Chapter Two: The Zeroth Law of Thermodynamics.

1- Introduction

In its various transformations, a system goes through a range of thermal phenomena, where it can exchange heat with the external environment (absorbing heat from or releasing it to the surroundings). This heat exchange has significant effects on the nature of the system and the state it evolves into, which can be summarized in the following physical effects:

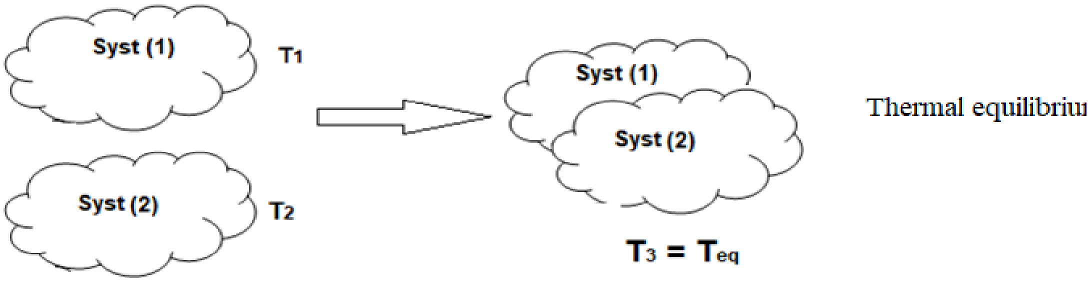
- Either the substance absorbs a quantity of heat, resulting in an increase in its temperature. This is reflected in its heating (i.e., an increase in its temperature) or in a change in its physical state (melting, dissolving, evaporating, etc.).
- Or the substance releases a quantity of heat, leading to a decrease in its temperature. This is reflected in its cooling (i.e., a decrease in its temperature) or in a change in its physical state (freezing, diluting, or condensing).

2- The Zeroth Law

The Zeroth Law is the principle of thermal equilibrium for an isolated system, and its statement is as follows:

If two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.

All systems in thermal equilibrium with each other have the same quantity of heat, denoted as Q (the amount of heat).



$$\int_1^2 Q_i = 0 \Rightarrow Q_1 + Q_2 = 0$$

If : $(T_1 < T_2) \Longrightarrow T_1 < T_3 = T_{eq} < T_2$

So, the Zeroth Law of an isolated system $\Longrightarrow \sum_{i=1}^{i=n} Q_i = 0$

3- The Concept of Heat and Temperature: When two objects are placed side by side, one hot and the other cold, we observe that the hot object contracts, meaning its temperature decreases, while the cold object expands, leading to an increase in its temperature. This observation aligns with the Zeroth Law of an isolated system.

$$\sum_{i=1}^{i=n} Q_i = 0$$

- If the first object is much larger than the second one, then the temperature of the first object changes by a very small amount, unlike the temperature of the second object, which changes significantly.
- Temperature is considered a relative quantity associated with the sensation of hotness or coldness.
- Physically, heat is defined as the degree of thermal motion of molecules in a substance, where it increases with the increased motion of the molecules.

4-Temperature Scales: Every measurable physical phenomenon directly related to the body's heat can be used as an indicator of temperature. Commonly used temperature scales include:

4-1- Celsius Scale (Celsius °C): Invented by the Swedish Scientist Celsius, it is based on two reference points:

- The freezing point of pure water is 0°C at atmospheric pressure (1 atm).
- The boiling point of pure water is 100°C at atmospheric pressure (1 atm).

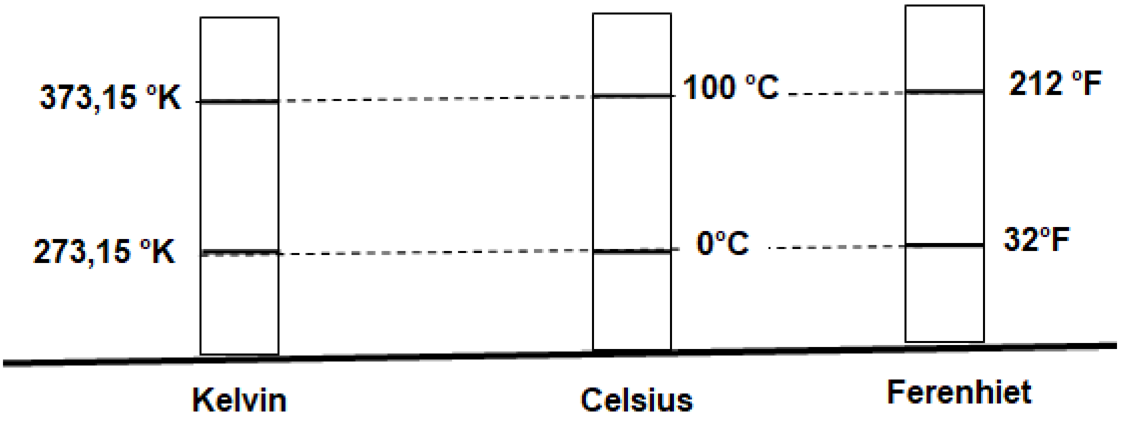
Examples of Celsius thermometers include alcohol and mercury thermometers.

4-2- Fahrenheit Scale (Fahrenheit °F): It is based on two reference points:

- The freezing point of ice is 32°F.
- The boiling point of water is 212°F.

4-3- Kelvin Scale (Kelvin °K): This scale is used in the field of thermodynamics and was discovered by the scientist William Thomson, known as Lord Kelvin. It is based on two reference points :

- The freezing point of ice is 273.15 °K.
- The boiling point of water is 373.15 °K.



The relationships between different temperature scales are as follows:

$$\boldsymbol{T\ (°K) = T(°C) + \ 273,15}$$

$$\boldsymbol{T(°F) = \frac{9}{5}\,T(°C) + 32}$$

Application: Find the equivalent temperature values in both the Fahrenheit and Celsius scales.

$$T(°C) = T\ (°F) \Longrightarrow T(°C) = \frac{9}{5}\ T(°C) + 32$$

$$\Longrightarrow T(°C)\left(1 - \frac{9}{5}\right) = 32\ \ \Longrightarrow T(°C) = \ -40\ °C = \ -40°F$$

5- Heat Quantity: Let's consider two substances placed in proximity to each other at different temperatures. A heat transfer occurs between them (according to the Zeroth Law) until we reach a state of equilibrium, expressed by the equilibrium temperature Tf = Teq.

To calculate the equilibrium temperature, we have three cases:

- **Case 1:** Both substances are of the same nature and have the same quantity.

$$T_{eq} = \frac{T_1 + T_2}{2}$$

Example: Suppose we have a mixture consisting of 1 kg of water at a temperature of 60°C and 1 kg of water at a temperature of 20°C. What is the equilibrium temperature?

$$T_{eq} = \frac{T_1 + T_2}{2} = \frac{60 + 20}{2} = 40\ °C$$

- **Case 2:** Both substances are of the same nature but have different quantities.

In this case:

$$T_{eq} = \frac{m_1T_1 + m_2T_2}{m_1 + m_2}$$

Where:

m_1 and m_2 are the masses of the first and second substances, respectively.
T_1 and T_2 are the temperatures of the first and second substances, respectively.
The relationship can be written as:

$$m_1\left(T_{eq} - T_1\right) + m_2\left(T_{eq} - T_2\right) = 0$$

For several substances, it becomes:

$$\sum_{i=1}^{n} m_i(T_{eq} - T_i) = 0$$

Meaning :

$$T_{eq} = \frac{\sum_{i=1}^{n} m_i T_i}{\sum_{i=1}^{n} m_i}$$

Example:

Substance (1) consists of 10 g of water at 50°C.

Substance (2) consists of 20 g of water at 35°C.

$$T_{eq} = \frac{m_1T_1+m_2T_2}{m_1+m_2} = \frac{(10\times50)+(20\times35)}{10+20} = 40\ °C$$

Case 3: The two substances are different in nature and quantity. In this case :

$$T_{eq} = \frac{m_1c_1T_1 + m_2c_2T_2}{m_1c_1 + m_2c_2}$$

$$\Rightarrow m_1c_1\left(T_{eq} - T_1\right) + m_2c_2\left(T_{eq} - T_2\right) = 0$$

In the case of multiple systems:

$$T_{eq} = \frac{\sum_{i=1}^{n} m_ic_iT_i}{\sum_{i=1}^{n} m_ic_i}$$

So:

$$\sum_{i=1}^{n} m_ic_i(T_{eq} - T_i) = 0$$

Where c_i is a coefficient associated with the nature of the substance (material type and physical state of the substance) and is referred to as specific heat capacity . The product m_ic_i is known as heat capacity.

Heat Capacity: It is the amount of heat required to raise the temperature of a specific body or a certain amount of substance by one degree Celsius, and its units are cal/°C; J/°C; cal/°K; J/°K...

That is, temperature unit per energy unit.

6- Heat Quantity Expression:

In theory, for a small transformation, the quantity of heat dQ represents the amount of heat received by the system, whether it is due to heating or cooling, where:

$$dQ = \underset{\nearrow\ \textbf{Heat capacity}}{C}dT$$

dT represents the change in temperature.
C is called the heat capacity.

Where:

$$\begin{cases} C = nc_n \\ \quad\textbf{or} \\ C = mc_m \end{cases} \qquad \textbf{So} \qquad \begin{cases} dQ = nc_ndT \\ \quad\textbf{or} \\ dQ = mc_mdT \end{cases}$$

c_m represents specific heat capacity per unit mass.
c_n represents specific molar heat capacity.
Note: Specific heat c_n or c_m can be:
c_V: Specific heat at constant volume (a transformation with constant volume).
c_P: Specific heat at constant pressure (a transformation with constant pressure).

7- Specific Heat Capacity cm: It is the amount of heat required to raise the temperature of a body with a mass of 1 gram by one degree, and its units are: cal/g.K; J/g.K.

8- Specific Molar Heat Capacity cn: It is the amount of heat required to raise the temperature of a substance with a quantity of 1 mole by one degree, and its units are: cal/mol.K; J/mol.K.

Notes:

- The specific heat of 1 gram of water is 1 cal/g.K, which is the amount of heat required to raise the temperature of 1 gram of water from 14.5°C to 15.5°C under a pressure of 1 atmosphere.
- Sign of Heat Quantity:
  Positive (+) ⇒ The system or the sentence gained an amount of heat ($Q > 0$).
  Negative (-) ⇒ The system or the sentence lost an amount of heat ($Q < 0$).
- Specific heat can be constant or variable with temperature, and thus it can be expressed in the following form:

$$c = a + bT + dT^2 = f(T)$$

If : $c = a + bT$

So, we can calculate the quantity of heat using the following method:

$$dQ = mc_m dT \Rightarrow Q = \int_{T_i}^{T_f} mc_m dT = m\int_{T_i}^{T_f} c_m dT$$

$$dQ = nc_n dT \Rightarrow Q = \int_{T_i}^{T_f} nc_n dT = n\int_{T_i}^{T_f} c_n dT$$

9- Latent Heat L: In the case of phase transitions, the quantity of heat is given by the relationship:

$$Q = nL \quad \text{or} \quad Q = mL$$

Where L is defined as latent heat.
Latent heat is the quantity of heat required to change the phase of one unit, either 1 mole or 1 gram, at constant temperature and pressure. Its units are: cal/g; cal/mol; J/mol; J/kg.
While Q is measured in calories (cal) or joules (J).

Example:

For water:

- at a temperature of 0°C or 273 K, the latent heat of fusion is called L_{fusion}

$$\begin{array}{ccc} H_2O_{solid} & \xrightarrow{\mathbf{Q}} & H_2O_{liquid} \\ T = 0°C & & T = 0°C \\ P = 1\ atm & & P = 1\ atm \\ Q = nL_{fusion} & \text{أو} & Q = mL_{fusion} \\ \nearrow & & \nearrow \\ \text{(J/mol ; cal/mol)} & & \text{(J/g; cal/g)} \end{array}$$

- At a temperature of 0°C or 373 K, the latent heat of vaporization for water is called $L_{vaporization}$.

$$\begin{array}{ccc} H_2O_{Liquid} & \xrightarrow{\mathbf{Q}} & H_2O_{Vapor} \\ T = 100\ °C & & T = 100\ °C \\ P = 1\ atm & & P = 1\ atm \\ Q = nL_{vap} & \text{أو} & Q = mL_{vap} \\ \nearrow & & \nearrow \\ \text{J/mol ; cal/mol)} & & \text{(J/g; cal/g)} \end{array}$$

Example: Calculate the amount of heat required during the transformation of 1 mole of solid iodine (I_2) at 300 K to liquid iodine at 400 K.
Given Data:
c_P (I_2, solid) = 5.4 cal/mol·K
c_P (I_2, liquid) = 19.4 cal/mol·K
$L_{fus\ ,387\ K}$ = 3.74 Kcal/mole
$T_{vaporization}$ (I_2, liquid) = 475 K

Solution:

$$\begin{tikzcd} I_2(s) \arrow[r, "Q_1"] & I_2(s) \arrow[r, "Q_2"] & I_2(l) \arrow[r, "Q_3"] & I_2(l) \\ \mathbf{300\ K} \arrow[rrr, bend right] & \mathbf{387\ K} & \mathbf{387\ K} & \mathbf{400\ K} \end{tikzcd}$$

$$Q_T = Q_1 + Q_2 + Q_3$$

$$Q_1 = \int_{300K}^{387K} nc_p(I_2, s)dT$$

$$= nc_p(I_2, s) \int_{300K}^{387K} dT = 1 \times 5,4(387 - 300) = 469,8\ cal$$

$$Q_2 = nL_{fus}(I_2) = 1 \times 3,74 = 3,74\ Kcal$$

$$Q_3 = \int_{387K}^{400K} nc_p(I_2, l)dT$$

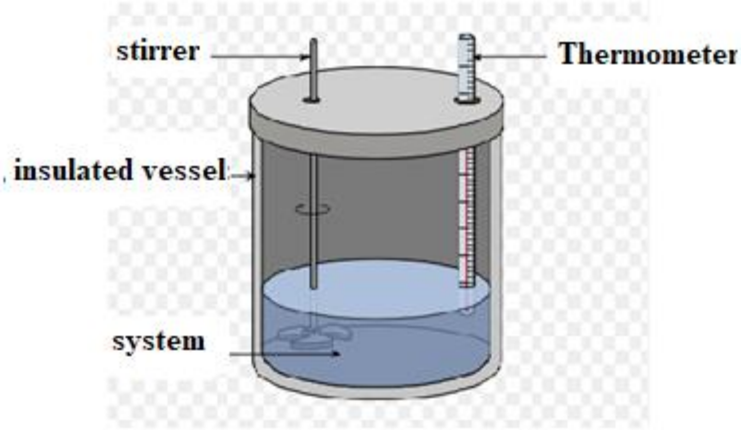
$$= nc_p(I_2, l) \int_{387K}^{400K} dT = 1 \times 19,5(400 - 387) = 253,5\ cal$$

$$Q_T = 469,8 + (3,74 \times 1000) + 253,5 = 4463,3\ cal$$

10- Measuring Heat Quantity: In practice, to calculate the quantity of heat, we use the calorimeter, which is based on the principle of the zeroth law of thermodynamics for isolated systems.

$$\sum Q_i = 0 \Rightarrow Q_{calorimeter} + Q_{\text{system}} = 0$$

Calorimeter Description: The calorimeter consists of a glass vessel insulated from the external environment by placing it inside an insulating casing.



- To measure the temperature inside the calorimeter vessel, we use a thermometer and a stirrer (agitator) to ensure homogeneous temperature within the vessel.
  The calorimeter system = Vessel + Accessories. Accessories = Stirrer (agitator) + Thermometer.

14- How to calculate the heat capacity of the calorimeter (in terms of water or water mass): To calculate the heat capacity of the calorimeter (in terms of water or water mass), we place a mass m_1 of water inside the calorimeter and record its initial temperature, which we'll call T_1. Then, we add a second mass m_2 of water at a different temperature, T_2, into the same calorimeter.
After thermal equilibrium is reached, we record the final equilibrium temperature T_f. Using the principle of the zeroth law of thermodynamics for an isolated system:

$$\sum Q_i = 0 \Rightarrow Q_{\text{calorimeter}} + Q_1 + Q_2 = 0$$

$$m_{\text{calorimeter}} c_{\text{calorimeter}} (T_f - T_1) + m_1 c_1 (T_f - T_1) + m_2 c_2 (T_f - T_2) = 0$$

Since the substance is water $\Rightarrow c_1 = c_2 = c$

And we put :

$$C_{\text{calorimeter}} = m_{\text{calorimeter}} \; c_{\text{calorimeter}}$$

The specific heat capacity of the calorimeter per unit mass

The heat capacity of the calorimeter

And consequently :

$$C_{calorimeter}(T_f - T_1) + m_1 c\,(T_f - T_1) + m_2 c\,(T_f - T_2) = 0 = 0$$

So :

$$C_{\text{calorimeter}} = -\frac{\left[m_1 c\,(T_f - T_1) + m_2 c\,(T_f - T_2)\right]}{(T_f - T_1)}$$

$$C_{\text{calorimeter}} = m_{\text{calorimeter}} \; c_{\text{calorimeter}} = \mu_{\text{eq}} \; c_{\text{water}} = \mu_{\text{eq}} \,.\, c$$

The heat capacity of the calorimeter

The specific heat capacity of the calorimeter per unit mass

Since : $c_{\text{water}} = 1\text{cal.}\,\text{g}^{-1}.\,\text{K}^{-1}$

$$so: \; C_{\text{calorimeter}} = \mu_{eq} . c_{\text{water}} = \mu_{eq}\;(g)$$

μ_{eq}: It is the amount of water that absorbs the same amount of heat absorbed by the calorimeter, meaning it is the equivalent mass of the calorimeter in terms of water.

Example (1): A calorimeter contains a quantity of water with a mass of 50 grams, where the temperature of the system (calorimeter + water) is 20°C. We add to this system another quantity of water with a mass of 50 grams and a temperature of 30°C. After thermal equilibrium is reached, the temperature is 24°C. Calculate the heat capacity of the calorimeter and the equivalent mass in water.

c_{water} = 1 cal/g·K

Solution:

According to the zeroth law of thermodynamics:

$$\sum_{i=1}^{i=n} Q_i = 0 \;\Rightarrow\; Q_{Cal} + Q_1 + Q_2 = 0$$

$$m_{\text{cal}}c_{\text{cal}}(T_f - T_1) + m_1c_1(T_f - T_1) + m_2c_2(T_f - T_2) = 0$$

$$C_{\text{cal}}(T_f - T_1) + m_1c\,(T_f - T_1) + m_2c\,(T_f - T_2) = 0$$

$$C_{\text{cal}} = -\frac{m_1c\,(T_f - T_1) + m_2c\,(T_f - T_2)}{(T_f - T_1)}$$

$$C_{\text{cal}} = -\frac{50 \times 1\,(24 - 20) + 50 \times 1\,(24 - 30)}{(24 - 20)} = 25\ cal/°K$$

The equivalent mass is :

$$C_{\text{cal}} = \mu_{eq}.c_{\text{water}} \Longrightarrow \mu_{eq} = C_{\text{cal}}(g)$$

Example 2:

In an isolated system, we placed 100 grams of zinc at a temperature of 95°C into 50 grams of water at a temperature of 15°C. If you know that the specific heat capacities of both zinc and water are 6.06 cal/mol·K and 1 cal/g·K, respectively, what is the final temperature of the system?

M(Zn) = 63.37 g/mole

Solution:

According to the zeroth law of thermodynamics:

$$\sum Q_i = 0 \Rightarrow Q_{Zn} + Q_{water} = 0$$

$$Q_{Zn} = n_{Zn}.c_{Zn}(T_f - T_1) = \frac{100}{63,37}.6,06(T_f - 95) = 9,56(T_f - 95)$$

$$Q_{\text{water}} = m_{\text{water}}.c_{\text{water}}(T_f - T_2) = 50.1(T_f - 15) = 50(T_f - 15)$$

$$9,56(T_f - 95) + 50(T_f - 15) = 0 \Rightarrow T_f = 27,84\ °C \approx 28°C$$

Example 3:

- What is the amount of heat in cal required to raise the temperature of 100 grams of copper from 10°C to 100°C, knowing that the specific heat capacity of copper is C_{Cu} = 0.093 cal/g·K.
- The same amount of heat is used to heat 100 grams of aluminum from 10°C, which one heats up more, aluminum or copper?

C_{Al} = 0.217 cal/g·K.

Solution:

$$Q_{Cu} = m_{Cu}.c_{Cu}\Delta T = 100 \times 0,093(100 - 10) = 837cal$$

$$Q_{Al} = Q_{Cu} = m_{Al}.c_{Al}\Delta T = m_{Al}.c_{Al}(T_f - 10) = 837$$

$$\Rightarrow T_f = \frac{837}{100 \times 0,217} + 10 = 48,57°C$$

Example 4:

Inside a calorimeter with a heat capacity C = 150 J/K, we place a mass m_1 (200 g) of water and measure the temperature, finding $T_1 = 70°C$. Then we add a mass m_2 (80 g) of ice with a temperature $T_2 = -23°C$. What is the temperature at thermal equilibrium, assuming all the ice turns into liquid water?

Given data:

$Cp(H_2O,l) = 4200$ J/kg·K

$Cp(H_2O,s) = 2100$ J/kg·K

$L_{fus}(H_2O,s) = 3.34 \times 10^5$ J/kg

Solution:

According to the zeroth law of thermodynamics:

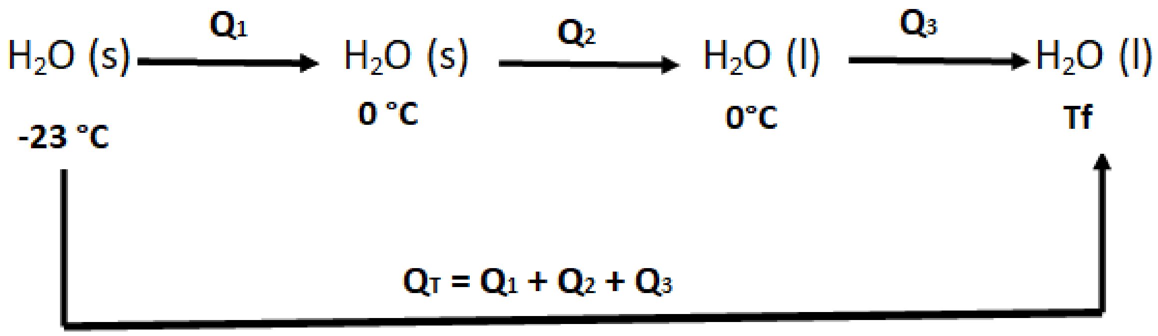
$$\sum Q_i = 0 \ \Rightarrow \ Q_{hot\ water} + Q_{ice} + Q_{cal} = 0$$

$$Q_{hot\ water} = m_1 c_p.\left(T_f - 70\right) = 200.10^{-3} \times 4200\left(T_f - 70\right)$$

$$= 840\left(T_f - 70\right)$$

$$Q_{cal} = C_{\text{cal}}\left(T_f - 70\right) = 150\left(T_f - 70\right)$$

Transformations of the ice :



$$Q_1 = m_2c_p(H_2O,s)\times(0+23) = 80\times10^{-3}\times2100(0+23) = 3864\,J$$

$$Q_2 = m_2L_{fus}(H_2O,s) = 80\times10^{-3}\times3,34.10^5 = 26720\,J$$

$$Q_3 = m_2c_p(H_2O,l)\times(T_f-0) = 80\times10^{-3}\times4200T_f = 336T_f$$

$$Q_{ice} = Q_T = Q_1+Q_2+Q_3 = 8364+26720+336T_f$$

$$Q_{ice} = 30584+336T_f$$

$$Q_{\,hot\,water}+Q_{ice}+Q_{cal} = 840(T_f-70)+30584+336T_f+150(T_f-70) = 0$$

$$\Rightarrow T_f = \frac{70(840+150)-30584}{150+840+336} = 29,19\,°C$$

$$-23\,°C < T_f = 29,19\,°C < 70\,°C$$

12- The mechanical work (pressure forces):

Work is one form of energy exchanged by the system with the external surroundings and is measured in joules or calories.

In terminology:

$\delta w > 0 \Longrightarrow$ **If the system receives work**

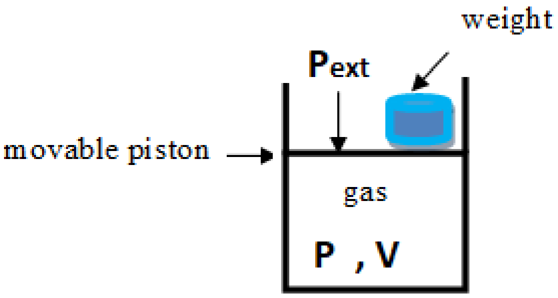
$\delta w < 0 \Longrightarrow$ **If the work is done by the system**

Example:

We consider a gas inside a cylinder with a movable piston, where the gas volume is V and the cylinder pressure is P.

Let's calculate the work done when the piston moves:

A) When we place a weight on the piston ⟹ the gas compresses ⟹ V (the volume) decreases. The external surroundings do work on the system, so dW > 0.



The work equation:

$$dW = Fdx$$

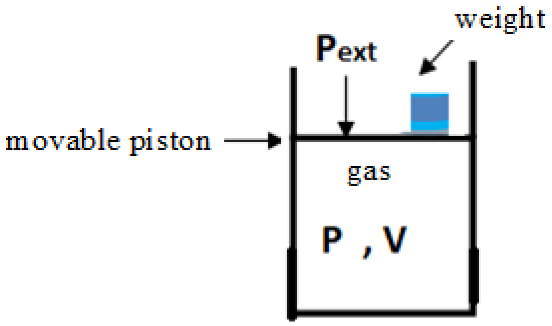
$$P_{ext} = \frac{F_{Force}}{S_{Surface}} \Rightarrow F = P_{ext}S$$

$$dW = P_{ext}Sdx = P_{ext}d(Sx) = P_{ext}dV \;/\quad S.x = Volume = V$$

In the case of compression ⇒ dV < 0 and In terminology dW > 0 , **so:**

$$dW = -P_{ext}dV$$

B) When lifting a weight ⇒ the gas expands ⇒ V (the volume) ↗ increases, so dV > 0



Terminologically:

since the work is done by the system on the external surroundings ⇒ **dW < 0**

And thus, the general relationship is:

$$dW = -P_{ext}dV$$

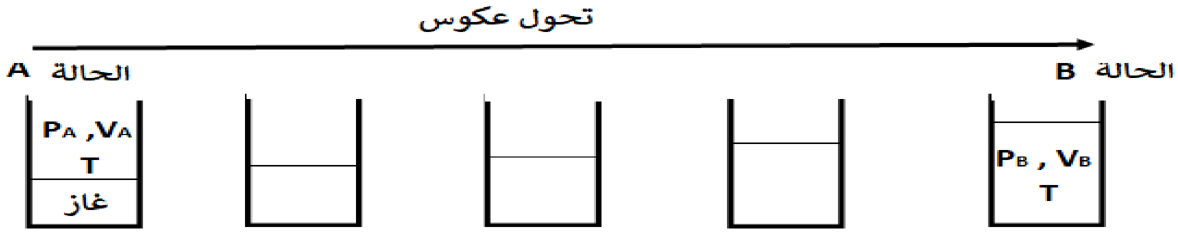
In general, for a small transformation:

$$dW = -P_{ext}dV \Rightarrow W = -\int_{V_1}^{V_2} P_{ext}dV$$

Note: Volume changes are considered significant for gases but negligible for solid and liquid materials.

12-1- Reversible work: It is a series of infinitesimal transformations, and a state of equilibrium can be determined at each moment in time.

Expansion:



$$W_{AB} = -\int_{V_A}^{V_B} P_{ext} dV$$

Reversible work $\Rightarrow P_{ext} = P_{int} = P_{Sys} = P_g = P$

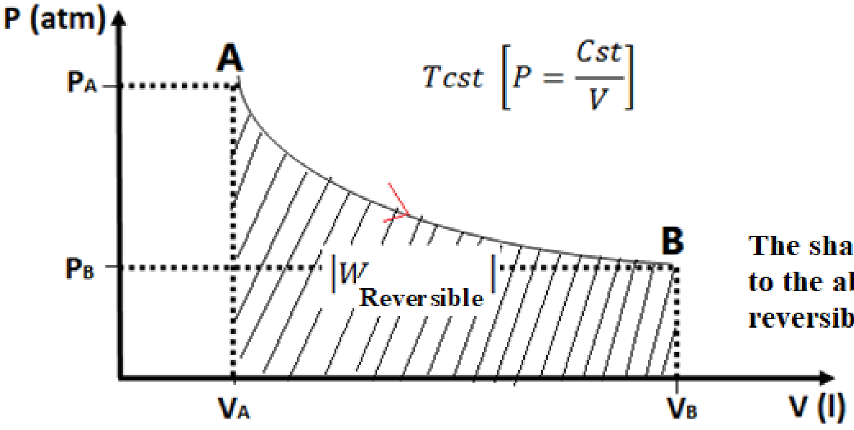
Ideal gas $\Rightarrow PV = nRT \Rightarrow p = \frac{nRT}{V}$

$$W_{AB} = -\int_{V_A}^{V_B} P_{ext} dV = -\int_{V_A}^{V_B} P dV = -\int_{V_A}^{V_B} \frac{nRT}{V} dV$$

If the temperature is constant $\Rightarrow W_{AB} = -nRT \int_{V_A}^{V_B} \frac{dV}{V}$

$$W_{AB} = -nRTLn\left(\frac{V_B}{V_A}\right)$$

$$V_B > V_A \Longrightarrow W_{AB} > 0$$



The shaded area corresponds to the absolute value of the reversible work

Clapeyron diagram P = f(V)

In this case, since the transformation occurs at constant temperature, according to Boyle's law relationship:

$$P_AV_A = P_BV_B \Longrightarrow \frac{P_A}{P_B} = \frac{V_B}{V_A}$$

Thus, during a reversible process at constant temperature for an ideal gas, the work is calculated using the following equation:

$$W_{AB} = -nRTLn\left(\frac{V_B}{V_A}\right) = -nRTLn\left(\frac{P_A}{P_B}\right)$$

Some characteristics of reversible work:

- Slow transformation.
- When the force is removed, the system returns to its initial state.
- This transformation is imaginary for mathematical simplification.

12-2) Irreversible work: Take, for example, the non-reversible expansion of an ideal gas at a constant temperature. In this case, there is a sudden change in pressure, where $P_A > P_B$ rapidly, and the external pressure becomes equal to P_B. During this transformation, the gas does work against this pressure.

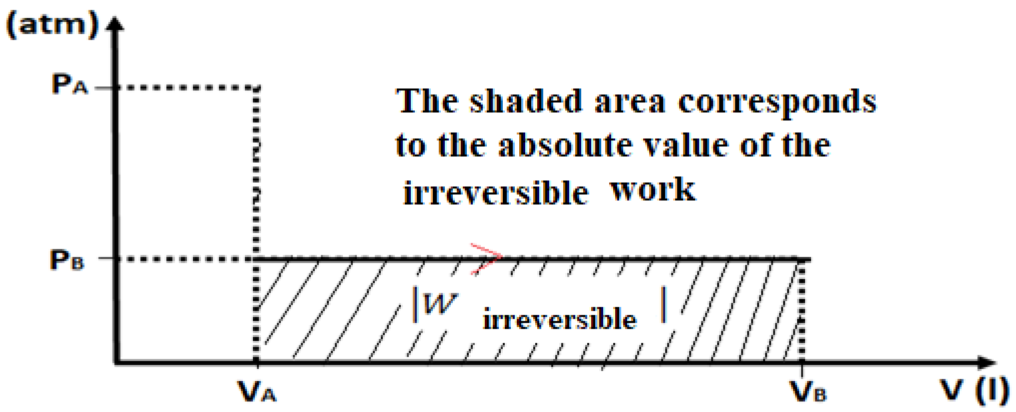
Initial state ⟶ **Final state**

P_A, V_A, T **P_B, V_B, T**

$$W_{AB} = -\int_{V_A}^{V_B} P_{ext} dV$$

reversible work $\Rightarrow P_{ext} = P_f = P_B$

$$W_{AB} = -\int_{V_A}^{V_B} P_B dV = -P_B \int_{V_A}^{V_B} dV = -P_B(V_B - V_A)$$



Clapeyron diagram P = f(V)

Note :

- The absolute value of the work done by the system against the external surroundings is greater in the case of reversible transformation than in the case of irreversible transformation.
- One of the characteristics of irreversible work is that it is a natural, very rapid transformation, and when the force that caused this transformation is removed, the system does not return to its initial state.

Example (1): Calculate the work done by a gas with a volume of 2 L at 25°C and 5 atm pressure when it expands at constant temperature to occupy a volume of 10 L.
• Using the reverse method.
• Using the non-reverse method.
Draw a Clapeyron chart in both cases.

Solution:

Initial state ⟹ **Final state**

$V_1 = 2$ l
$T_1 = 25°C = 298$ °K
$P_1 = 5$ atm

$V_2 = 10$ l
$T_2 = T_1 = 25°C = 298$ °K
$P_2 = ?$

since the transformation occurs at constant temperature , according to Boyle's law relationship:

⇓

$P_1V_1 = P_2V_2$

So :

$$P_2 = \frac{P_1V_1}{V_2} = \frac{5 \times 2}{10} = 1\ atm$$

- **Reversible transformation**

$$W_{12} = -\int_{V_1}^{V_2} P_{ext} dV$$

$$reversible\ transformation \Rightarrow P_{ext} = P_{int} = P_{Sys} = P_g = P$$

$$\text{Ideal gas} \Rightarrow PV = nRT \Rightarrow p = \frac{nRT}{V}$$

$$W_{12} = -\int_{V_1}^{V_2} P_{ext}dV = -\int_{V_1}^{V_2} PdV = -\int_{V_1}^{V_2} \frac{nRT}{V}dV$$

$$If\ the\ temperature\ is\ constant \quad \Rightarrow W_{12} = -nRT_1 \int_{V_A}^{V_B} \frac{dV}{V}$$

$$W_{12} = -nRT_1 Ln\left(\frac{V_2}{V_1}\right) = -nRT_1 Ln\left(\frac{P_1}{P_2}\right)$$

$$n = \frac{P_1V_1}{RT}$$

$$W_{12} = -nRT_1 Ln\left(\frac{P_1}{P_2}\right) = -\frac{P_1V_1}{RT}.RT_1 Ln\left(\frac{P_1}{P_2}\right) =$$

$$-P_1V_1.RT_1 Ln\left(\frac{P_1}{P_2}\right)$$

$$W_{12} = -5 \times 2Ln\left(\frac{5}{1}\right) = -16,09\ atm.l$$

$$1\ atm.l = 1,01325.10^2\ J = 24,24\ cal$$

$$W_{12} = -16,09 \times 1,01325.10^2 = -1630,32\ J = -390,02\ cal$$

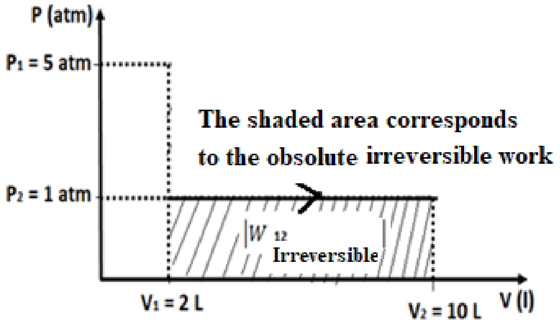
- **Irreversible transformation**

$$W_{12} = -\int_{V_1}^{V_2} P_{ext}dV$$

Irreversible transformation $\Rightarrow P_{ext} = P_f = P_2$

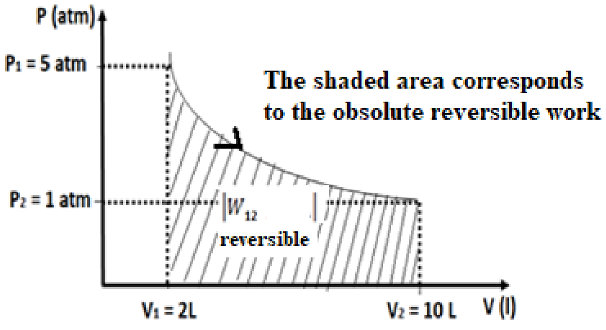
$$W_{12} = -\int_{V_1}^{V_2} P_2dV = P_2(V_2 - V_1) = -1 \times (10 - 2) = -8\ atm.l$$

$$W_{12} = -8 \times 1,01325.10^2 = -810,6\ J = -193,92\ cal$$



The shaded area corresponds to the obsolute irreversible work

Clapeyron diagram **P = f(V)**



The shaded area corresponds to the obsolute reversible work

Clapeyron diagram **P = f(V)**