u>Reversible transformation:</u>

$\Delta U = Q_{rev} + W_{rev} = 0$ (isothermal)

$Q_{rev} = - W_{rev} = nRT\ln\frac{V_2}{V_1}$

$\Delta S_{sys} = \frac{Q_{rev}}{T} = nR\ln\frac{V_2}{V_1}$

Since the transformation is reversible, the work done by the system will be equal to the work received by the surroundings. Therefore, the heat received by the system is equal to the heat released by the surroundings.

$Q_{ext} = -Q_{sys} = - Q_{rev} = - nR\ln\frac{V_2}{V_1}$

$\Delta S_{ext} = - nR\ln\frac{V_2}{V_1}$

$\Delta S_{univers} = \Delta S_{sys} + \Delta S_{ME} = 0$

The increase in entropy of the system is equal to the decrease in entropy of the surroundings, thus the entropy of the universe remains constant. There is conservation of entropy in the universe during a reversible transformation.

Irreversible transformation:

$\Delta S_{sys} = \frac{Q_{rev}}{T} = - \frac{W_{rev}}{T} = nR\ln\frac{V_2}{V_1} > 0$

$\Delta U = Q_{irr} + W_{irr} = 0 \Longrightarrow Q_{irr} = - W_{irr} = P_{ext}(V_2-V_1)$

$\Delta S_{ext} = -\frac{Q_{irr}}{T} = \frac{W_{irr}}{T} = -\frac{P_{ext}(V_2-V_1)}{T} < 0$

$\Delta S_{univers} = \Delta S_{sys} + \Delta S_{ME} = \frac{Q_{rev}-Q_{irr}}{T} = nR\ln\frac{V_2}{V_1} - \frac{P_{ext}(V_2-V_1)}{T} > 0$ Therefore, creation of entropy occurs.

The entropy of the universe increases during an irreversible process.

4.2.4. Entropy of solids and liquids:

Solids and liquids are incompressible. $c_p \approx c_v = c$

$dS = \frac{\delta Q}{T} \Longrightarrow \Delta S = \int_A^B \frac{\delta Q}{T}$ / $\delta Q = ncdT$

$\Delta S = \int_{T_A}^{T_B} nc\frac{dT}{T} \Longrightarrow \Delta S = nc\ln\frac{T_B}{T_A}$ Solid

4.2.5. Entropy of ideal gases:

a. Isothermal transformation:

$\Delta U = Q + W = 0 \Longrightarrow Q = -W = nRT\ln\frac{V_2}{V_1} = nRT\ln\frac{P_1}{P_2}$

$\Delta S = \int_1^2 \frac{Q_{rev}}{T} = \frac{Q}{T} = nR\ln\frac{V_2}{V_1}$

$$\boldsymbol{\Delta S = nR\ln\frac{V_2}{V_1} = nR\ln\frac{P_1}{P_2}}$$

b. Isochoric transformation:

$\Delta S = \int_{T_1}^{T_2} \frac{\delta Q_{rev}}{T}$ $\delta Q_{rev} = nc_v dt$, $\Delta S = \int_{T_1}^{T_2} nc_v \frac{dT}{T}$

$$\boldsymbol{\Delta S = nc_v\ln\frac{T_2}{T_1}}$$

c. Isobaric transformation :

$\Delta S = \int_{T_1}^{T_2} \frac{\delta Q_{rev}}{T}$ $\delta Q_{rev} = nc_p dt$, $\Delta S = \int_{T_1}^{T_2} nc_p \frac{dT}{T}$

$$\boldsymbol{\Delta S = nc_p\ln\frac{T_2}{T_1}}$$

d. Reversible adiabatic transformation:

For an adiabatic transformation. $\delta Q_{rev} = 0$, as a result,

$$\boldsymbol{\Delta S = 0}$$

4.2.6. Expression of entropy for ideal gases:

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

$dS = \frac{\delta Q}{T} \Longrightarrow \delta Q = TdS$

$dU = \delta Q + \delta W \Longrightarrow nc_v dT = TdS - PdV$ $PV = nRT$

$nc_v dT = TdS - nRT\frac{dV}{V}$

$$dS = nc_v\frac{dT}{T} + nR\frac{dV}{V}$$

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

$H = U + PV$, $dH = dU + PdV + VdP$

$nc_p dT = TdS - PdV + PdV + VdP$

$nc_p dT = TdS + VdP \quad V = \frac{nRT}{P}$

$nc_p dT = TdS + nRT\frac{dP}{P}$

Solid $$dS = nc_P\frac{dT}{T} - nR\frac{dP}{P}$$

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

$dS = nc_v\frac{dT}{T} + nR\frac{dV}{V}$ et $dS = nc_P\frac{dT}{T} - nR\frac{dP}{P}$

$nc_v\frac{dT}{T} + nR\frac{dV}{V} = nc_P\frac{dT}{T} - nR\frac{dP}{P}$

$n(c_p - c_v)\frac{dT}{T} = nR(\frac{dP}{P} + \frac{dV}{V})$

According to Mayer's relation $c_p - c_v = R$

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

$dS = nc_P\frac{dT}{T} - nR\frac{dP}{P} = nc_P(\frac{dP}{P} + \frac{dV}{V}) - nR\frac{dP}{P}$

$$dS = nc_v\frac{dP}{P} + nc_p\frac{dV}{V}$$

4.2.7. Variation of entropy for phase changes:

Definition:

In the case where the system undergoes a change in physical state, such as fusion, vaporization, or sublimation, ΔS is given by:

$$\Delta S = n\ (ou\ m)\ \frac{\Delta H_{changement}}{T_{changement}} = n\ (ou\ m)\ \frac{L_{changement}}{T_{changement}}$$

Fusion : $\Delta S_{fus} = n\ (ou\ m)\ \frac{\Delta H_{fus}}{T_{fus}}$

Vaporization: $\Delta S_{vap} = n\ (ou\ m)\ \frac{\Delta H_{vap}}{T_{vap}}$

2. Calculation of entropy change during heating of a pure substance:

Consider a pure substance in the solid state characterized by an initial temperature T1. It is heated at constant pressure until it reaches the gaseous state characterized by a final temperature T2. The change in entropy is expressed as follows:

$$\Delta S = n_{cp\ solide} \ln\frac{T_{fus}}{T_1} + n\frac{L_{fus}}{T_{fus}} + n_{cp\ liquide} \ln\frac{T_{vap}}{T_{fus}} + n\frac{L_{vap}}{T_{vap}} + n_{cp\ gaz} \ln\frac{T_2}{T_{vap}}$$

Exercise:

Calculate:

a) The amount of heat involved.
b) The change in internal energy.
c) The change in enthalpy.
d) The change in entropy.

When:

1. Heating 2 kg of air from 30 to 100°C at constant pressure.
2. Heating 2 kg of air enclosed in a rigid balloon from 30 to 100°C.

- In the case where 2 kg of air is heated from 30 to 100°C at constant pressure:
  $Q_p = mc_p(T_2 - T_1) = 33{,}18$ kcal
  Solid
- $\Delta U = mc_v\ (T_2 - T_1)$ avec $c_v = \frac{c_p}{\gamma} = 0{,}168$ kcal/K.mol

Therefore, $\Delta U = 23{,}52$ Kcal

The work can be deduced from this:

- $\Delta U = Q_p + W \Longrightarrow W = \Delta U - Q_p = -9{,}66$ kcal $= -40{,}38$ KJ
- $\Delta H = Q_p = mc_p(T_2 - T_1) = 33{,}18$ kcal
- $\Delta S = mc_p \ln\frac{T_2}{T_1} = 0{,}0985$ kcal

- In the case where 2 kg of air enclosed in a rigid balloon is heated from 30 to 100°C.
  At constant volume: $Q_v = mc_v(T_2 - T_1) = 23{,}52$ kcal.
- $W = 0$
- $\Delta U = Q_v = 23{,}52$ kcal.
- $\Delta H = mc_p(T_2 - T_1) = 33{,}18$ kcal.
- $\Delta S = mc_v \ln\frac{T_2}{T_1} = 0{,}0698$ kcal

4.3. Statement of the Third Law:

The Third Law of thermodynamics states that:

"At absolute zero (0 K), the entropy of a pure crystal (a solid with ordered structure) is zero, $S_{0K} = 0$."

This principle, also known as the "Nernst's postulate," asserts that at 0 K, there is perfect order, meaning there is no thermal agitation at this temperature, and the crystal is in a perfect state.

4.4. Absolute molar entropy:

The third principle makes it possible to attribute an absolute entropy to any pure body brought to temperature T. In the standard state, the absolute molar entropy is denoted $S°_T$.

4.5. Calculation of the absolute molar entropy of a pure substance:

A ⟶ A

Initial state — Final state

$T_{initial} = 0$ K — $T_{final} = T$

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

Absolute molar entropy at temperature T   Absolute molar entropy at T = 0 K

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

4.6. Entropy of a chemical reaction:

Consider a chemical reaction taking place at constant temperature and pressure:

$$aA + Bb \longrightarrow cC + dD$$

$\Delta S_R = S_{final} - S_{initial} = cS\ (C) + d\ S(D) - aS\ (A) - b\ S\ (B)$
Solid

$$\mathbf{\Delta S_R = \sum \upsilon_j\ S_T\ (products) - \sum \upsilon_i\ S_T\ (reactants)}$$

Under standard conditions at 298 K, the entropy change ΔS°298K is:

$$\mathbf{\Delta S°_{298} = \sum \upsilon_j\ S°_{298}\ (products) - \sum \upsilon_i\ S°_{298}\ (reactants)}$$

Example 1:

Let's determine the entropy change $\Delta S°_{298}$ during the formation of one mole of hydrochloric acid according to the following reaction carried out at 298 K, under a pressure of 1 atmosphere:

$\frac{1}{2} H_2\ (g) + \frac{1}{2} Cl_2 \longrightarrow HCl\ (g)$

$\Delta S°_{298} = S°_{298}(HCl) - \frac{1}{2} S°_{298}\ (Cl_2) - \frac{1}{2} S°298(H_2) = 2{,}35$ cal/mol.K > 0

Example 2:

$CaCO_3\ (s) \longrightarrow CaO\ (s) + CO_2\ (g)$

$\Delta S°_{298} = S°_{298}\ (CaO) + S°_{298}\ (CO_2) - S°_{298}\ (CaCO_3) = 38{,}4$ cal/mol.k > 0 (appearance of a new phase).

Example 3:

$2\ C\ (s) + 3\ H_2 \longrightarrow C_2H_6\ (g)$

$\Delta S°_{298} = S°_{298}\ (C_2H_6) - 2\ S°_{298}\ (C) - 3\ S°_{298}\ (H_2) = -\ 41{,}57$ cal/mol.k < 0

$\Delta S°_{298} < 0 \Longrightarrow$ The disorder decreases as the number of gas moles has decreased.

4.7. Variation of $\Delta S°_R$ with temperature:

Consider a chemical reaction taking place at constant pressure:

$aA + Bb \longrightarrow cC + dD$

By knowing ΔS°298 of this reaction, we can determine ΔS°T using the following Kirchhoff's equation:

$$\mathbf{\Delta S°_T = \Delta S°_{298} + \int_{298}^{T} \Delta c_p \frac{dT}{T} \qquad at\ p = constant}$$

$$\mathbf{\Delta c_p = \sum \upsilon_j\ c_{p,j}\ (products) - \sum \upsilon_i\ c_{p,i}\ (reactants)}$$

If the reaction occurs at constant volume, Kirchhoff's relation becomes:

$$\Delta S^\circ_T = \Delta S^\circ_{298} + \int_{298}^{T} \Delta c_V \frac{dT}{T} \qquad \text{à } V = \text{constant}$$

$$\Delta c_p = \sum \upsilon_j \, c_{v,j} \text{ (products)} - \sum \upsilon_i \, c_{v,i} \text{ (reactants)}$$

<u>Exercise:</u>

1. Calculate the entropy change of formation of one mole of liquid water from its elements under standard conditions of temperature and pressure. Interpret the result.
2. Calculate this change in the case of one mole of liquid water at 80°C and 1 atm. Interpret the result.

Given:

Compound	S°_{298} (J/K.mol)	C_p (J/K.mol)
H_2 Solid	130,45	28,42
O_2	204,83	29,16
H_2O	69,85	75,22

1. The reaction involved is H_2 (g) + ½ O_2 (g) ⟶ H_2O (l)

The entropy change of this reaction is given by Hess's Law:

$\Delta S^\circ_{298} = S^\circ_{298} (H_2O) – ½\, S^\circ_{298} (O_2) – S^\circ_{298} (H_2) = - 163,02$ J/k.mol

This value reflects a significant decrease in disorder: we start with 1.5 moles of gas and end up with 1 mole of liquid.

2. At 80°C (353 K) and under 1 atm, the entropy change is given by Kirchhoff's equation:

$$\Delta S^\circ_{353} = \Delta S^\circ_{298} + \int_{298}^{353} \Delta c_p \frac{dT}{T}$$

$$\Delta c_p = \sum \upsilon_j \, c_{p,j} \text{ (products)} - \sum \upsilon_i \, c_{p,i} \text{ (reactants)}$$

$\Delta c_p = c_p (H_2O) – c_p(H_2) – ½\, c_p (O_2) = 32,22$ J/mol

ΔS°_{353} = -157,56 J/K.mol

If we compare the entropy change at the two temperatures, we can make the following observation:

The formation reaction at 25°C results in a slightly greater decrease in disorder compared to that at 80°C (the state of liquid water at 80°C is less ordered than at 25°C); molecular disorder increases with temperature.