chapiter 3: 1st Principle of Thermodynamics

III.1 Equivalence between heat and work

Benjamin Thomson (1798), Lord of Rumford, was the first to put forward the idea equivalence between heat and work, which can be transformed into each other. There a simple relationship between the mechanical work performed on a system and the heat heat it generates. James Prescott Joule first experimentally found that the heat produced in a system is directly proportional to the mechanical work performed on it.

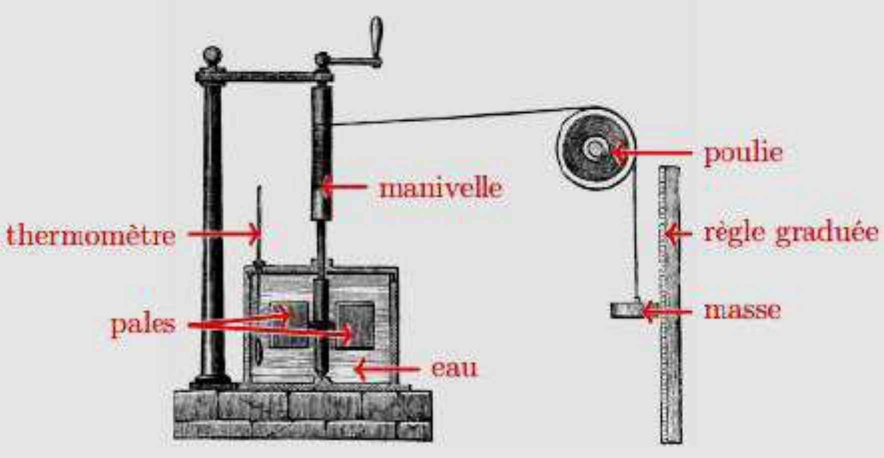


Fig.III.1: Joule apparatus for measuring measuring the mechanical equivalent of heat |[6].

He also calculated the constant of proportionality in a unique experiment which we will also describe in this article.

If W is the work done on a system and Q is the amount of heat produced thanks to this work, then :

$$W \propto Q \Rightarrow W = J \times Q \Rightarrow J = \frac{W}{Q} \quad \text{..} (III.1)$$

$$J = 4.186 KJ / Kcal$$

The expression J says that the mechanical equivalent of heat is the number of units of work

units of work to be performed on a system to produce a single unit of heat.

III.2 Statement of the first principle

The thermodynamic balance W+Q of exchanges between a system and the external environment has the same value for all transformations that take the system from the same initial the same initial state to the same final state. For two transformations with the same beginnings and end states :

$$W_1 + Q_1 = W_2 + Q_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.2)$$

$${}_{A}^{B}\left[W + Q\right] = Cste$$

wherever you are. Only the initial and final states count.

III.3 General expression of the first principle

For a closed system, the equivalence principle leads to the following general expression of the first principle (in a unified system of units):

$$\Delta U = U_2 - U_1 = W + Q \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.3)$$

- The quantity U2 - U1 corresponds to the increase in the system's energy U between initial state 1 and final state 2.
- The quantity Q is the heat received by the system, and W is the work supplied to the external environment.

It is often convenient to have the differential form of the first principle available

application to infinitesimal transformations. In this case, we write :

$$dU = dW + dQ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.4)$$

Where :

- Q: designates the quantity of elementary heat received by the system during time dt.
- dW: the corresponding work supplied to the external environment.

Application examples:

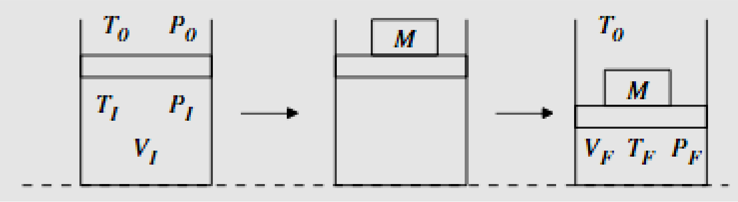
Compression of a gas

We're interested in the evolution of one mole of a perfect diatomic gas enclosed in an enclosure.

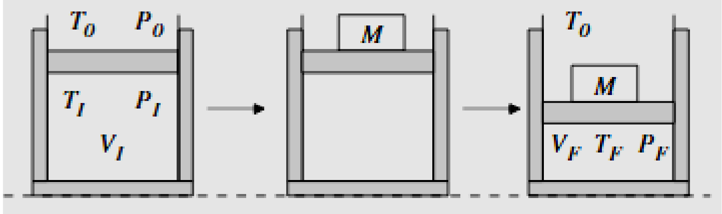
an enclosure. The enclosure is in contact with the atmosphere (pressure P0 , temperature T0), adding a mass M to the piston is equivalent to doubling the external pressure.

For each of these evolutions, starting from the initial state PI= P0 and TI = T0, we aim to determine the final state, as well as the energy balance, i.e. the quantities ΔU, W and Q.

First experience:



Second experiment: the enclosure is now insulated.



Third experiment: we repeat the set-up from the first experiment, now increasing slowly increasing the pressure from P0 to 2P0.

III.4. Definition of internal energy U

The internal energy of a thermodynamic system is the energy it contains. It is an an extensive state function associated with the system. This energy accounts for the system's internal agitation at the atomic level. Like all energies, it is defined to within one constant.

III.5 Differential expression of internal energy

According to the first principle of thermodynamics :

$$dU = \delta Q + \delta W \ldots\ldots(III.5)$$

$$or$$

$$\delta Q = C_v \times dT + l \times dV \ldots\ldots(III.6)$$

If only pressure forces are involved :

$$\delta W = -PdV \ldots\ldots(III.7)$$

$$donc :$$

$$dU = C_v \times dT + (l - P) \times dV \ldots\ldots(III.8)$$

III.6. Differential expression of the first principle

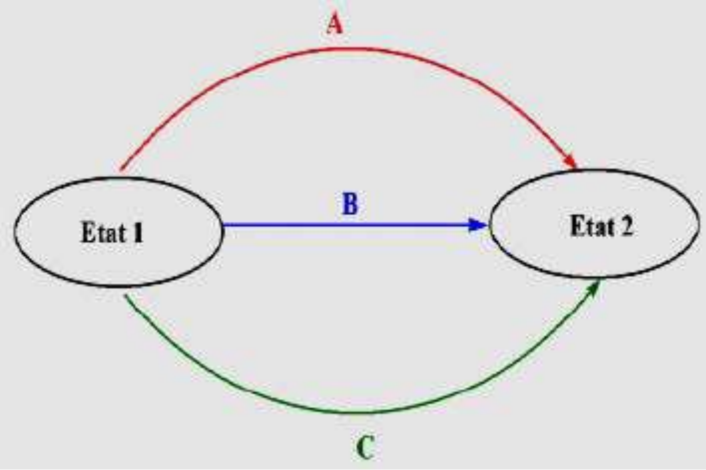
Let two states A and A' be infinitely close:

$$dU = U_A - U_{A'} \ldots\ldots(III.9)$$

$$dU = dW + dQ \ldots\ldots(III.10)$$

The sum W+Q is constant whatever the nature of the transformation:

$$W_A + Q_A = W_B + Q_B = W_C + Q_C = U_2 - U_1 = \Delta U$$



Sign convention:

- Si $\Delta U>0$: system receives energy.
- Si ΔU□< 0 : the system gives up energy.

The same applies to Q and W.

III.7. Calculating the change in internal energy ΔU

"During a transformation of a system, the variation in total energy (ΔE_T) is equal to the sum of all energy quantities exchanged with the external medium external environment:

$$\Delta E_T = Q + W \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.11)$$

$$\Delta.(E_C + E_P + U) = Q + W \Rightarrow \Delta E_C + \Delta E_P + \Delta U = Q + W \ldots\ldots\ldots\ldots (III.12)$$

Generally, for thermodynamic transformations :

E_c = Cste and **E_p = Cste** hence:

$$\Delta U = Q + W \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.13)$$

Therefore, for an isolated system: ΔU =0 (U remains constant)

Example:

Over a period of time, the electric motor of an aquarium pump (system) does work of 555 kJ on the pump and releases 124 kJ of heat to the outside environment.

What is the energy change?

$$\Delta U = U_2 - U_1 = Q + W = -125 - 555 = -679 \ \ kJ$$

III.7.1. Joule's 1st law; the variation of the internal energy of a perfect gas

For one mole of a perfect monoatomic gas, the internal energy is given by :

$$U = \frac{3}{2} RT \ldots\ldots\ldots soit \ldots\ldots dU = \frac{3}{2} RdT \ldots\ldots\ldots\ldots\ldots\ldots (III.14)$$

Suppose the system undergoes a transformation from state (1) [P1, V1,T1] to state (2) [P2, V2,T2]. Therefore :

$$\Delta U = U_2 - U_1 = \frac{3}{2}R(T_2 - T_1) = \frac{3}{2}(P_2V_2 - P_1V_1) \ldots\ldots (III.15)$$

$$\Delta U = U_2 - U_1 = C_v \times \Delta T \ldots\ldots (III.16)$$

Joule's 1st law: The internal energy U of a perfect gas depends only on its temperature T.

temperature T. (For a monoatomic perfect gas): **Cv = 3/2 R**

- If the transformation is adiabatic (thermally isolated): Q = 0 => U =W in this case W is independent of the path followed.

- If the system is mechanically isolated;W =0 => U = Q => Q is independent of the path followed. independent of the path followed.

III.7.2. Isochore transformation

According to the first principle, an elementary variation dU of U is written :

$$dU = \delta W + \delta Q \Rightarrow \delta W = -P_{ext}dV = 0 \ldots\ldots (III.17)$$

Because (V=Cste).

The change in internal energy is therefore reduced to the amount of heat exchanged:

$$dU = \delta Q \Rightarrow \Delta U = Q = \int nC_v dT \ldots\ldots (III.18)$$

In this case, the thermal energy Q exchanged at constant volume depends only on the final and initial states of the system under study.

initial state of the system under study, because its variation is determined by that of a that of a state function U.

III.7.3. Isobaric transformation

Most transformations are carried out at constant pressure, usually at atmospheric pressure.

atmospheric pressure. The system can then exchange heat and work and work with the external environment.

For an elementary transformation : $dU = \delta W + \delta Q$

with δQ = heat exchanged at constant P :

$\delta W = -P_{ext} dV = -PdV$ since $P_{ext} = P$ we can see :

$$dU = \delta Q - PdV \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.19)$$

III.7.4. Relationship between QP and QV

This relationship is mainly used for gas-phase or heterogeneous-phase reactions or heterogeneous-phase reactions, where the reactants and products of the reaction are gases, leading to a significant variation in Δ(P.V).

- At constant volume, dV = 0 and dU = dQ i.e. integrating: Δ U = Q .
- At constant pressure, dP = 0 and dH = dQ, i.e. integrating: Δ H = Q .

The heat exchanged with the external medium at constant pressure is equal to the enthalpy variation ΔH of the system.

Example:

One mole of N2, considered as a perfect gas, rises from 20°C to 100°C.

Calculate the heat Q .

1- for an isochoric transformation

2- for an isobaric transformation.

$$C_P = 33\ J.mol^{-1}.K^{-1} \qquad R = 8{,}31\ J.mol^{-1}.K^{-1}$$

Solution:

1. Transformation isochore : (V=Cste)

$$Q_V = ?????$$

$$\delta Q_V = nC_V dT \Rightarrow Q_V = \int nC_V dT = nC_V \Delta T = nC_V (T_2 - T_1)$$

2.

$$n = 1.mole \quad , \Delta T = 80°C \quad , C_V = C_P - R = 33 - 8.31 = 24{,}69$$

$$Q_V = 1 \times 24.69 \times 80 = 1975.2J$$

Transformation isobare : (P=Cste)

$$Q = Q_P = ?????$$

$$Q_P = \int \delta Q_P = \int nC_P dT = nC_P \int_{T2}^{T1} dT = nC_P (T_2 - T_1)$$

$$n = 1mole \quad , \Delta T = 80°C \quad , C_P = 33J.mol^{-1}K^{-1}$$

$$Q_P = 1 \times 33 \times 80 = 2640J$$

$$\Delta H = Q_P = 2640J$$

III.7.4.1. For a perfect gas (Mayer's relation)

In physics, and more particularly in thermodynamics, the Mayer relation, established in the 19th century by Julius Robert von Mayer, is a formula relating the heat capacities CP at constant pressure and Cv at constant volume of a perfect of a perfect gas according to :

$$C_P - C_v = \frac{PV}{T} = nR \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.19)$$

Mayer relationship :

With :

- n: the quantity of matter (number of moles);
- R: the universal perfect gas constant.

$$C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_{V,n}\left(\frac{\partial V}{\partial T}\right)_{P,n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(III.20)$$

This relationship can be generalized to real bodies as follows:

Example:

For one mole, Mayer found :

$$C_p - C_v = 2{,}24 \ \ cal.K^{-1} \quad et \quad J = \frac{8{,}314}{2{,}24} = 3{,}7 \ \ J.cal^{-1}$$

While the precise value of J is 4.18 J.cal-1

III.7.4.2. For chemical reactions

In thermochemistry, Qp and Qv correspond respectively to the heats of reaction At constant pressure and constant volume.

If we rewrite H = U + PV in the form: ΔH = ΔU + Δ(PV) we obtain:

$$Q_p = Q_v + \Delta(PV) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(III.21)$$

Example:

Combustion of methane releases 2000 kJ at 25°C.

Deduce the reaction

$$(Q_P = \Delta H).$$

$$Q_v = Q_P - \Delta nRT \Rightarrow Q_P = Q_v + \Delta nRT$$

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$

$$Q_v = -2000 \ \ kJ \quad ; \quad \Delta n = 1 - 3 = -2$$

$$Q_P = -2000 + (8{,}314).(298).(2) \times 10^{-3} = -2004{,}95 \ \ kJ$$

III.7.5. Reversible adiabatic work - Laplace's equation

In the case of a thermodynamic system, only the internal energy varies:

dU= δW + δQ, the mechanical work δW is the product of the change in volume dV by the external pressure P exerted for this change in volume dW = - PdV . If this process is adiabatic, i.e. without heat exchange heat exchange: δQ= 0 , hence :

$$dU = -PdV \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(III.22)$$

Let's now consider the enthalpy of the system (H = U + PV) and its variation:

$$dH = dU + PdV + VdP \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(III.23)$$
$$dH = -PdV + PdV + VdP \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(III.24)$$
$$dH = VdP \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(III.25)$$

If we assume that this gas behaves like a perfect gas, the variations, internal energy and enthalpy of the system depend only on temperature, according to depend only on temperature, according to the Joule-Gay-Lussac and Joule-Thomson laws respectively.

Lussac and Joule-Thomson laws respectively. It follows that :

$$dU = C_v dT \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(III.26)$$
$$dH = C_p dT \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(III.27)$$

Where C_p and Cv are respectively the heat capacities at constant volume and pressure and T is the temperature. The unit of C_p and C_v is the joule per kelvin (J/K).

From this we can deduce two relationships: by internal energy: C_v dT= - PdV , by enthalpy: C_p dT= -PdV from which we also derive :

$$dT = -\frac{P}{C_v} dV = \frac{V}{C_P} dP \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(III.28)$$

$$\frac{C_P}{C_v}\frac{dV}{V} = -\frac{dP}{P} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(III.29)$$

Laplace's coefficient ɣ, or adiabatic index, defined by the ratio of of isobaric and isochoric heat capacities :

$$\gamma = \frac{C_P}{C_v} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.30)$$

We rewrite the relationship established above:

$$\gamma \frac{dV}{V} = -\frac{dP}{P} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.31)$$

Let's integrate this relationship between two states (P0 ,V0 , T0) and (P1 ,V1 , T1) , for the quantity of gas, with :

$$\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1} = nR \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.32)$$

We'll assume that ɣ is constant during the transformation, despite the temperature change. We obtain :

$$\gamma \int_{V0}^{V} \frac{dV}{V} = -\int_{P0}^{P} \frac{dP}{P} \Rightarrow \gamma \times \ln\left(\frac{V}{V_0}\right) = -\ln\left(\frac{P}{P_0}\right) \ldots\ldots\ldots\ldots\ldots\ldots (III.33)$$

and therefore :

$$PV^{\gamma} = P_0 V_0{}^{\gamma} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.34)$$

If we substitute in (III.34) :

$$\begin{array}{l} P_0 = \dfrac{nRT_0}{V_0} \\ P = \dfrac{nRT}{V} \end{array} \Rightarrow TV^{\gamma-1} = T_0 V^{\gamma-1} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.35)$$

If we also substitute in (III.34) :

$$\begin{array}{l} V_0 = \dfrac{nRT_0}{P_0} \\ V = \dfrac{nRT}{P} \end{array} \Rightarrow P^{1-\gamma}T^{\gamma} = P_0^{1-\gamma}T_0^{\gamma} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.36)$$

Example:

Defining the coefficient ɣ as the ratio C_p /C_v and using the Mayer relation, find the expressions

relationship, find the expressions Cp and Cv as a function of R. for application, considering an adiabatic transformation.

Give the expressions for Laplace's law and Laplace's law of work.

Solution:

Defining Cp and Cv as the molar heat capacities at constant pressure and constant volume respectively, we have at constant pressure and constant volume, we have : According to Mayer :

$$C_P - C_v = R \quad et \quad \gamma = \frac{C_P}{C_v} \Rightarrow C_v = \frac{R}{\gamma - 1} \quad et \quad C_P = \frac{\gamma R}{\gamma - 1}$$

III.7.6. Irreversible adiabatic work

There is no exchange of heat or work between the gas and the outside world. For the gas system, ΔU = 0 and, if the gas is perfect, U depends only on T, and temperature does not vary.

on T, and temperature does not vary.

If we're dealing with a perfect gas (PV = nRT), since there is no variation in the product PV must be constant, i.e. : PiVi =PfVf

$$dW = -\int_{Vi}^{Vf} PdV \Rightarrow W = P\left(V_i - V_f\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.37)$$

Example:

Calculate the work done when one mole of perfect gas expands isothermally at 298 K from P1= 10 atm to P2= 5atm.

a) Reversible

b) Irreversible

Solution:

The work of the pressure forces is expressed by : W = -P_{ext} dV

a) Reversible :

$$P_{ext} = P_{\text{int}} = P_{gaz} = \frac{nRT}{V} \quad \text{Donc : } W_{rev} = -\frac{nRT}{V}.dV \Rightarrow W_{rév} = -\int \frac{nRT}{V}.dV$$

Isothermal transformation :

$$\Rightarrow T = Cste \text{ et } P_1V_1 = P_1V_2 \Rightarrow \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$W_{rev} = -nRT\int\frac{dV}{V} = -nRT.\ln\frac{V_2}{V_1} = -nRT.\ln\frac{P_1}{P_2} = nRT.\ln\frac{P_2}{P_1}$$

$$W_{rev} = 1\times 8.314\times 298\times \ln\left(\frac{5}{10}\right) = -1717.3.J$$

b) Irreversible :

$$P_{ext} = P_2$$

$$\delta W_{irrev} = -P_2dV \Rightarrow W_{irrev} = -\int P_2dV = -P_2(V_2 - V_1) = P_2(V_1 - V_2) \quad avec\ V\frac{nRT}{P}$$

Donc :

$$W_{irrev} = P_2\left(\frac{nRT}{P_1} - \frac{nRT}{P_2}\right) = nRT\left(\frac{P_2}{P_1} - 1\right) \Rightarrow W_{irrev} = 1\times 8.314\times 298\times\left(\frac{5}{10} - 1\right) = -1238.8.J$$

Note that :

$$|W_{rev}| \rangle . |W_{irrev}|$$

III.8. Notion of enthalpy H

In physics, the variable enthalpy is a quantity related to the energy of a system thermodynamic system. It comprises the system's internal energy (denoted U), to which is added the product of pressure and volume (denoted PV).

$$H = U + PV \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.38)$$

III.8.1. The enthalpy function

Let's consider a monobaric transformation in which the system moves from a state A to a state B of equilibrium, exchanging heat Q_p and work solely through the pressure forces $W_{f,p}$. The first principle allows us to write :

$$\Delta U = U_A - U_B = Q_P - W_{f,P} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.39)$$

U being the internal energy state function at constant pressure, the work of the pressure forces is equal to :

$$W_{f,P} = -P\Delta V = -P(V_B - V_A) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.40)$$

$$U_B - U_A = Q_P - P(V_B - V_A) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.41)$$

Hence :

$$Q_P = (U_B + PV_B) - (U_A + PV_A) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.42)$$

This defines a new state function, the enthalpy function H(U,P,V) :

$$H = U + PV \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.43)$$

It follows that :

$$Q_P = H_B - H_A = \Delta H \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.44)$$

III.8.2. Differential expression of enthalpy

$$H = U + PV \Rightarrow dH = dU + PdV + VdP \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.45)$$

Let's apply the 1st principle:

$$dU = \delta Q - PdV \Rightarrow dH = \delta Q - PdV + PdV + VdP = \delta Q + VdP \ldots\ldots\ldots (III.46)$$

III.8.3. Joule's 2nd law; enthalpy variation of perfect gases

Joule's second law: The enthalpy of a perfect gas depends only on its temperature, hence :

$$H = C_P.T \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.47)$$

Applying the second principle for ΔH we have :

$$\begin{aligned} &\Delta H = \Delta U + \Delta PV \Rightarrow \Delta H = \Delta U + \left(P V_2 - P_1 V_1\right) \Rightarrow \\ &\Delta H = nC_v\left(T_2 - T_1\right) + \left(nRT_2 - nRT_1\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.48) \end{aligned}$$

(2nd Joule's law).

$$\Delta H = nC_P\left(T_2 - T_1\right) = m_{Cp}\left(T_2 - T_1\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.49)$$

Where :

Cp: is the molar heat capacity at constant pressure in J.mol-1.K-1.

Cp :is the mass heat capacity at constant pressure in J.kg-1.K-1.

Since both heat capacities are such that :

$$\gamma = \frac{C_P}{C_V} = \frac{c_P}{c_V} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.50)$$

We deduce :

$$\Delta H = \gamma.\Delta U \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (III.51)$$