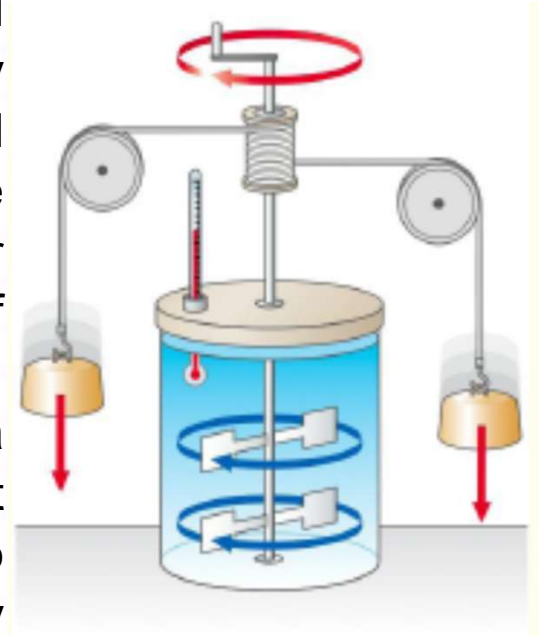


# The Joule experiment and the mechanical equivalent of calory

**The mixture calorimeter.** It is a container isolated from the external environment: there is no  $\Delta Q$  exchanged. The two masses are properly bound to the central axis that can rotate. When the two masses fall down they induce rotation of the axis with the shovels (some mechanical energy is transferred to the system). Therefore, the water temperature increases (the shovels rotation will heat water because of viscosity).

Mechanical energy dissipation because of water viscosity, will induce a measurable water-T growth. From this we can calculate the heat transferred to the system and its T increase. This heat is due to dissipation of an equal amount of potential energy (energy conservation). The ratio between the work by the weight on the system ( $U_p$  potential energy of weight,  $mgh$ ) and  $\Delta Q$  is a constant. This constant is a conversion factor between different units and is referred to as the **mechanical equivalent of calory**.



**MECHANICAL EQUIVALENT of CALORY, J:**

$$J = \frac{L}{\Delta Q} = \frac{4,186 J}{1 cal} = \frac{4186 J}{1Kcal}$$

# 1st Principle of Thermodynamics

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## I PRINCIPLE of THERMODYNAMICS – INTERNAL ENERGY

This principle can be viewed as a generalized form of the energy conservation.

$$\Delta Q = L + \Delta U$$

**$\Delta Q$**  = heat exchanged by the system ( $\Delta Q > 0$  absorbed by the system,  $\Delta Q < 0$  given by the system)

**$L$**  = work made by the system onto the exterior ( $L > 0$ , when the system expands)

**$\Delta U$**  = a new thermodynamical function, the internal energy.

**$U$ , internal energy:** it is the sum of kinetic and potential energy of all the particles of the system.

# Internal energy

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INTERNAL ENERGY:

$$U = \sum_i (K_i + U_i)$$

$U_i$  = potential energy of the  $i$ -th particle.

$U$  is a state function, namely it only depends on the thermodynamical state of the system

$\Delta U = U(B) - U(A) = \Delta U(A,B)$ , i.e. it is transformation-path independent to go from  $A$  to  $B$ .

Moving to infinitesimal transformations:

$dU \Rightarrow$  “ $d$ ” indicates an infinitesimal variation of  $U$  that is path independent and only depends on the initial and final states (the latin « $d$ »).

$$dU = \delta Q - \delta L$$

$\delta Q, \delta L \Rightarrow$  “ $\delta$ ” (greek) indicates that the  $Q$  and  $L$  variations depend also on the transformation path and not only on the initial and final states.

# 1<sup>st</sup> principle for cyclic transformations

$$\Delta U^{(1)} (A \rightarrow B) = \Delta U^{(2)} (A \rightarrow B)$$

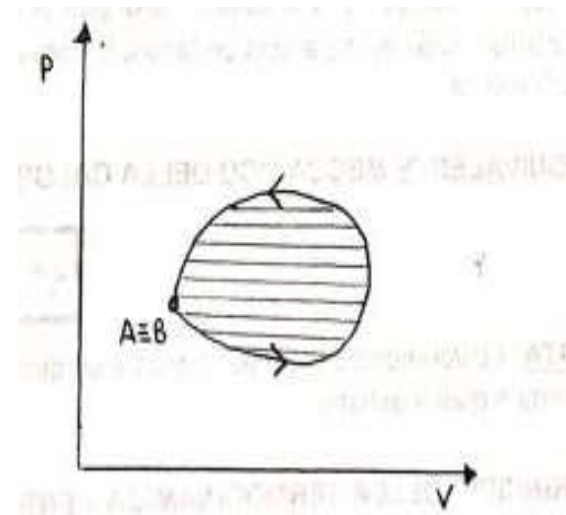
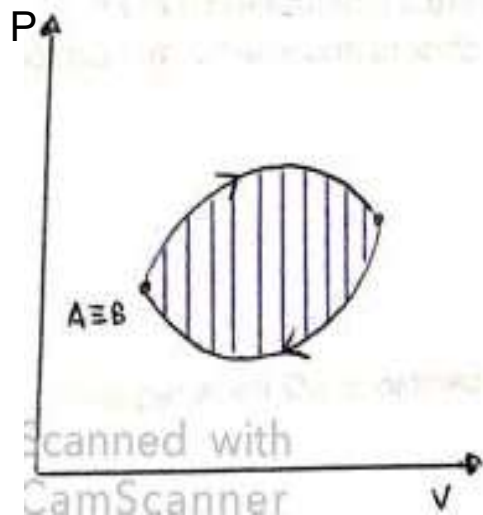
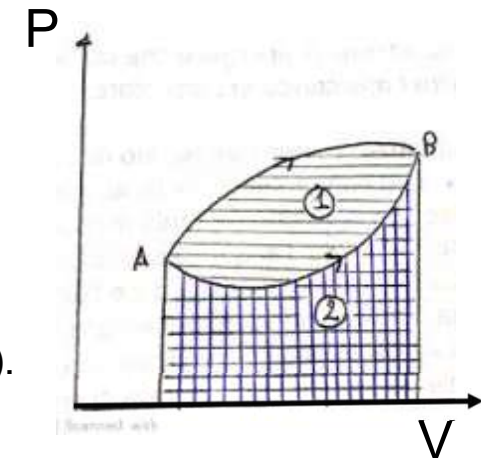
$L^{(1)} (A \rightarrow B) \neq L^{(2)} (A \rightarrow B)$  green area  $\neq$  blue area

In particular  $L^{(1)} (A \rightarrow B) > L^{(2)} (A \rightarrow B)$

Analogously in general:

$$\Delta Q^{(1)} (A \rightarrow B) \neq \Delta Q^{(2)} (A \rightarrow B)$$

For cyclic transformations we have  $A = B$  (initial and final states coincide).



$$\Delta U = U^{(B)} - U^{(A)} \quad L (A \rightarrow B) > 0 \text{ clockwise}$$

$$L (A \rightarrow B) < 0 \text{ anti-clockwise}$$

$$\Delta U = 0 \quad \Delta Q = L \quad (\text{that can be } > \text{ or } < 0) \text{ for } \mathbf{Cyclic Transformations}$$

# Thermodynamical transformations

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A transformation is said reversible (or quasi static) when, by changing by whatever small amount  $\epsilon$  the transformation conditions, the direction of the transformation will be reversed. When this does not occur, the transformation is irreversible. Any real transformation is actually irreversible. Reversible transformation is an ideal case.

**Isobare:**  $P = \text{cost}$

**Isovolumic (isochore):**  $V = \text{cost}$

**Adiabatic:**  $\Delta Q = 0$  (no heat exchange between system and exterior)

**Isothermal:**  $T = \text{cost}$

As for the graphs representing irreversible transformations in the Clapeyron's plane, it is not possible to draw a precise curve. Any irreversible transformation is not made of equilibrium states and thus we can identify no intermediate point in the Clapeyron's plane as the system is not at equilibrium.

# Ideal gases

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A gas is ideal when (1) interactions with the wall are elastic, (2) the volume of its molecules is negligible and, mainly, (3) the molecule-molecule interaction is negligible. In ideal gases there is no potential energy but only kinetic, associated to its particles. Hence, **its internal energy only depends on temperature. Any gas at sufficiently high T and low P behaves as ideal. At equilibrium the state equation holds true.**

STATE EQUATION:

$$PV = nRT$$

**P** = pressure

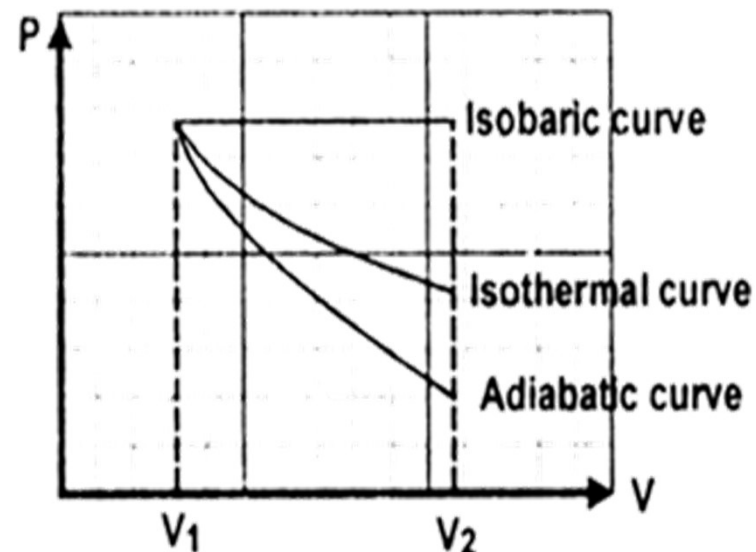
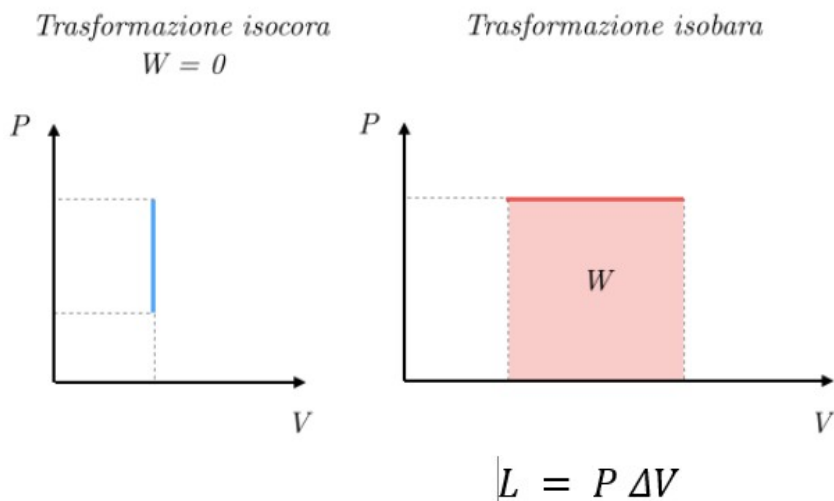
**N** = number of moles

**V** = volume

**T** = absolute temperature

**R** = is called ideal gas constant and is universal:  $0.0821 \text{ (L} \cdot \text{Atm)/(K} \cdot \text{mole)} = 8.31 \text{ Joule/(K} \cdot \text{mole)}$

# Graphs of transformations in the Clapeyron's plane



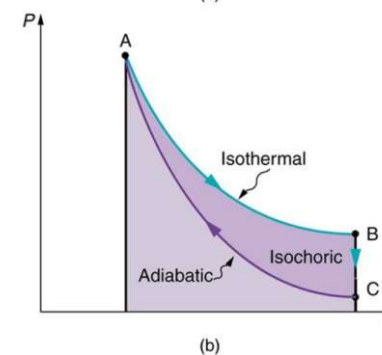
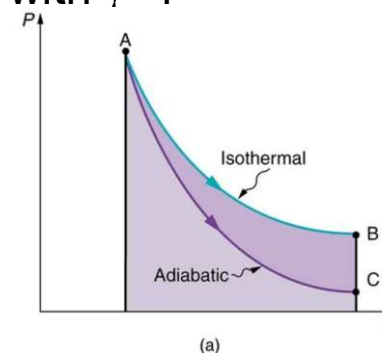
**Isobare:** by the work definition, where  $p = \text{const.}$  we'll have  $L = p \Delta V$ , the simplest case where  $L$  coincides with the rectangle area.

**Isochore:** by the definition of work, where  $V = \text{const.}$ ,  $V_i = V_f$  we'll have  $L = 0$ .

**Isothermal:** from  $pV = nRT$ , for  $n$  and  $T = \text{const.}$ ,  $pV = \text{const.}$  e  $V = \text{const}/p$ . Mathematically, we have an equilateral hyperbola branch (having form  $y = 1/x$ ). The curve has a negative slope ( $p \propto 1/V$ ), i.e  $p$  and  $V$  are inversely proportional.

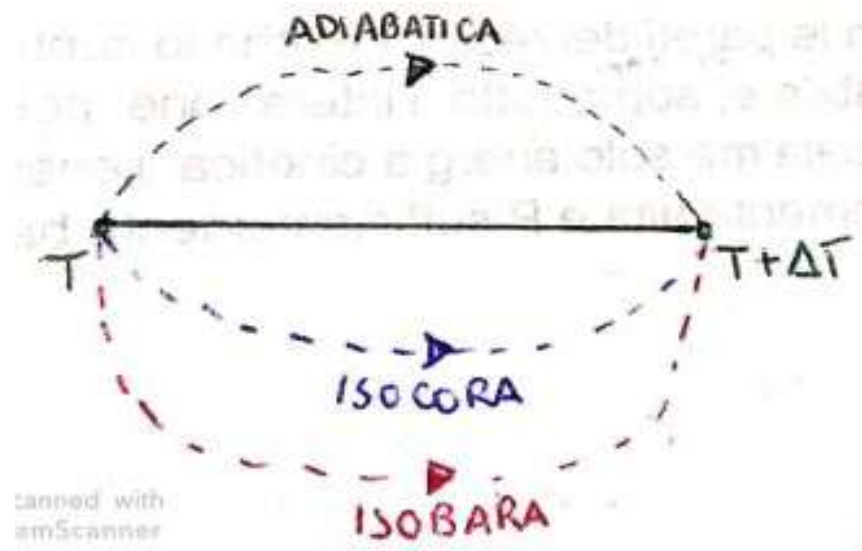
**Adiabatic:** the relation between  $p$  and  $V$  is  $p \propto 1/V^\gamma$ . Since  $\gamma > 1$  the curve has a slope more negative than the Isothermal. The Adiabatic is more rapidly decreasing than Isothermal. Thus, it will never be possible starting from the same initial point to reach the same final state by following an Adiabatic and an Isothermal. For each single point we have one and only one Adiabatic and one and only one Isothermal.

ISOTHERMAL (equilateral hyperbola)  $p \propto 1/V$   
ADIABATIC  $p \propto 1/V^\gamma$  with  $\gamma > 1$



# Thermal capacity and specific heat of ideal gases

In gases specific heats at constant pressure and constant volume are not equal, as for solids and liquids. Let us consider a system starting from  $T$  and arriving in  $T + \Delta T$ , by following whatever transformation.

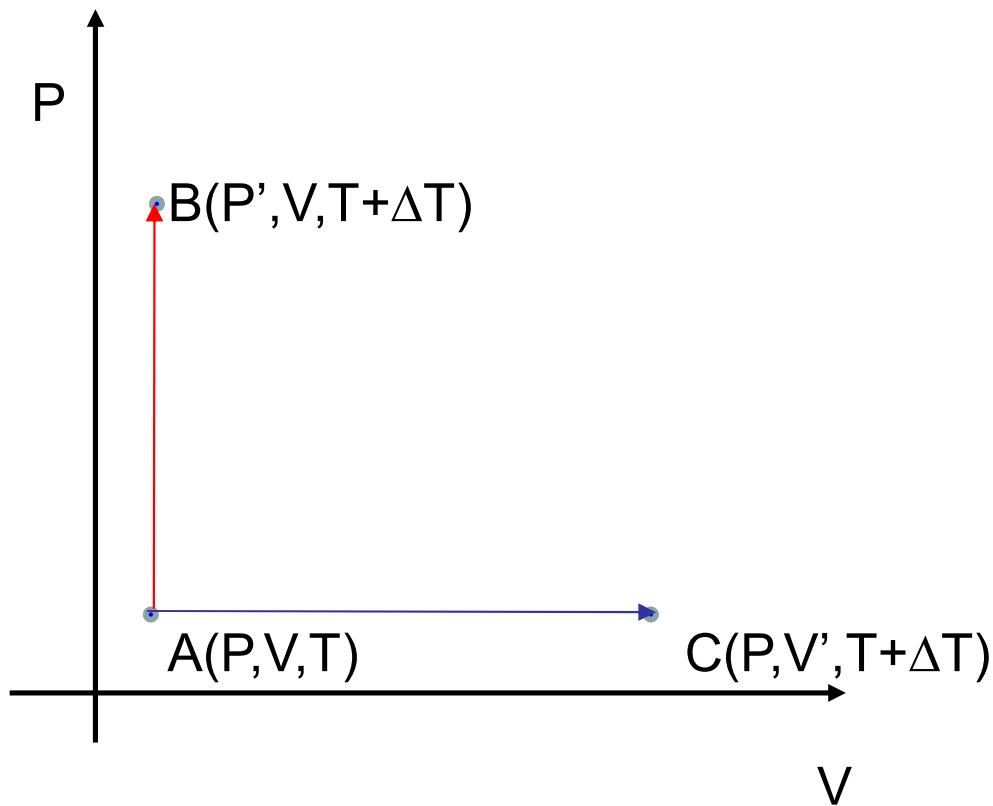


$$\Delta Q_{\text{adiab.}} = 0$$

$$\Delta Q_{\text{isoc.}} \neq \Delta Q_{\text{isob.}} \neq 0$$

**Note:** in an ideal gas  $\Delta U$  only depends on  $T$  as there is no potential energy due to interactions between molecules and molecule-molecule and molecule-wall bumps are elastic.  $\Delta U = \Delta U(T)$

For an Isochore and an Isobare in the  $p$ - $V$  plane, we obtain:



$$A \rightarrow B \quad L_{A \rightarrow B} = 0 \rightarrow U(B) - U(A) = \Delta Q_{\text{isoc.}}$$

$$A \rightarrow C \quad L_{A \rightarrow C} = p \Delta V \rightarrow U(C) - U(A) = \Delta Q_{\text{isob.}} - p \Delta V$$

$$\Delta Q_{\text{isob.}} = p \Delta V + (U(C) - U(A))$$

where  $U(C) - U(A) = U(B) - U(A)$   
and  $U(B) - U(A) = \Delta Q_{\text{isoc.}}$

Therefore

$$\Delta Q_{\text{isob.}} = p \Delta V + \Delta Q_{\text{isoc.}}$$

For  $c_v$  we have

$$c_v = \left( \frac{\Delta Q}{\Delta T} \right)_v = \frac{\Delta U}{\Delta T}$$

Since  $L=0$ . For the molar specific heat  $c_p$  we have

$$c_p = \left( \frac{\Delta Q}{\Delta T} \right)_p$$

Since  $\Delta Q_{isob} = \Delta Q_{isoc} + p \Delta V$ , we have

$$c_p = \left( \frac{\Delta Q}{\Delta T} \right)_p = \left( \frac{\Delta Q}{\Delta T} \right)_v + p \left( \frac{\Delta V}{\Delta T} \right)_p$$

For  $n=1$  mole of ideal gas (molar specific heats), from the state equation we find

$$V = \frac{RT}{p} \rightarrow p = \text{const.}, \quad \Delta V = R \frac{\Delta T}{p}, \quad p \left( \frac{\Delta V}{\Delta T} \right)_p = R$$

# Mayer's relation

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Thus

**MAYER'S RELATION:**

$$C_p = C_v + R$$

HOLDS TRUE for IDEAL GASES

This equation relates the molar specific heats at constant pressure and constant volume.

From the Equipartition Theorem (Classical Statistical Physics), we can determine one of the two quantities and so retrieve the latter. This theorem states that at equilibrium at T for each mole of ideal gas we have an average energy contribution  $\frac{1}{2} RT$  per each degree of freedom.

**Degree of freedom:** it is the way a particle (atom or molecule) can move or can change its configuration. Given this definition we know that:

For monoatomic gases ( He, Ne, Ar, Kr. Xe. Rn. metallic vapors)

$$C_v = \frac{3}{2} R \rightarrow C_p = \frac{5}{2} R$$

In such a case the particles, assumed to be point-like, possess only 3 degrees of freedom given by the 3 possible spatial directions they can move on; for each of such particles (point-like) we shall only need 3 spatial coordinates to locate unambiguously the particle position.

NOTE. We have 3 contributions per each single mole  $U(T)$  = from which

$$C_v = \frac{dU(T)}{dT} \rightarrow C_v = \frac{3}{2} R$$

# $C_p$ e $C_v$ for diatomic and polyatomic gases

For molecular diatomic gases (  $H_2$ ,  $N_2$ ,  $O_2$ ,  $CO_2$ ..)  $C_v = \frac{5}{2}R \rightarrow C_p = \frac{7}{2}R$

In such a case we can assume the particles to be like rods, simple objects but with their extension, the position of which can be identified unambiguously by 5 degrees of freedom: 3 for the spatial moves of the centre of mass and 2 additional for any possible rotation of the rod around its centre of mass (longitude and latitude).

For molecular polyatomic gases (  $CO_2$ ,  $NH_3$ , ..)

$$C_v \sim \left( \frac{6}{2} : \frac{7}{2} \right) R \rightarrow C_p \sim \left( \frac{8}{2} : \frac{9}{2} \right) R$$

To separate different degrees of freedom becomes more complex (it depends on whether molecules are linear or not, for example).

For air in standard conditions we have:  $C_p \sim 0,25 \frac{cal}{g K} = \frac{1}{4} C_p$  of  $H_2O$