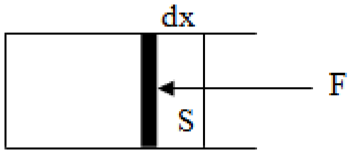
2.1. Concept of work:

2.1.1. Expression of the work of the pressure forces:

Work (**W**) is defined as a force **F** acting through a displacement **x**, the displacement being in the direction of the force.



$$\partial \mathbf{W} = -\mathbf{F.dx}$$

$$\mathbf{P} = \frac{\mathbf{F}}{\mathbf{S}} \rightarrow \mathbf{F} = \mathbf{P.S}$$

$$\partial \mathbf{W} = -\mathbf{P.S.dx} \quad ; \quad \mathbf{S.dx} = \mathbf{dV}$$

$$\partial \mathbf{W} = -\mathbf{P.dV} \longrightarrow \mathbf{W} = -\int \mathbf{P.dV}$$

***Units of work :**

$[W] = Pa.m^3 = Joule\ (J)$

[W] = calorie (cal)

Remark :

*If : $V_2 > V_1 \longrightarrow \Delta V > 0 \longrightarrow W < 0$ (**Expansion**).

*If : $V_2 < V_1 \longrightarrow \Delta V < 0 \longrightarrow W > 0$ (**Compression**).

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

a) Isochoric transformation:

V = constant $\longrightarrow$ dV = 0

W = 0

b) Isobaric transformation:

P = constant ; and ; $W = -P\int_{V_1}^{V_2} dV$

$$\mathbf{W = -P\,(V_2 - V_1)}$$

$$V = \frac{nRT}{P} \rightarrow W = -P\left(\frac{nRT_2}{P} - \frac{nRT_1}{P}\right)$$

$$\mathbf{W = -\,nR\,(T_2 - T_1)}$$

c) Isothermal transformation:

T = constant

$$W = -\int P.dV = -\int nRT\frac{dV}{V} = -nRT\int_{V_1}^{V_2}\frac{dV}{V} = -nRT\,[LnV]_{V_1}^{V_2}$$

$$\mathbf{W = -nRT.Ln\left(\frac{V_2}{V_1}\right)}$$

$$P_1V_1 = P_2V_2 \rightarrow \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\mathbf{W = -nRT.Ln\left(\frac{P_1}{P_2}\right)}$$

2.2. Concept of heat:

2.2.1. Definition:

Heat or **quantity of heat** (**Q**) is the thermal energy that is transferred from one system at a higher temperature to another system (or the surroundings) at a lower temperature as the result of a temperature difference.

The expression for the quantity of heat is:

$\partial Q = m.c'.dT \rightarrow Q = \int_{T_1}^{T_2} m.c'.dT$

If **c'** is constant, we will have: $Q = m.c'.\Delta T$

With: $\Delta T = T_2 - T_1$

m: Mass of the substance.

c': ***Specific heat capacity*** (***J/g.K***, ***cal/g.K***).

ΔT: Temperature change.

T_1: Initial temperature.

T_2: Final temperature.

Note: We can also write:

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

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 heat capacity*** (***cal/mol.K***, ***J/mol.K***).

Units of heat :

[Q] = Joule (J)

[Q] = calorie (cal)

2.1.2. Specific heat capacity (c):

Specific heat capacity, also called ***specific heat*** is the quantity of heat required to raise the temperature of 1g (or 1mol) of a substance by 1 °C.

We distinguish the following different types of specific heat capacity :

- Specific heat capacity “c'_v” (molar heat capacity “c_v”) at constant volume.
- Specific heat capacity “c'_p” (molar heat capacity “c_p”) at constant pressure.

2.1.3. Heat capacity (C):

Is the product of the specific heat capacity (molar heat capacity) of a substance by its mass (number of moles). **C = m.c'= n.c**

So: **Q = C.ΔT**

C: Heat capacity (**cal /K** ; **J/ K)**

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 substances in the solid or liquid states: $c_p \approx c_v$, and, $C_p \approx C_v$

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

2.1.4. Heat capacity for ideal gases:

- **Monatomic 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 index)

From these two relationships; we find:

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

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

2.1.5. Quantities of heat for the different transformations:

***Isochoric transformation:**

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

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

***Isobaric transformation:**

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

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

***Isothermal transformation:**

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

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

***Adiabatic transformation:**

$$\mathbf{Q = 0}$$

2.1.6. Latent heat of physical state change:

Latent heat is the quantity of heat absorbed or released by 1g (or 1mol) of a substance during a change in its physical state that occurs at constant temperature. It is denoted **L'** (or **L**).

The quantity of heat for physical state change is given by:

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

[L'] = cal/g, J/g

[L] = cal/mole, J/mole

Solid → Liquid: Latent heat of fusion or melting ($L_f>0$)

Liquid → Solid: Latent heat of solidification or freezing ($L_s = - L_f < 0$)

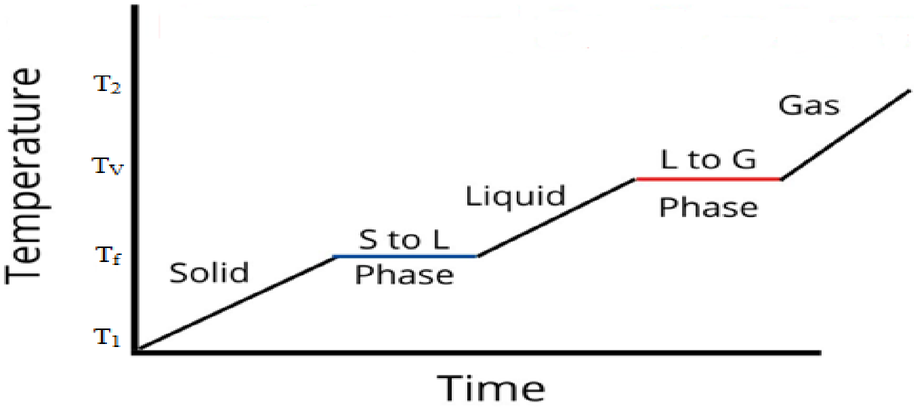
Liquid → Gas: Latent heat of vaporization ($L_v >0$)

Gas → Liquid: Latent heat of liquefaction ($L_{liq} = - L_v < 0$)
Solid → Gas: Latent heat of sublimation ($L_{sub} > 0$)
Gas → Solid: Latent heat of condensation ($L_{cond} = - L_{sub} < 0$)

Examples :

For water: $L_f = 80$ cal/g (p = 1atm ; T = 0°C)
$L_v = 535$ cal/g (p = 1atm ; T = 100°C)

*** Calculating (Q) during the heating of a pure substance :**



The quantity of heat for 1g of a pure substance undergoing fusion and vaporization, transitioning from temperature T_1 to temperature T_2, is expressed as:

$Q = Q_1 + Q_2 + Q_3 + Q_4 + Q_5$

$$\mathbf{Q = m.c'_{p(solid)}.(T_f - T_1) + m.L'_f + m.c'_{p(liquid)}.(T_v - T_f) + m.L'_v + m.c'_{p(vapor)}.(T_2 - T_v)}$$

T_f: temperature of fusion (melting).
T_V: temperature of vaporization.

2.3. First principle of thermodynamics:

2.3.1. Statement of the first principle of thermodynamics:

First principle of thermodynamics is thus *conventionally* stated as: « **The change in internal energy of a system is equal to the energy exchanged between the system and the surroundings in the form of work and heat.** »

Mathematically, this can be put as :

$$\mathbf{dU = \partial W + \partial Q} \longrightarrow \mathbf{\Delta U = W + Q}$$

U: is the internal energy; it is a state function.
W and Q are not state functions.

2.3.2. Internal energy (U):

Is the sum of potential and kinetic energies of all particles in a system. Its differential expression is:

$$\mathbf{dU = n.c_V.dT}$$

[U] = joule, calorie.

***1st law of Joule:**

For an ideal gas, the internal energy (U) only depends on the temperature, it is independent of pressure and volume.

2.3.3. Enthalpy (H):

Enthalpy is defined as the sum of a system's internal energy (U) and the work that the system has done on its surroundings. It is a state function.

$\mathbf{H = U + P.V}$

The differential expression for enthalpy is:

$\mathbf{dH = n.c_P.dT}$

[H] = joule, calorie

***2nd law of Joule:**

For an ideal gas, the enthalpy (H) only depends on the temperature, it is independent of pressure and volume.

2.3.4. Internal energy change for the different transformations:

a) Isochoric transformation:

$\int_{U1}^{U2} dU = \int_{T_1}^{T_2} n.c_V.dT = n.c_V \int_{T_1}^{T_2} dT$

$\mathbf{\Delta U = U_2 - U_1 = n.c_V.(T_2 - T_1)}$

$V = Cte \rightarrow W = 0$; and; $\Delta U = W + Q$; Hence $\mathbf{\Delta U = Q_V}$

b) Isobaric transformation:

$\int_{U1}^{U2} dU = \int_{T_1}^{T_2} n.c_V.dT$

$\mathbf{\Delta U = U_2 - U_1 = n.c_V.(T_2 - T_1)}$

c) Isothermal transformation:

$T = cte \longrightarrow \Delta T = 0$

$\int_{U1}^{U2} dU = \int_{T_1}^{T_2} n.c_V.dT \rightarrow \Delta U = n.c_V.\Delta T$

$\mathbf{\Delta U = 0}$

We have: $\mathbf{\Delta U = W + Q}$ (According to the 1st principle of thermodynamics)

and : $\mathbf{\Delta U = 0}$ (According to the 1st law of Joule)

So: $\mathbf{Q = -W}$

d) Adiabatic transformation:

$\int_{U1}^{U2} dU = \int_{T_1}^{T_2} n.c_V.dT = n.c_V \int_{T_1}^{T_2} dT$

$\mathbf{\Delta U = U_2 - U_1 = n.c_V.(T_2 - T_1)}$

We have: $\mathbf{\Delta U = W + Q}$; and; $\mathbf{Q = 0}$

Hence : $\mathbf{\Delta U = W}$

2.3.5. Enthalpy change for the different transformations:

a) Isochoric transformation:

$\int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} n.c_P.dT = n.c_P \int_{T_1}^{T_2} dT$

$\mathbf{\Delta H = H_2 - H_1 = n.c_p.(T_2 - T_1)}$

b) Isobaric transformation:

$\int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} n.c_P.dT = n.c_P \int_{T_1}^{T_2} dT$

$\mathbf{\Delta H = H_2 - H_1 = n.c_p.(T_2 - T_1)}$

$P = Cte \rightarrow W = -P(V_2 - V_1)$

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

$Q_P = (U_2 + P.V_2) - (U_1 + P.V_1)$

We have: $H = U + P.V$

Hence: $Q_P = H_2 - H_1 = \Delta H$

$\mathbf{Q_P = \Delta H}$

c) Isothermal transformation:

$T = cte \longrightarrow \Delta T = 0$

$\int_{H}^{H_2} dH = \int_{T_1}^{T_2} n.c_P.dT \rightarrow \Delta H = n.c_P.\Delta T$

$\Delta H = 0$ (According to the 2nd law of Joule)

d) Adiabatic transformation:

$\int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} n.c_P.dT = n.c_P \int_{T_1}^{T_2} dT$

$\mathbf{\Delta H = H_2 - H_1 = n.c_p.(T_2 - T_1)}$

Note:

$\Delta H = n.c_P.\Delta T$

$\Delta U = N.C_V.\Delta T$

$\frac{\Delta H}{\Delta U} = \frac{c_p}{c_V} = \gamma \rightarrow \boldsymbol{\Delta H = \gamma.\Delta U}$

2.3.6. Reversible adiabatic transformation:

$dU = \partial Q + \partial W$, and, $\partial Q = 0$ (adiabatic), so : $dU = \partial W$

$dU = n\, c_V\, dT = n\, \frac{R}{\gamma - 1} dT$, and, $\partial W = -P\, dV = -nRT\frac{dV}{V}$

So : $n\, \frac{R}{\gamma - 1} dT = -nRT\frac{dV}{V} \rightarrow \int \frac{dT}{T} = -(\gamma - 1) \int \frac{dV}{V}$

$LnT = -(\gamma - 1)LnV + Cte \rightarrow LnT + LnV^{(\gamma-1)} = Cte \rightarrow Ln\left(T.V^{(\gamma-1)}\right) = Cte$

$\mathbf{T.V^{(\gamma-1)} = K}$

We have also:

$T.V^{(\gamma-1)} = K$; and; $T = \frac{P\,V}{n\,R}$

Hence: $\left(\frac{P\,V}{n\,R}\right).V^{(\gamma-1)} = K \rightarrow P.V^{\gamma} = K.n.R = k'$

$\mathbf{P.V^{\gamma} = k'}$

And we have also:

$T.V^{(\gamma-1)} = K$; and ; $V = \frac{nRT}{P}$

$T.(\frac{nRT}{P})^{(\gamma-1)} = K \rightarrow T^{\gamma}.P^{(1-\gamma)} = \frac{K}{(n.R)^{(\gamma-1)}} = K''$

$\mathbf{T^{\gamma}.P^{(1-\gamma)} = K''}$

$$\left.\begin{aligned}&\mathbf{T.V^{(\gamma-1)} = K}\\&\mathbf{P.V^{\gamma} = k'}\\&\mathbf{T^{\gamma}.P^{(1-\gamma)} = K''}\end{aligned}\right\}\ \textbf{Laws of LAPLACE}$$

2.3.7. Reversible adiabatic work:

Adiabatic transformation : $\mathbf{Q = 0}$; So :

$W = \Delta U = n.c_V.(T_2 - T_1)$; and ; $c_v = \frac{R}{\gamma-1}$

$$\mathbf{W = n\frac{R}{\gamma-1}(T_2 - T_1)}$$

$W = \frac{1}{\gamma-1}(nRT_2 - nRT_1)$; and ; $PV = nRT$

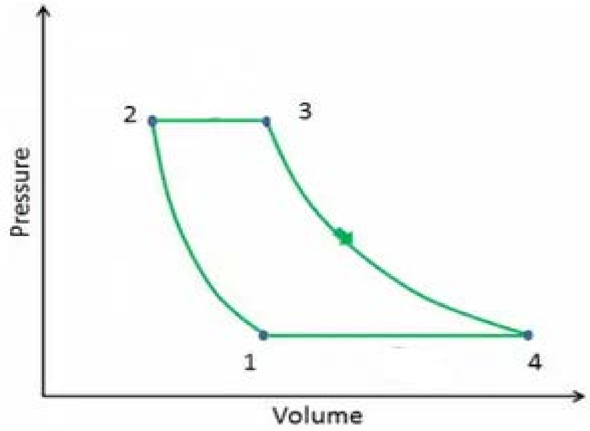
Hence : $W = (\frac{1}{\gamma-1})(P_2V_2 - P_1V_1)$

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

2.3.8. Special cases:

a) Cyclic transformation (Cyclic process):

Is a process in which the initial and final states are the same. It is a sequence of processes that leave the system in the same state in which it started.



$\mathbf{U_1 = U_2 \rightarrow \Delta U = U_2 - U_1 = 0}$

$\mathbf{\Delta U = Q + W = 0 \rightarrow Q = -W}$ $\mathbf{Q \neq 0}$; and; $\mathbf{W \neq 0}$

b) Isolated system:

The isolated system does not exchange energy with the surroundings.

$\mathbf{Q = 0}$; and; $\mathbf{W = 0}$

$\mathbf{\Delta U = Q + W = 0 \rightarrow \Delta U = U_2 - U_1 = 0 \rightarrow U_2 = U_1}$