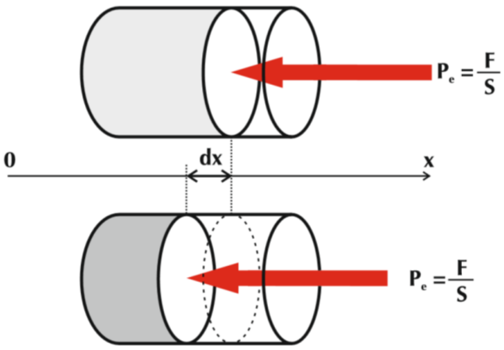
2.1. Concept of work:

2.1.1. Expression of the work of the pressure forces:

Work is defined as the action of an external force on an object over a distance. It is equal to the product of the force (F) times the displacement (x).



$\delta W = - F_e\, dx = - P_e\, S dx = -P_e\, dV$ (S : Surface)

After integration, we find: $W = -\int_1^2 P_e\, dV$ (P_e : external pressure)

For a reversible transformation, we have: $P_e = P$ (P: system pressure)

As a result, $\mathbf{W = -\int_1^2 P\, dV}$

Units of work :

$[W] = Pa.m^3$ = Joules	
[W] = l. atm	**1 l.atm = 101.325 J**
[W] = Cal	**1 Cal = 4.185 J**

Note:

$W = -\int_1^2 P\, dV$

- If $V_2 < V_1$ (compression), $\Delta V < 0$ and $W > 0$, indicating that the system receives work from the external surroundings.
- If $V_2 > V_1$ (expansion), $\Delta V > 0$ and $W < 0$, indicating that the system provides work to the external surroundings.

2.1.2. Work for the different transformations for an ideal gas:

Reversible case:

a) **Isochoric Transformation (V constant , dV =0) :**

$W_{rev} = 0$

b) **Isobaric Transformation:**

$W_{rev} = -P_{ext}(V_2 - V_1) = -P(V_2 - V_1) = -nR(T_2 - T_1)$

c) **Isothermal Transformation:**

$$W = -\int_1^2 P\, dV = -nRT\int_{V1}^{V2} \frac{dV}{V} = -nRT\ln\frac{V_2}{V_1} = nRT\ln\frac{V_1}{V_2} = nRT\ln\frac{P_2}{P_1} = P_1V_1\ln\frac{P_2}{P_1}$$

$(P_1V_1 = P_2V_2)$

Irreversible Case

a) **Isochoric Transformation (V constant, dV =0) :**

$W_{irr} = 0$

b) **Isobaric Transformation:**

$W_{irr} = -P_{ext}(V_2-V_1) = -P_2(V_2-V_1)$

c) **Isothermal Transformation:**

$W_{irr} = -P_{ext}(V_2-V_1) = -P_2(V_2 - V_1) = -P_2(\frac{nRT}{P_2} - \frac{nRT}{P_1}) = nRT(\frac{P_2}{P_1} - 1)$

2.2. Concept of Heat Q :

2.2.1. Définition :

Heat (Q) is a form of energy that is transferred from one part of a system to another or to another system by virtue of a difference in temperature.

In this case, the amount of heat exchanged is proportional to the temperature difference. ($\Delta T = T_2-T_1$) and to the mass (m) of the system.

The expression for the quantity of heat (or heat) is:

$$\delta Q = m.\ c'.\ dT$$

$$Q = \int_{T_1}^{T_2} mc'dT$$

m: mass of the substance (g or Kg).

c': Specific heat capacity (cal (J) / g(Kg).°C(K)).

ΔT: temperature variation (°C or K).

T_1: initial temperature (K).

T_2: final temperature (K).

m : masse du corps (système) s'exprime en g ou en Kg

Units of heat :

[Q] = Joule (J)

[Q] = calorie (cal)

Note:

We can also write:

$\delta Q = n.c.dT \rightarrow Q = \int_{T_1}^{T_2} n.c.dT$

If **c'** is constant, we will have:

$Q = n.c.\Delta T$

With: $\Delta T = T_2 - T_1$

n: number of moles.

c: Molar specific heat capacity (cal (J) / mol.°C(K)).

Note:

$Q<0 \Longrightarrow$ the reaction is exothermic.

$Q>0 \Longrightarrow$ the reaction is endothermic

$Q = 0 \Longrightarrow$ the reaction is athermic

2.2.2. Specific heat capacity (c):

Specific heat, also called **specific heat capacity** is the quantity of heat required to raise the temperature of one unit mass (1g) or one mole (1mol) of a substance by one degree celsius (1 °C) (or one kelvin (1 K)).

We distinguish the following different types of specific heat capacity:

- Specific heat capacity "$\mathbf{c'_v}$" (molar "$\mathbf{c_v}$") at constant volume.
- Specific heat capacity "$\mathbf{c'_p}$" (molar "$\mathbf{c_p}$") at constant pressure.

Example

c water, liquid = 1 cal/g °C = 18 cal/mol °C

2.2.3. Heat capacity (C):

Is the product of the specific heat capacity (molar) of a substance by its mass (number of moles). It is expressed in **cal (J) / K.**

$$\mathbf{C = m.c' = n.c}$$

$$\mathbf{c' = \frac{n.c}{m} = \frac{m/M}{m}\,c = \frac{c}{M}}$$

So: $\mathbf{Q = C.\Delta T}$

There are two types of heat capacity:

C_v: heat capacity at constant volume.

C_p: heat capacity at constant pressure.

For C_p, C_v, c_p and c_v; we have the following two cases:

Case of pure bodies in the solid or liquid states: $c_p \approx c_v$, and, $C_p \approx C_v$

Case of pure bodies in the gaseous state: $c_p \neq c_v$, and, $C_p \neq C_v$

2.2.4. Heat capacity for ideal gases:

- **Monoatomic ideal gases:**

Examples : He, Ar, Ne...

$$\mathbf{C_P = \frac{5}{2}nR}$$

$$\mathbf{C_V = \frac{3}{2}nR}$$

With:

n: number of moles.

R: ideal gas constant.

- **Diatomic ideal gases:**

Examples : O_2, N_2, H_2...

$$\mathbf{C_P = \frac{7}{2}nR}$$

$$\mathbf{C_V = \frac{5}{2}nR}$$

- **Relationship between c_p and c_v for an ideal gas:**

c_p and c_v are linked by the **Mayer** relation: $\mathbf{c_p - c_v = R}$

We also have : $\mathbf{\frac{c_P}{c_V} = \gamma}$ (γ: adiabatic constant)

From these two relationships; we find:

$$\mathbf{c_V = \frac{R}{\gamma - 1}}$$

$\mathbf{c_P = \frac{\gamma.R}{\gamma-1}}$

	c_p (cal/mol.K)	c_v (cal/mol.K)	$\gamma = \frac{c_p}{c_V}$
Monoatomic gas: Ar, Ne, He	5	3	1,66
Diatomic gas : H_2, N_2, O_2	7	5	1,40
Other gases: H_2O, CO_2	8	6	1,33

2.2.5. Quantities of heat for the different transformations:

***Isochoric transformation:**

$$\delta Q = m.c'_V.dT = n.c_V.dT \rightarrow \int_1^2 \delta Q = \int_{T_1}^{T_2} m.c'_V.dT = \int_{T_1}^{T_2} n.c_V.dT$$

$$\mathbf{Q = m.c'_V.(T_2 - T_1) = n.c_V.(T_2 - T_1)}$$

***Isobaric transformation:**

$$\delta Q = m.c'_P.dT = n.c_P.dT \rightarrow \int_1^2 \delta Q = \int_{T_1}^{T_2} m.c'_P.dT = \int_{T_1}^{T_2} n.c_P.dT$$

$$\mathbf{Q = m.c'_p.(T_2 - T_1) = n.c_p.(T_2 - T_1)}$$

***Isothermal transformation:**

$\mathbf{Q = -W}$ (According to the first law of thermodynamics)

$$\mathbf{Q = nRT.Ln\left(\frac{P_1}{P_2}\right) = nRT.Ln\left(\frac{V_2}{V_1}\right)}$$

***Adiabatic transformation:**

$\mathbf{Q = 0}$

2.2.6. Latent heat

Latent heat of a substance is the amount of energy absorbed or released by the substance during a change in its physical state that occurs without changing its temperature.

Or: The latent heat, denoted L, is the amount of heat required to transform one unit of mass (or one mole) of a pure substance from one physical state to another at p=1atm.

$$\mathbf{Q = m.L}$$

Where,

L is Latent Heat in $J.kg^{-1}$ ou $cal.kg^{-1}$

Q is Amount of Heat Released or Absorbed

m is Mass of substance

Or $\mathbf{Q = n\,L}$

Where: n is the number of moles and L is the latent heat expressed in $J.mol^{-1}$ or en $cal.mol^{-1}$.

Latent heat is called by various names depending upon the phase it changes.

- Solid-to-Liquid: Latent Heat of Fusion $L_f>0$

Liquid to solid: Latent Heat of Solidification $L_s = -L_f < 0$

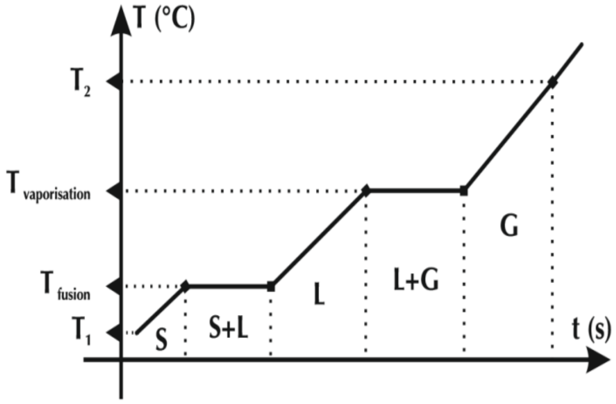
- Liquid-to-Gas: Latent Heat of Vaporization $L_v > 0$
- Solid-to-Gas: Latent Heat of Sublimation $L_{sub}>0$

Exemple :

- The latent heat of fusion of water at 0°C under P = 1atm, L_f = 80.4 cal / g
- The latent heat of vaporization of water at 100°C under P = 1atm, L_v = 535 cal / g

Calculating Heat Required for Phase Change

For a pure substance with mass m in a solid state at temperature T_1, receiving heat quantity Q leads it to a gaseous state at temperature T_2. The heat quantity necessary for this mass to transition from T_1 to T_2 is:



$$\mathbf{Q = Q_1 + Q_2 + Q_3 + Q_4 + Q_5}$$

$$\mathbf{Q} = \int_{T_1}^{T_f} mc_{cp\ solid}dT + mL_f + \int_{T_f}^{T_v} mc_{cp\ liquid}dT + mL_v + \int_{T_v}^{T_2} mc_{p\ gaz}dT$$

$$\mathbf{Q = m_{cp\ solid}(T_f - T_1) + mL_f + m_{cp\ liquid}(T_v - T_f) + mL_v + m_{cp\ gaz}(T_2 - T_v)}$$

2.3. Internal energy:

2.3.1. Définition :

Internal energy, **U** is the total energy of a system. It includes the kinetic energy, potential energy, chemical energy, Electrostatic energy etc. of the system. Thermodynamics is not concerned about calculating the internal energy of a system. However, it is more important to observe **the change in internal energy** (**ΔU**) of a system.

The change in internal energy during a transformation from an initial state to a final state is:

$$\mathbf{\Delta U = W + Q}$$

2.3.2. First principle of thermodynamics

The first principle of thermodynamics, also known as the law of conservation of energy, states that the total energy of an isolated system remains constant. This means that energy cannot be created or destroyed, but it can be converted from one form to another. The principle is based on the concept of energy conservation.

2.3.3. Other statement of the first principle:

a) Conservation principle:

For an isolated system, we have: $Q = W = 0$, therefore: $\Delta U = U_2 - U_1 = Q + W = 0$

Thus, $U_1 = U_2$

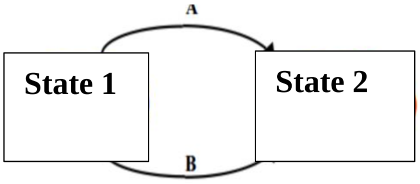
The internal energy of an isolated system remains constant.

b) Equivalence principle:

Consider a closed system undergoing a cyclic transformation. The initial state and the final state coincide. There fore: $U_1 = U_2$

c) Initial and final state principle:

Consider a set of transformations that take a system from an initial equilibrium state 1 to a final equilibrium state 2.



$$\Delta \mathbf{U} = \mathbf{U_2} - \mathbf{U_1} = \mathbf{W_A} + \mathbf{Q_A} = \mathbf{W_B} + \mathbf{Q_B}$$

But $\mathbf{W_A} \neq \mathbf{W_B}$ et $\mathbf{Q_A} \neq \mathbf{Q_B}$

ΔU depends only on the initial and final states and not on the path taken. This principle implies that the internal energy U is a state function.

Note:

Q and W are not state functions.

2.3.4. Differential expression of internal energy:

For an elemental transformation, we have: $\mathbf{dU = \delta Q + \delta W}$

2.3.5. Consequences of the first principle:

a) At constant volume:

$\Delta U = U_2 - U_1 = Q_v + W = Q_v - \int_1^2 P\,dV$

Isochoric transformation V = constant $\Longrightarrow$ dV = 0 $\Longrightarrow$ W = 0

$\mathbf{\Delta U = U_2 - U_1 = Q_v}$

ΔU represents the heat exchanged at constant volume.

b) At constant pressure:

$\Delta U = U_2 - U_1 = Q_p + W = Q_p - p\,(V_2 - V_1)$

$U_2 - U_1 = PV_1 - PV_2 + Q_p \Longrightarrow Q_p = (U_2 + PV_2) - (U_1 + PV_1)$

We define a new state function **H = U + PV** **H : Enthalpy of the system.**

$\mathbf{Q_p = H_2 - H_1 = \Delta H}$

ΔH <0 $\Longrightarrow$ the reaction is exothermic.

ΔH >0 $\Longrightarrow$ the reaction is endothermic.

The heat of reaction at constant pressure is equal to the change in enthalpy of the system, and therefore it only depends on the initial and final states.

- **Relationship between heat of reaction at constant volume and heat of reaction at constant pressure:**

$Q_p = H_2 - H_1 = (U_2 + PV_2) - (U_1 + PV_1) = U_2 - U_1 + PV_2 - PV_1$

$Q_p = Q_v + n_2RT - n_1RT \Longrightarrow \mathbf{Q_P = Q_v + \Delta nRT}$

2.3.6. Applications of the first principle

1. Joule's laws:

- **Joule's first law:**

The internal energy is only a function of temperature.

$U = U(T)$; $dU = C_VdT$; $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

$\Delta U = Q_V = \int_{T_1}^{T_2} C_v dT = \int_{T_1}^{T_2} nc_v dT$

If c_v is constant $\mathbf{\Delta U = nc_v\Delta T}$

- **Joule's second law:**

Enthalpy is only a function of temperature

$H = H(T)$; $dH = C_pdT$; $C_p = \left(\frac{\partial H}{\partial T}\right)_p$

$\Delta H = Q_p = \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} nc_p dT$

If c_p is constant $\mathbf{\Delta H = nc_p\Delta T}$

- Relationship between ΔU et ΔH :

$$\left.\begin{array}{l}\mathbf{\Delta H = nc_p\Delta T} \\ \mathbf{\Delta U = nc_v\Delta T}\end{array}\right\} \quad \frac{\Delta H}{\Delta U} = \frac{c_p}{c_V} = \gamma \qquad \mathbf{\Delta H = \gamma\, \Delta U}$$

2.3.7. Specific transformations:

1. Isothermal transformation:

$$\begin{array}{ccc}\textbf{State 1} & \boxed{T_1 = T_2 = T} & \textbf{State 2} \\ \boxed{n, P_1, V_1, T} & \xrightarrow{\qquad\qquad} & \boxed{n, P_2, V_2, T}\end{array}$$

$P_1V_1 = nRT$ $\qquad\qquad$ $P_2V_2 = nRT$

$$\mathbf{P_1V_1 = P_2V_2}$$

- $\Delta U = nc_v\Delta T = 0$
- $\Delta H = nc_p\Delta T = 0$

$\Delta U = Q + W = 0 \Longrightarrow Q = -W$

- $W = -nRT\ln\frac{V_2}{V_1} = nRT\ln\frac{V_1}{V_2} = nRT\ln\frac{P_2}{P_1} = P_1V_1\ln\frac{P_2}{P_1}$
- $Q = nRT\ln\frac{V_2}{V_1} = nRT\ln\frac{p_1}{p_2}$

Isochoric transformation :

State 1 **State 2**

$$\boxed{n, P_1, T_1, V} \xrightarrow{\boxed{V_1 = V_2 = V}} \boxed{n, P_2, T_2, V}$$

$P_1V = nRT_1$ $P_2V = nRT_2$

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

- $W = 0$
- $\Delta U = Q + W = Qv = nc_v\Delta T$
- $\Delta H = \gamma\ \Delta U = nc_p\Delta T$

Isobaric transformation:

State 1 **State 2**

$$\boxed{n, V_1, T_1, P} \xrightarrow{\boxed{P_1 = P_2 = P}} \boxed{n, V_2, T_2, P}$$

$PV_1 = nRT_1$ $PV_2 = nRT_2$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

- $W =-P\ (V_2 - V_1)$
- $\Delta U = Q + W = nc_v\Delta T$
- $Q_p = \Delta H = nc_p\Delta T$

Adiabatic transformation:

State 1 **State 2**

$$\boxed{n, P_1, T_1, V_1} \xrightarrow{\boxed{Q = 0}} \boxed{n, P_2, T_2, V_2}$$

$P_1V_1 = nRT_1$ $P_2V_2 = nRT_2$

$dU = \delta Q + \delta W$

$\delta Q = 0$, donc $dU = \delta W$

Pour un gaz parfait nous avons:

$dU = nc_V\ dT = n\ (R\ /\gamma\text{-}1)\ dT$

$\delta W = -\ PdV = (-nRT\ /\ V)\ dV$

As a result

$n\ (R/\ \gamma\ \text{-}1)\ dT = (-nRT/V)\ dV \Longrightarrow dT/T = -(\gamma\ \text{-}1)\ (dV/V\ )$

$\ln\ (T) = -(\ \gamma\ -\ 1)\ \ln\ (V) + cst$

$\ln\ (T) + \ln\ (V\ )^{\gamma - 1} = \ln\ (TV^{\gamma - 1}) = cst$

$TV^{\gamma - 1} = cst$

Therefore, : $\mathbf{T_1V_1^{\gamma - 1} = T_2V_2^{\gamma - 1}}$

$$\left.TV^{\gamma - 1} = k\ \right\}\ PV^{\gamma} = K' \Longrightarrow \mathbf{P_1V_1^{\gamma} = P_2V_2^{\gamma}}$$

$T = PV / nR$

$$\left.\begin{array}{l} TV^{\gamma -1} = k \\ V = nRT/ P \end{array}\right\} \quad T^{\gamma}P^{1-\gamma} = K'' \Longrightarrow \quad \mathbf{T_1^{\gamma}P_1^{1-\gamma} = T_2^{\gamma}P_2^{1-\gamma}}$$

$$\left.\begin{array}{l} \mathbf{T_1V_1^{\gamma -1} = T_2V_2^{\gamma -1}} \\ \mathbf{P_1V_1^{\gamma} = P_2V_2^{\gamma}} \\ \mathbf{T_1^{\gamma}P_1^{1-\gamma} = T_2^{\gamma}P_2^{1-\gamma}} \end{array}\right\} \quad \textbf{Laplace's law}$$

Work done by pressure forces during a reversible adiabatic transformation of an ideal gas.:

$\Delta U = Q + W = nc_v\Delta T = nc_v(T_2\text{-}T_1) = nc_v\frac{P_2V_2-P_1V_1}{nR} = \frac{c_V}{R}(P_2V_2 - P_1V_1)$

On a $c_p\text{-}c_v = R$, $\gamma = \frac{c_p}{c_v}$

$\mathbf{W} = \frac{c_V}{c_P-c_V}(P_2V_2 - P_1V_1) = \frac{P_2V_2-P_1V_1}{\gamma-1}$

$$\mathbf{W = \frac{P_2V_2-P_1V_1}{\gamma-1}}$$

Exercice d'application :

1mol of NO (supposedly perfect gas) is subjected to the following successive transformations:

- An isothermal reversible compression from an initial state to state 2.
- An adiabatic reversible expansion from state 2 to state 3.
- An isobaric heating that brings it back to the initial state.

1) Calculate V_1, V_2, T_2, T_3 if P_1=2atm=P_3. P_2=10 atm and T_1=300K.
2) Calculate for each transformation (in joules) the following quantities: Q, W, ΔU, ΔH.

Given: **Cv= 3/2R ; Cp=5/2R**

Solution :

1) Calculation of parameters

$P_1V_1 = nRT_1 \longrightarrow V_1 = nRT_1/P_1 \longrightarrow V_1 = 12{,}3$ L

- V2 will be obtained using the relation:

$P_1V_1 = P_2V_2 \longrightarrow V_2 = V_1 (P_1/P_2) \longrightarrow V_2 = 2{,}46$ L

$T_1=T_2=300K$ (isothermal transformation)

- To determine V_3, we apply the relation

$P_2V_2^{\gamma}= P_3V_3^{\gamma} \longrightarrow V_3= V_2 (P_2/P_3)^{1/\gamma} \longrightarrow V_3 = 6{,}46$ L

- The temperature T_3 is obtained by applying the relation for ideal gases;

$P_3V_3= n RT_3 \longrightarrow T_3= P_3 V_3 /nR \longrightarrow T_3=157{,}6$ K

2) Calcul des différentes grandeurs :

Isothermal transformation 1→2

$\Delta U_{12}= 0$, $\Delta H_{12}= 0$ (since there is no temperature variation)

$\Delta U_{12} =0= Q_{12} +W_{12} \quad Q_{12} = - W_{12} \longrightarrow W_{12} = -nRT\ln\frac{V_2}{V_1} \longrightarrow W = 4014{,}26J$

$Q_{12} = - 4014{,}26J$

Adiabatic transformation 2→3

$Q_{23} = 0 \Rightarrow W_{23} = \Delta U_{23} = n\,c_v\,(T_3 - T_2) = -1776$ J

$\Delta H = nc_p\,(T_3 - T_2) = -2960$ J

IsobaricTransformation 3→1

$W_{31} = -P\Delta V = -P\,(V_1 - V_3) = 2\,(12{,}3 - 6{,}46) = -11{,}68$ L .atm = - 1184J

$\Delta U_{31} = -\,nc_v\,(T_1 - T_3) = 1\,.3/2.\,8{,}31\,(300 - 157{,}6) = 1776$ J

$Q_{23} = \Delta H_{23} = nc_P\,(T_1 - T_3) = 1.\,5/2.\,8{,}31\,(300 - 157{,}6) = 2960$ J