

Chapter II :

First principle of thermodynamics

I- Introduction :

In this lecture we shall study the first law of thermodynamics and explore possible thermodynamic processes through which heat can be converted into work.

II- Notion of heat (Q)

- When a container is placed over a fire, the temperature of the water rises. It is said that the heat source has given heat to the water.
- When water cools, it loses heat.

The amount of energy transferred to water is called 'heat'.

it is given by the relation:

$$Q = m.C. \Delta T$$

C : specific heat

II-1- Specific heat (C) :

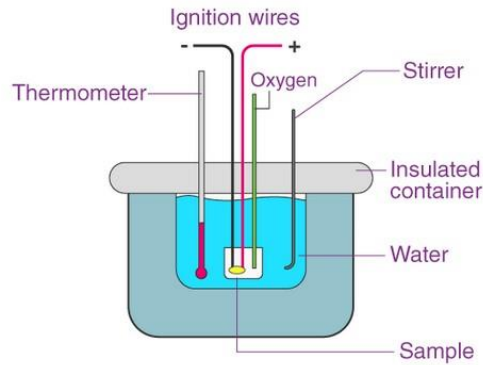
is the quantity of heat required to raise the temperature of one gram of a substance by one Celsius degree. The units of specific heat are usually calories or joules per gram per Celsius degree. For example, the specific heat of water is 1 calorie (or 4.186 joules) per gram per Celsius degree. The Scottish scientist Joseph Black, in the 18th century, noticed that equal masses of different substances needed different amounts of heat to raise them through the same temperature interval, and, from this observation, he founded the concept of specific heat.

The SI unit for heat is a form of energy called the joule (J). Heat is frequently also measured in the calorie (cal), which is defined as "the amount of heat required to raise the temperature of one gram of water from 14.5 degrees Celsius to 15.5 degrees Celsius."

II-2- Measuring the Heat :

A **calorimeter** is an object used for calorimetry, or the process of measuring the heat of chemical reactions or physical changes as well as heat capacity. It mainly consists of a metallic vessel made of materials which are good conductors of electricity such as copper and aluminium etc. There is also a facility for stirring the contents of the vessel. This metallic vessel with a

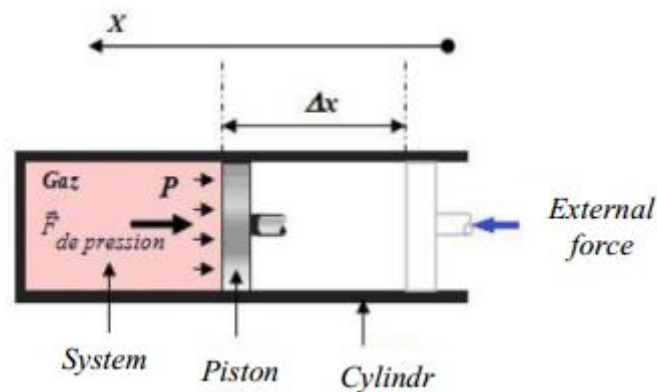
stirrer is kept in an insulating jacket to prevent heat loss to the environment. There is just one opening through which a thermometer can be inserted to measure the change in thermal properties inside.



III-Notion of work (W) :

Work is defined, for mechanical systems, as the action of an external force on an object over a distance.

Consider a cylinder containing a gas at pressure 'P'; the piston has cross-section 'S'.



$$\vec{F} = \vec{P} \times S$$

When an external operator exerts a force on the piston, it moves to the left: the gas then exerts a force 'F' ; Where: 'F' is in Newton (N); 'S' is in square meter (m²).

* Work is equal to the product of force (F) times displacement (dx) according to the equation:

$$\delta W = \vec{F} \times \vec{dx}$$

*The volume (V) represents the surface by a distance (x):

$$V = S.x$$

$$\delta W = F. dx = P. S. dx \quad \text{and} \quad V = S.x \Rightarrow dV = S. dx \Rightarrow dx = \frac{dV}{S}$$

$$\Rightarrow W = P \cdot S \cdot \frac{dV}{S} \Rightarrow \delta W = P \cdot dV$$

III-1- Expression of the work in case of reversible transformation:

Example :

- ✓ When the gas expansion is reversible and this involves the external pressure being less than the internal pressure, by a small extent throughout the expansion process and in this case $P = P_{ext}$.

We have :

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

By integrating the previous equation with gas being considered ideal and consisting of a number of moles, so the law can be used :

$$\text{Perfect gas} \Rightarrow PV = nRT$$

If the transformation is isothermal :

$$W = - \int_{V_1}^{V_2} \frac{nRT}{V} \cdot dV$$

$$\Rightarrow W = -nRT \ln \frac{V_2}{V_1}$$

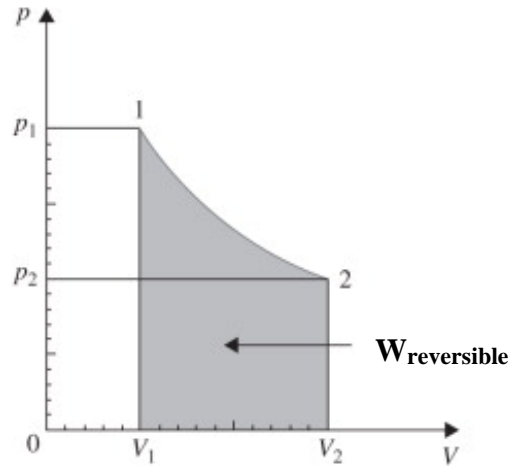
From **Boyle's Law**:

Becomes the previous equation

$$W = -nRT \ln \frac{P_1}{P_2}$$

- **Calculation of work graphically :**

The work is equal to the area calculated between the curve and the axis of the volumes and the two lines $1V_1$ and $1V_2$



III-2- Expression of the work in case of irreversible transformation:

Example :

- ✓ When the gas expansion is irreversible, this involves a sudden change of pressure, in which case: $P = P_2$ (final pressure).

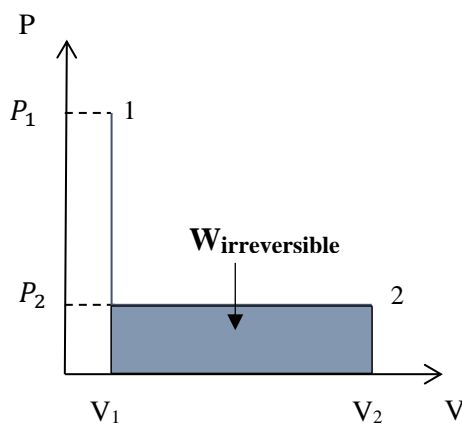
We have :

$$W = - \int_{V_1}^{V_2} P_2 \cdot dV$$

By integrating the previous equation:

$$W = -P_2 \int_{V_1}^{V_2} (V_2 - V_1)$$

- Calculation of work graphically :



IV- First principle of thermodynamics :

Internal energy definition is given as:

The energy contained within the system associated with random motions of the particles along with the potential energies of the molecules due to their orientation.

The energy due to random motion includes translational, rotational, and vibrational energy. It is represented as U . So now we can say, since internal energy is a state function and in all the processes shown above the change in internal energy from state, 'a' to state 'b' will be the same.

IV-1- Text of the first principle of the thermodynamic :

The first law of thermodynamics is based on the law of conservation of energy, which states that energy cannot be created or destroyed, but can be transferred from one form to another.

Many power plants and engines operate by turning heat energy into work. The reason is that a heated gas can do work on mechanical turbines or pistons, causing them to move. The first law of thermodynamics applies the conservation of energy principle to systems where heat transfer and doing work are the methods of transferring energy into and out of the system. The first law of thermodynamics states that the change in internal energy of a system ΔU equals the net heat transfer into the system Q , plus the net work done on the system W . In equation form, the first law of thermodynamics is, $\Delta U=Q+W$.

Where,

- ΔU is the internal energy
- Q is the heat added to the system
- W is the work done by the system

Note :

❖ We have to be very careful with the first law. About half of textbooks, teachers, and professors write the first law of thermodynamics as $\Delta U=Q+W$ and the other half write it as

$$\Delta U = Q-W.$$

Both equations are correct, and they say the same thing. The reason for the difference is that in the formula $\Delta U = Q + W_{\text{on gas}}$, we are assuming that W represents the **work done on the system**, and when we use $\Delta U=Q-W_{\text{by gas}}$, we are assuming that W represents the **work done by the system**.

The two different equations are equivalent since, $W_{\text{on gas}} = - W_{\text{by gas}}$

When **work is done on a system**, the work done adds to the internal energy of the system (hence the plus sign in $\Delta U = Q + W_{\text{on gas}}$)

When **work is done by a system**, the work done takes away from the internal energy of the system (hence the minus sign in $\Delta U = Q - W_{\text{by gas}}$)

❖ It is a state function that depends only on the equilibrium state the system is in (it does not depend on the path followed by the system during the transformation);

❖ It is expressed in Joule (J) or calorie (cal);

❖ By convention: if $\Delta U > 0$, energy is supplied to the system, if $\Delta U < 0$, energy is given up by the system.

IV-2-Application to transformations :

IV-2-1-Isochore transformation ($V = \text{cte}$) :

At: $V = \text{Cte}$; $W = 0 \implies \Delta U = Q_V + 0 \implies \Delta U = Q_V$

$$\Delta U = Q_V = m \cdot C_V \cdot \Delta T ; \Delta U = Q_V = n \cdot C_V \cdot \Delta T$$

IV-2-2-Isobaric transformation ($P = \text{cte}$) :

According to the first principle :

$$\Delta U = Q + W$$

$$P = \text{Cte} \Rightarrow W = - \int_{V_1}^{V_2} P \cdot dV = -P(V_2 - V_1)$$

So :

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

✓ Enthalpy :

During the transformation being made at constant pressure it can be written :

According to the first principle :

$$\Delta U = Q_P + W_P$$

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

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

And from it we know a new H function so that:

$$H = U + P V$$

the equation becomes:

$$Q_P = H_2 - H_1 = \Delta H \Rightarrow Q_P = \Delta H$$

Note :

U: is a state function, P.V: is a state function, so H is a state function

✓ **Heat capacity :**

Mass or molar heat capacity or mass or molar specific heat is the heat required to raise the temperature of a unit mass or mole of a substance by one degree.

It is measured at constant pressure (C_P) or constant volume (C_V).

The heat capacities C_p and C_V of a pure body are respectively the derivatives of its enthalpy and internal energy with respect to temperature:

$$C_P = \left[\frac{\delta Q}{dT} \right]_P = \frac{\delta Q_p}{dT} = \frac{dH}{dT}$$

$$C_V = \left[\frac{\delta Q}{dT} \right]_V = \frac{\delta Q_V}{dT} = \frac{dU}{dT}$$

The amount of heat required to raise the temperature of 'n' moles of 1 pure substance from T_1 to T_2 is:

At : P = Cte : $\delta Q_P = dH = n.C_P.dT \Rightarrow \Delta H = Q_P =$

$$\Delta H = n \int_{T_1}^{T_2} C_p \cdot dT$$

At : V = Cte : $\delta Q_V = dU = n.C_V.dT \Rightarrow \Delta U = Q_V =$

$$\Delta U = n \int_{T_1}^{T_2} C_v \cdot dT$$

The amount of heat required to raise the temperature of 'm' grammes of 1 pure substance from T_1 to T_2 is:

At : P = Cte : $\Delta H = Q_P = m \int_{T_1}^{T_2} C_p \cdot dT$

At : V = Cte : $\Delta U = Q_V = m \int_{T_1}^{T_2} C_v \cdot dT$

Note:

Both C_p and C_V functions relate to temperature in shape: $aT^2 + bT + C$

In the case of C_p and C_V fixed numbers independent of temperature, it can be written:

$$\Delta U = n C_V \cdot \Delta T, \quad \Delta H = n C_p \cdot \Delta T$$

✓ **Relation between C_p and C_v (MAYER relation) :**

We have: $dH = dU + d(P.V) \dots (1)$

$$dH = n.C_p. dT \dots (2)$$

$$dU = n.C_v dT \dots (3)$$

By exploiting equations: (1), (2) and (3) :

$$dH = dU + d(PV) \Rightarrow n.C_p. dT = n.C_v dT + d(PV) ; (P.V = n. R.T)$$

$$\Rightarrow n.C_p. dT = n.C_v dT + d(n.R.T) = n.C_v dT + nRdT \text{ (ividing by 'n dT')}$$

so we'll have: $C_p = C_v + R \Rightarrow \mathbf{C_p - C_v = R}$ **MAYER Relation**

- γ is the ratio between C_p and C_v ; $\gamma = \frac{C_p}{C_v} > 1$ (γ is called the adiabatic constant).

IV-2-3-Isothermal transformation (T = cte):

Characteristic equation

In Initial state: $P_1.V_1 = n. R.T \dots (1)$

In the final state: $P_2.V_2 = n. R.T \dots (2)$

Expression of work

$$P \neq \text{Cte and } P.V = n. R. T \Rightarrow P = \frac{nRT}{V} \dots \dots \dots (2)$$

Replacing (2) in (1) gives:

$$W = - \int_1^2 n. R. T. \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2} ; \text{ (Since } \frac{P_1}{P_2} = \frac{V_2}{V_1} \text{)}$$

$$W = -nRT \ln \frac{V_2}{V_1}$$

$$W = -nRT \ln \frac{P_1}{P_2}$$

Expression of heat quantity :

Since $U = f(T)$: so $\Delta U = 0 \Rightarrow Q + W = 0 \Rightarrow Q = - W$

$$Q = nRT \ln \frac{V_2}{V_1}$$

$$Q = nRT \ln \frac{P_1}{P_2}$$

Expression of internal energy :

Since $U = f(T)$: so $\Delta U = 0$

Expression of enthalpy :

Since $H = f(T)$: so $\Delta H = 0$

IV-2-4-Adiabatic transformation ($Q = 0$) :

An adiabatic transformation is one that takes place without any change in heat ($Q = 0$).

We have:

$$dU = \delta Q + \delta W = 0 + \delta W \Rightarrow dU = \delta W = -PdV$$

$$\Delta U = W = \int nC_V dT = - \int PdV$$

This equation can be written:

$$nC_V dT = -PdV$$

According to the ideal gas relationship:

$$nC_V dT = -\frac{nRT}{V} dV$$

$$\frac{dT}{T} = -\frac{R}{C_V} \cdot \frac{dV}{V}$$

According to Meyer's relationship

$$C_p - C_V = R$$

Dividing both sides of the equation by C_V :

$$\frac{C_p - C_V}{C_V} = \frac{R}{C_V} = \frac{C_p}{C_V} - 1 = \gamma - 1$$

So:

$$\frac{dT}{T} = -(\gamma - 1) \frac{dV}{V}$$

By integration we get :

$$\ln T + \ln V^{\gamma-1} = K \Rightarrow$$

$$T V^{\gamma-1} = K'$$

During reversible adiabatic transformation, $T V^{\gamma-1}$ remains constant and writes the previous relationship:

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

It's the first equation of **Laplace**.

The adiabatic equation of state can also be described:

- ❖ Temperature as a function of volume;
- ❖ Pressure as a function of pressure.
- We have: $P.V = n.R.T \Rightarrow V = \frac{nRT}{P}$

By replacing in the relation:

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

We get the second equation of **Laplace**:

$$T_i^\gamma P_i^{1-\gamma} = T_f^\gamma P_f^{1-\gamma}$$

- We have: $P.V = n.R.T \Rightarrow T = \frac{PV}{nR}$

By replacing in the relation:

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

We get the third equation of **Laplace**:

$$P_i V_i^\gamma = P_f V_f^\gamma$$

✓ Expression of adiabatic transformation work :

Based on the first principle of Thermodynamics:

$$\delta U = \delta Q + \delta W = \delta W$$

As $Q = 0$:

$$W = \Delta U = \int_{T_f}^{T_i} nC_V dT = nC_V(T_f - T_i)$$

$$T_f = \frac{P_f V_f}{nR}, \quad T_i = \frac{P_i V_i}{nR}$$

With compensation we find:

$$W = nC_V \left(\frac{P_f V_f}{nR} - \frac{P_i V_i}{nR} \right)$$

$$\frac{C_V}{R} = (\gamma - 1)^{-1}$$

$$W_{ad} = \frac{1}{\gamma - 1} (P_f V_f - P_i V_i)$$

Note :

For diatomic gases : $\gamma = 7/5 = 1,4$

For monoatomic gases : $\gamma = 5/3 = 1,66$

The following table shows recipes for calculating Q , W , ΔU , and ΔH for an ideal gas undergoing a reversible change along the specified pathway.

Table 1: Thermodynamics Properties for a Reversible Expansion or Compression.

Pathway	Q	W	ΔU	ΔH
Isothermal	$Q = -W$	$-nRT \ln(V_2/V_1)$	0	0
Isochoric	$n \int_{T_1}^{T_2} C_V \cdot dT$	0	$\Delta U = Q_V$	$n \int_{T_1}^{T_2} C_p \cdot dT$
Isobaric	$n \int_{T_1}^{T_2} C_p \cdot dT$	$-p\Delta V$	$\Delta U = Q_p + W$ $n \int_{T_1}^{T_2} C_V \cdot dT$	$n \int_{T_1}^{T_2} C_p \cdot dT$
Adiabatic	0	$\frac{1}{\gamma - 1} (P_f V_f - P_i V_i)$ $= \Delta U$	$n \int_{T_1}^{T_2} C_V \cdot dT$ $= W$	$n \int_{T_1}^{T_2} C_p \cdot dT$

For the ring :

$$\Delta U_{cycle} = \Delta H_{cycle} = 0$$

$$Q_{cycle} = \sum Q = -W_{cycle}$$