CHAPTER IV: Applications of the 1st Principle of Thermodynamics to Thermochemistry

IV.1 Heat of reaction: Q_R; Q_p; Q_v

Let Q be the quantity of heat exchanged with the external environment (at constant pressure or constant volume) when the chemical system passes from the initial state to the final state.
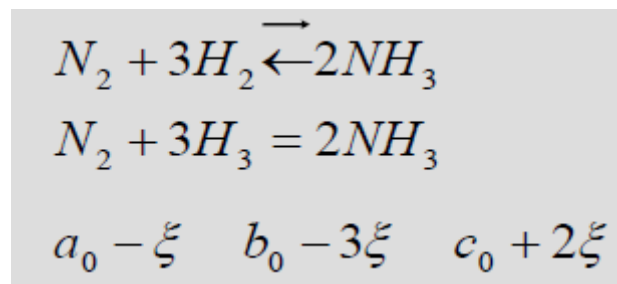
IV.1.1 Heat of reaction Q_R

The heat of reaction Q_R is the quantity of elementary heat exchanged (consumed or released) by the chemical system under consideration, at temperature T and for an elementary reaction rate dξ :

$$Q_R = \left(\frac{\delta Q}{\delta \xi} \right)_T \quad \text{..(IV.1)}$$

Chemical reactions generally take place at constant volume or constant pressure pressure for a given temperature T :

Example:

$$N_2 + 3H_2 \xleftarrow{\longrightarrow} 2NH_3$$
$$N_2 + 3H_3 = 2NH_3$$
$$a_0 - \xi \quad b_0 - 3\xi \quad c_0 + 2\xi$$

ξ Can be negative or positive.

IV.1.2 Heat of reaction at constant pressure Q_p :

Let's consider the previous chemical system in evolution. The first principle allows us to write, for an elementary rate of advance dξ:

$$dH = d(U + PV) = dU + d(PV) \quad \text{...(IV.2)}$$
$$dH = \delta Q + \delta W + PdV + VdP \quad \text{......}|\text{.................................(IV.3)}$$
$$dH = \delta Q - PdV + PdV + VdP \quad \text{.......................................(IV.4)}$$

Like P = P_{ext} = Cte, VdP = 0, So:

$$\delta H = \delta Q_p \quad \text{...(IV.5)}$$

We can express an elementary variation of the enthalpy function

H (T,P,ξ) as :

$$dH = \left(\frac{\partial H}{\partial T}\right)_{P,\xi} dT + \left(\frac{\partial H}{\partial P}\right)_{T,\xi} dP + \left(\frac{\partial H}{\partial \xi}\right)_{T,P} d\xi \dots\dots\dots\dots\dots(IV.6)$$

At constant T and P :

$$Q_P = \sum V_i H_{m,i} = \Delta r H \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(IV.8)$$

$$dH = \left(\frac{\partial H}{\partial \xi}\right)_{T,P} d\xi = \delta Q_P \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(IV.7)$$

With:

- $H_{m,i}$: Molar enthalpy of component

- Ai *and* Vi : Algebraic stoichiometric coefficient.

The term Δr H, enthalpy of reaction, represents the amount of heat exchanged by the chemical system under monothermal and isobaric conditions for a reaction progress ξ de reduced to one mol.

The heat exchanged by a reaction system for a given state of advancement is :

$$\Delta H_T = Q_P = \xi \Delta r H_T \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(IV.9)$$

$\Delta r H_T :$ Is the enthalpy of reaction at temperature T per unit advance (for ξ = 1mol).

IV.1.3 Heat of reaction at constant volume Qv :

Still considering the previous reaction, we can write, on the one hand :

$$dU = \delta Q + \delta W \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(IV.10)$$
$$avec: \delta W = -PdV = 0 \to (V = Cste)$$
$$dU = \delta Q_V \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(IV.11)$$

And on the other hand, the differential of the function :

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,\xi} dT + \left(\frac{\partial U}{\partial V}\right)_{T,\xi} dV + \left(\frac{\partial U}{\partial V}\right)_{T,V} d\xi \dots\dots\dots\dots\dots(IV.12)$$

At constant T and V :

$$dU = \left(\frac{\partial U}{\partial \xi}\right)_{T,V} d\xi = \delta Q_P \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (IV.13)$$

$$Q_V = \sum v_i U_{m,i} = \Delta rU \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (IV.14)$$

The term ΔUr, internal energy of reaction, represents the amount of heat exchanged by the chemical system under monothermal and isochoric conditions for a the reaction progresses ξ to one mol.

Example:

One mole of N2 (g), considered as a perfect gas, is heated from 20°C to 100°C.

Calculate the amount of heat Q received by this system, its change in internal energy and its change in enthalpy in the following two cases enthalpy in the following two cases:

- When the transformation is isochoric.
- When the transformation is isobaric.

We give: Cp (N2,g)=33 J.mol-1.K-1 and R=8.31 J.mol-1.K-1

Solution:

The change in internal energy is equal to the amount of heat released at constant volume.

volume.

- Since the transformation is isochoric (constant volume), we have :

$$C_P - C_V = R \Rightarrow C_V = C_P - R = (33 - 8.31) = 24.69 mol^{-1}K^{-1}$$

$$Q_V = \Delta U = n \int_{T1}^{T2} C_V dT = 1975.2 J$$

La variation d'enthalpie est égale à la quantité de chaleur dégagée à pression constante.

- La transformation étant isobare (pression constante) nous avons :

$$Q_P = \Delta H = n \int_{T_1}^{T_2} C_P dT = -2640 J$$

IV.2 The standard state

The evolution of a real system is studied by comparison with an associated fictitious system called the standard system:

- For a gas or gas mixture, the standard state is that of the perfect gas " PV=nRT" at pressure P = 1bar and temperature T.

- For a component in the condensed phase (liquid or solid), the standard state is that of the pure body in the same physical state at temperature T and P = 1bar.

- The standard reference state of a chemical element is the standard state of the most stable most stable simple pure body, in its most stable physical state at the temperature T and P = 1bar (1bar = 105 Pa (1N/m2) and 1atm = 1.013bar).

Example:

Standard reference states of some elements at T= 25°C :

Gases: O2(g), Cl2 (g), H2 (g) .

Liquids: Br2 (l), Hg (l),....

Solids: C(graphite), S (s), Fe (s), Cu (s), ...

IV.3. Standard enthalpy of formation ΔH_f^0

This is the enthalpy of formation of one mole of a chemical substance in a standard state from simple pure bodies taken in their standard reference state.

Example (at 298 K and P=1bar) :

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \Delta H^0_{f,298K}(H_2O,g)$$

$$H_2O_{(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \dots\dots\dots\dots\dots\dots\dots\dots\dots \Delta H^0_{f,298K}(H_2O,l)$$

$$Fe_{(s)} + 2S_{(s)} \rightarrow FeS_{2(s)} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \Delta H^0_{f,298K}(FeS_2,s)$$

The enthalpy of formation of simple bodies in their standard reference state at a temperature T, is equal to zero. $\Delta H^0_{f,T}(O_2,g)=0$ whatever T.

IV.4. Enthalpy of dissociation

The dissociation energy of a bond (D0) refers to one of the measures of the energy of a chemical bond. It corresponds to the change in enthalpy during hemolytic cleavage1 with reactants and products of the homolysis reaction at 0 K (absolute zero).

Example (at 298 K and P=1bar) :

$$CH_3CH_3 - H \rightarrow CH_3CH_3 + H$$
$$avec: D_0 = \Delta H = 101{,}1 \ kCal/mol = 423 \ kJ/mol$$
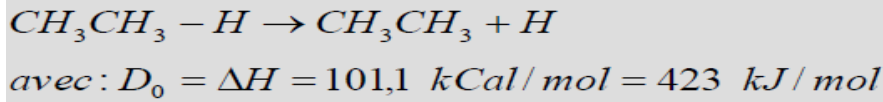
IV.5. The enthalpy of change of physical state (ΔH fus , ΔH vapo, ΔH Sub)

During a change of state of a pure body, there is a variation in enthalpy. For example, for a body of mass m going from state 1 to state 2 at temperature :

$$\Delta H_{1,2} = mL_{1,2} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (IV.15)$$

$\Delta H_{1,2}$: Change in enthalpy in J.

$L_{1,2}$: Enthalpy of mass change of state expressed in J/kg

m: Mass in kg

IV.5.1 Enthalpy of fusion ΔH_f :

The enthalpy of fusion is the energy absorbed by heat by a body when it passes from the solid state to the liquid state at constant temperature and pressure. The enthalpy of solidification (reverse transformation) is the opposite of the enthalpy of fusion:

$$\Delta H(solidification) = -\Delta H(fusion)\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(IV.16)$$

IV.5.2 Enthalpy of vaporization ΔH_{vap}:

The enthalpy of vaporization of a chemical compound is the difference in enthalpy involved in the vaporization of one mole of that compound. The enthalpy of liquefaction (reverse transformation) is the opposite of the enthalpy of vaporization:

$$\Delta H(liquéfication) = -\Delta H(vaporisation)\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(IV.17)$$

IV.5.3 Enthalpy of sublimation ΔH_{sub}:

The enthalpy of sublimation, formerly latent heat of sublimation, is the energy absorbed by heat by a body when it passes from the solid state to the gaseous state at constant temperature and pressure. The enthalpy of deposition (reverse transformation) is the opposite of the enthalpy of sublimation:

$$\Delta H(d\acute{e}position) = -\Delta H(sub\lim ation)..(IV.18)$$

Example:

$$H_2O_{(l)} \rightarrow H_2O_{(g)}$$

$$\Delta_{vap}H^0 = \Delta H^0_{f,(H2o,g)} - \Delta H^0_{f,(H2O,l)} = -214,83 + 285,84 = 44 \ kJ/mol$$

Si $\Delta_{vap}H^0$ ou L^0_{vap} vaut *44 kJ / mol*, l'enthalpie de transformation inverse c-a-dire la

$$\Delta_{vap}H^0 = -\Delta_{liq}H^0$$

liquéfaction vaut *-44 kJ / mol*. $\Delta_{fus}H^0 = -\Delta_{sol}H^0$

$$\Delta_{sub}H^0 = -\Delta_{cond}H^0$$

IV.6. The enthalpy of a chemical reaction ΔH R:

The enthalpy of reaction **ΔH R** is a reaction quantity associated with writing the balance equation of a chemical reaction carried out at constant temperature T and pressure P.

It is expressed in joules per mole (J/mol) and corresponds to the enthalpy variation of the reaction mixture for an advancement ξ of the reaction in progress equal to 1mol. So, if we know the advancement of a reaction, we can calculate the enthalpy variation **ΔH** associated with this reaction according to the following relationship:
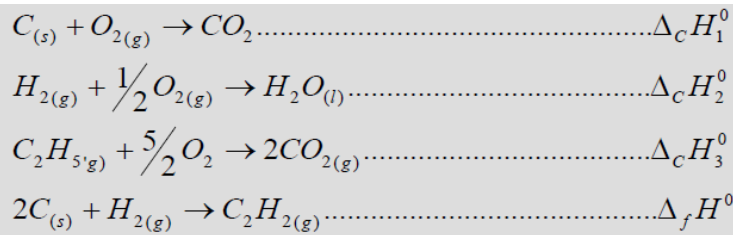
$$\Delta H = \int_0^\xi \Delta rH \times d\xi..(IV.19)$$
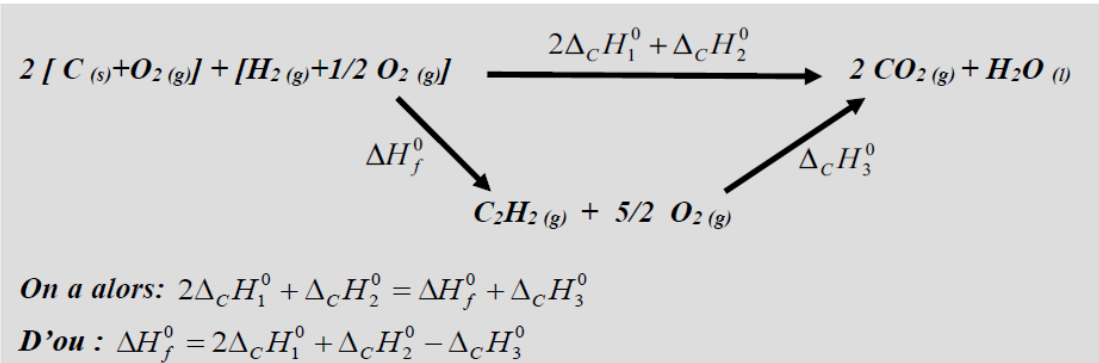
IV.6.1. Hess's law

Hess's law is a thermochemical law developed by the Swiss chemist Germain Henri Hess. It states: The enthalpy of reaction of a chemical reaction is equal to the sum of the enthalpies of formation of the products (final state), minus the sum of the enthalpies of formation of the reactants (initial state), taking into account the stoichiometry of the reaction.

Example:

Determine the standard enthalpy of formation of acetylene gas using the heats of combustion of heats of combustion of C(s) ; H2 (g) and C2H2 (g) :
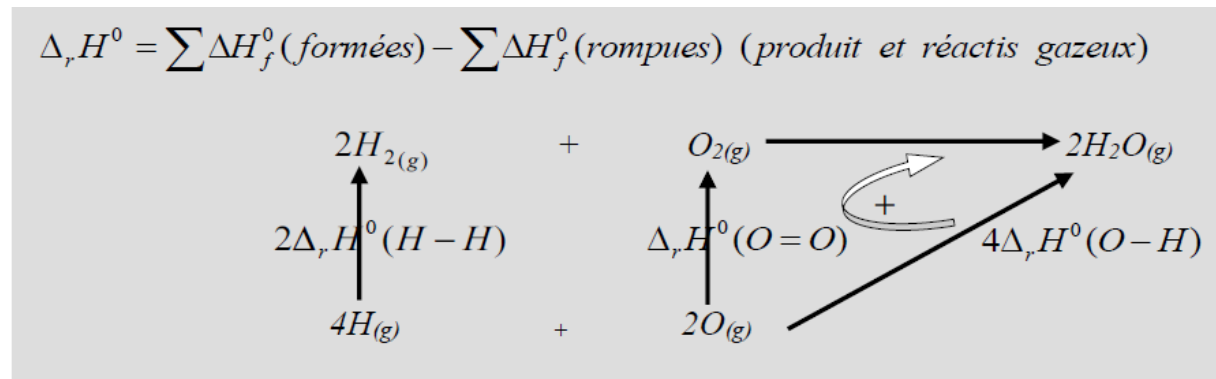
$$C_{(s)} + O_{2(g)} \rightarrow CO_2 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \Delta_c H_1^0$$

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2 O_{(l)} \dots\dots\dots\dots\dots\dots\dots\dots\dots \Delta_c H_2^0$$

$$C_2 H_{5'g)} + \frac{5}{2} O_2 \rightarrow 2CO_{2(g)} \dots\dots\dots\dots\dots\dots\dots\dots \Delta_c H_3^0$$

$$2C_{(s)} + H_{2(g)} \rightarrow C_2 H_{2(g)} \dots\dots\dots\dots\dots\dots\dots\dots\dots \Delta_f H^0$$

Solution :

On a alors: $2\Delta_c H_1^0 + \Delta_c H_2^0 = \Delta H_f^0 + \Delta_c H_3^0$

D'ou : $\Delta H_f^0 = 2\Delta_c H_1^0 + \Delta_c H_2^0 - \Delta_c H_3^0$
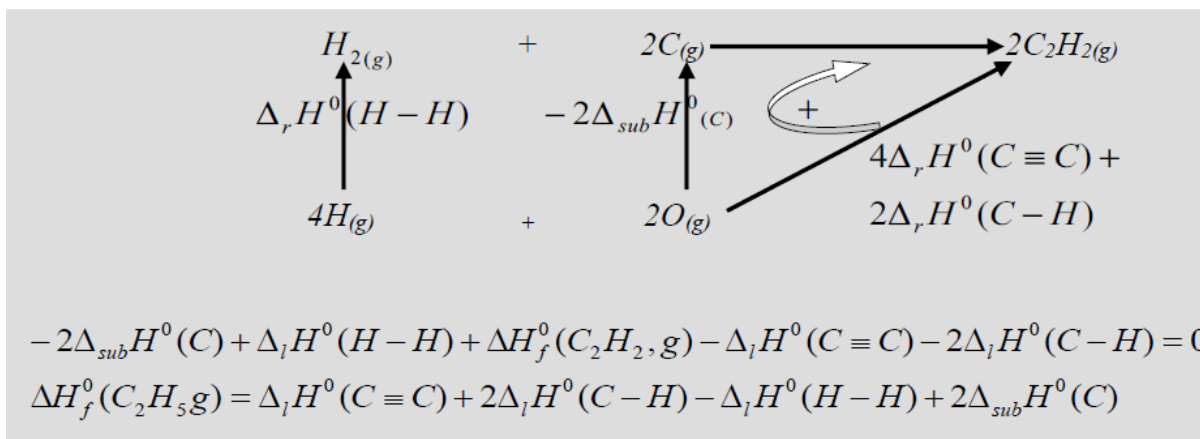
IV.6.2. Binding energy or binding enthalpy

In the case of a reaction involving only bodies in the gaseous state, the enthalpy of reaction is given by the expression:

$$\Delta_r H^0 = \sum \Delta H_f^0 (form\acute{e}es) - \sum \Delta H_f^0 (rompues) \quad (produit \ et \ r\acute{e}actis \ gazeux)$$

By applying Hess's law:

$$2\Delta_l H°(H-H) + \Delta_l H°(O=O) + \Delta_f H° - 4\Delta_l H°(O-H) = 0$$

$$\Delta_f H° = 4\Delta_l H°(O-H) - 2\Delta_l H(H-H) - \Delta_l H°(O=O)$$

If one of the components is in a solid or liquid state, the following must be taken into account

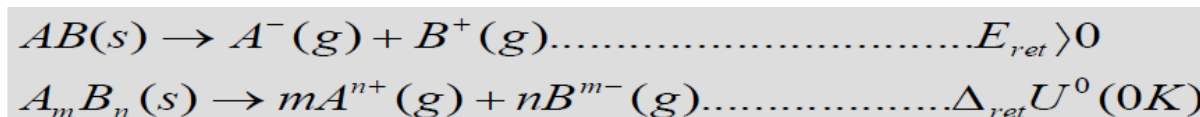$$H_{2(g)} \qquad + \qquad 2C_{(g)} \longrightarrow 2C_2H_{2(g)}$$

$$\Delta_r H^0(H-H) \qquad -2\Delta_{sub}H^0{}_{(C)} \qquad +$$

$$4\Delta_r H^0(C \equiv C)+$$

$$4H_{(g)} \qquad + \qquad 2O_{(g)} \qquad 2\Delta_r H^0(C-H)$$

$$-2\Delta_{sub}H^0(C)+\Delta_l H^0(H-H)+\Delta H_f^0(C_2H_2,g)-\Delta_l H^0(C \equiv C)-2\Delta_l H^0(C-H)=0$$
$$\Delta H_f^0(C_2H_5 g)=\Delta_l H^0(C \equiv C)+2\Delta_l H^0(C-H)-\Delta_l H^0(H-H)+2\Delta_{sub}H^0(C)$$

its transformation into a gas.

The energy of a bond depends on its environment in the molecule, and varies slightly from one molecule to another. The values of bond enthalpies given in thermodynamic tables are average values over several molecules.

Consequently, calculating reaction enthalpies $\Delta rH °$ from binding energies gives less accurate results than those determined from enthalpies of formation or combustion. The latter are often determined experimentally for a given substance.

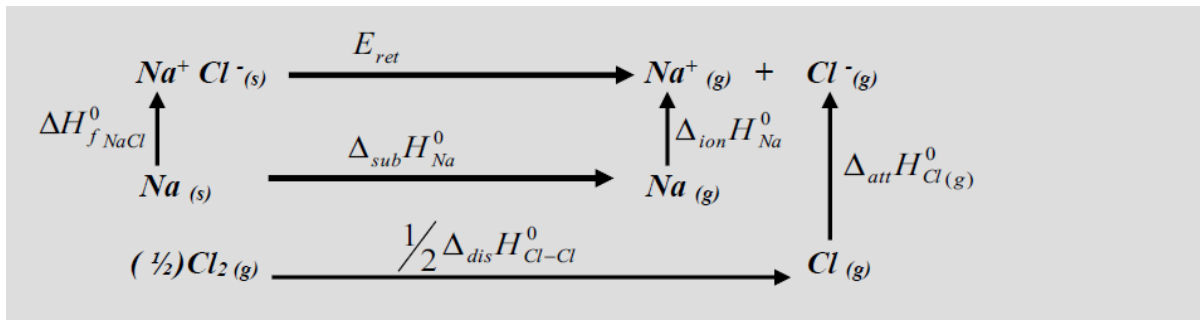### IV.6.3. Reticular energy (Born-Haber cycle)

Reticular energy is the standard internal energy, at 0K, of the dissociation reaction of the crystal into ions in the gas state:

$$AB(s) \rightarrow A^-(g)+B^+(g)\dots\dots\dots\dots\dots\dots E_{ret} \rangle 0$$
$$A_m B_n(s) \rightarrow mA^{n+}(g)+nB^{m-}(g)\dots\dots\dots\dots\Delta_{ret}U^0(0K)$$

$\Delta_{ret}H°(T)$:   is the standard reticular enthalpy.

E_{ret} :   cannot be measured. It can be calculated using the Born Haber cycle.

N.B.: Reticular energy is also defined as the enthalpy of the reaction to form one mole of the crystal from ions in the gas state.

Loi de Hess:

$$\Delta_{ret}H^0_{NaCl} - \Delta_{ion}H^0_{Na} - \Delta_{att}H^0_{Cl(g)} - \frac{1}{2}\Delta_{dis}H^0_{Cl-Cl} - \Delta_{subl}H^0_{NaCl} + \Delta H^0_{f,NaCl} = 0$$
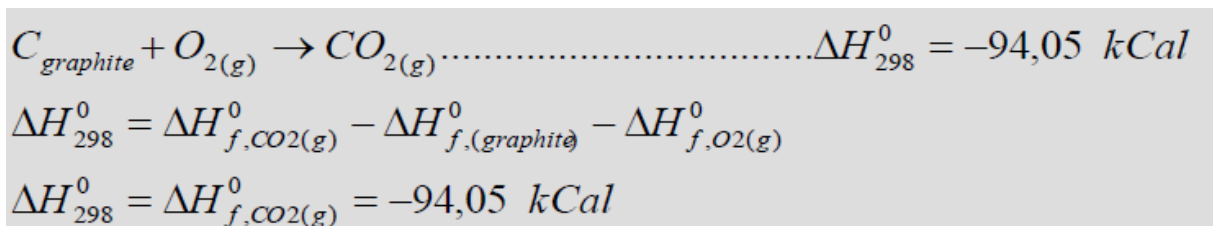
IV.6.4. The enthalpy of formation of gaseous atoms ΔH $_f$ (atoms, gaseous)

The Enthalpy of formation of a compound is the enthalpy of its synthesis reaction, from the constituent elements in the state of simple bodies under atmospheric pressure (standard state). The basic elements (simple bodies) have an enthalpy of formation. The bodies chosen are those made up of one kind of atom in the form in which they exist at equilibrium in the reference state O2, H2, Cl2, N2, Cgraphite.
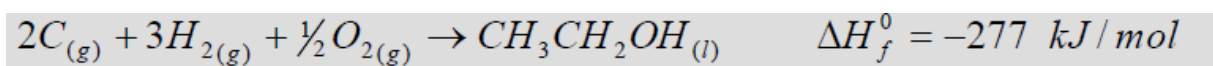
Example:

$$\Delta H_f(corps) = \Delta H^\circ_{298K} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(IV.20)$$

The standard enthalpy of formation at T of a chemical compound **ΔH $_f^0$ (T)**:

$$C_{graphite} + O_{2(g)} \rightarrow CO_{2(g)} \dots\dots\dots\dots\dots\dots\dots\dots\Delta H^0_{298} = -94{,}05 \ kCal$$

$$\Delta H^0_{298} = \Delta H^0_{f,CO2(g)} - \Delta H^0_{f,(graphite)} - \Delta H^0_{f,O2(g)}$$

$$\Delta H^0_{298} = \Delta H^0_{f,CO2(g)} = -94{,}05 \ kCal$$

Ethanol formation reaction :

$$2C_{(g)} + 3H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow CH_3CH_2OH_{(l)} \qquad \Delta H^0_f = -277 \ kJ/mol$$

The standard enthalpy of formation of a simple body in its reference state is zero.

IV.6.5. Kirchhoff's law.

A thermodynamic system is transformed from an initial state (1) to a final state (2). Assuming it takes place at constant pressure T, where it absorbs a quantity of heat Q :
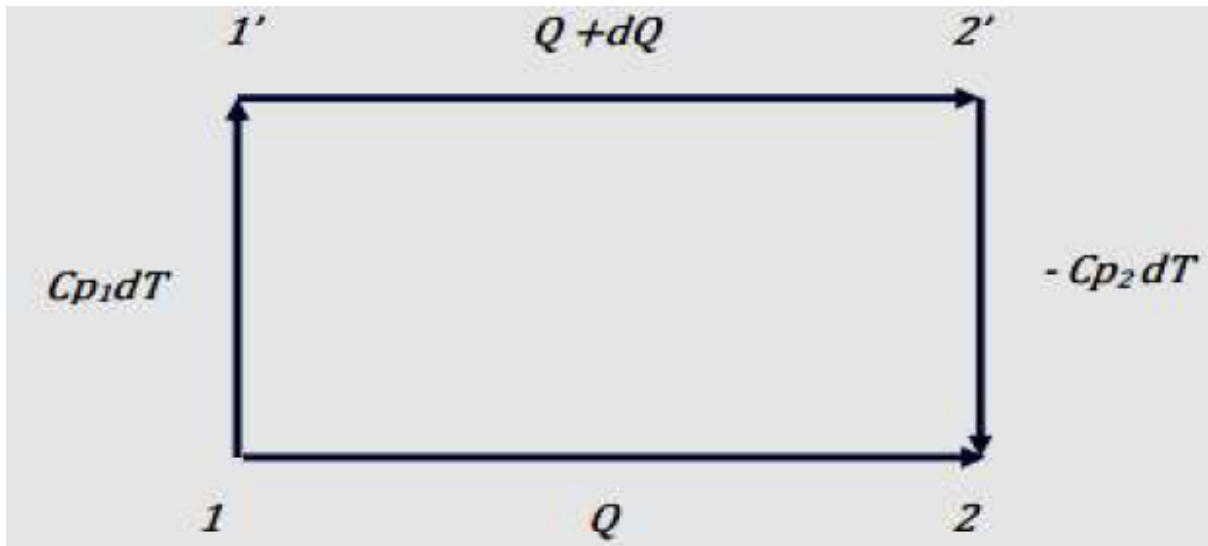

Fig.IV.1: Energy balance of heat of reaction variation with temperature [8].

Performing an energy balance on this system, we can write:

$$Q = C_{P1}dT + Q + dQ - C_{P2}dt \Rightarrow dQ = C_{P2}dT - C_{P1}dT = (C_{P2} - C_{P1})dT \Rightarrow$$

$$\frac{dQ}{dT} = C_{P2} - C_{P1} = \Delta C_p \dots\dots\dots\dots\dots\dots\dots\dots\dots(IV.21)$$

If we consider this thermodynamic system to be a chemical reaction, the quantity of heat (Q) is simply the change in enthalpy ΔH_R^0; therefore

$$\frac{d\Delta H_R^\circ}{dT} = \Delta C_p \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(IV.22)$$

Kirchhoff's law

$$\Delta C_P = \sum C_{P-produits} - \sum C_{P-réactifs} \dots\dots\dots\dots\dots\dots\dots\dots(IV.23)$$

Not forgetting the stoichiometric coefficients of the reaction products and reactants.

IV.6.7. Heat of reaction as a function of temperature

$$\Delta rH(T) = \Delta rH(298) + \Delta rC_p(T - 298)\dots\dots\dots\dots\dots\dots\dots(IV.24)$$

$$\Delta rH^\circ(T) = \Delta rH^\circ(298) + \Delta rC_p^\circ(T - 298)\dots\dots\dots\dots\dots\dots(IV.25)$$

$\Delta Cp\,^0 r$ Se calculated from thermodynamic tables.

If Cp is a function of T :

$$\Rightarrow \Delta rH(T) = \Delta rH(298) + \int_{...}^{T} \Delta rC_P dT \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(IV.26)$$

IV.6.8. Flame temperature and explosion pressure :

During a chemical reaction, there is often a variation in temperature. If this variation is too abrupt, it can be considered as adiabatic.

Two particular temperatures can then be defined:

- The flame temperature, which is the temperature reached by an adiabatic reaction at constant pressure.

- The explosion temperature, which is the temperature reached by an adiabatic reaction at constant volume.

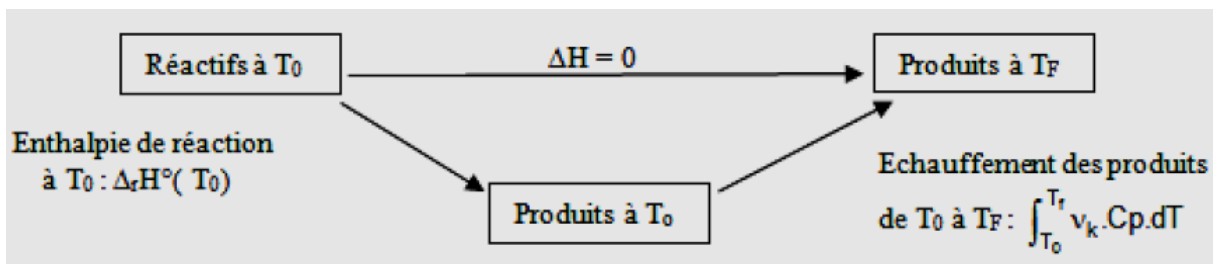To calculate them, we use the following thermochemical cycle:

Fig.IV.2: The thermochemical cycle for enthalpy calculations [8].

T_f is given by :

$$\Delta rH^{\circ}(T) + \int_{T0}^{T1} \sum_K v_K \times C_{Pk} dT = 0 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(IV.27)$$

For an explosion temperature, we reason in the same way, but with the variation in internal energy and heat capacities at constant volume.

Example:

The reaction to form methanol (CH3OH) at constant pressure releases a quantity of heat of the order of 49.5 kJ / mol at 298.15 K.

$$CO_{2(g)} + 3H_{2(g)} \rightarrow CH_3OH_{(l)} + H_2O_{(l)}$$
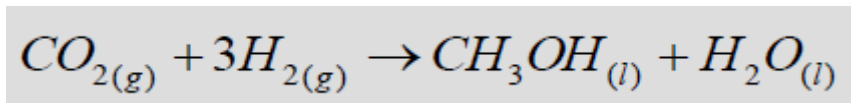
Determine the maximum temperature a methanol flame burning at constant pressure can reach. We give :

Composés	$CO_{2(g)}$	$H_{2(g)}$	$H_2O_{(l)}$	$H_2O_{(g)}$	$CH_3OH_{(l)}$	$CH_3OH_{(g)}$
$\Delta H^0_{f,298}(kCal/mol)$	-94,054	00	-68,315	-57,796	-57,23	-48,27
$C^0_{P,298}(Cal/mol.K)$	8,87	6,89	17,997	8,025	19,25	10,49

Solution:

The maximum temperature Tflame that can be reached by a methanol flame burning at constant pressure according to the reaction :

$$CO_{2(g)} \quad + \quad 3\,H_{2(g)} \quad \xrightarrow[\substack{P=Cste}]{T=737\ K} \quad CH_3OH_{(g)} \ + \ H_2O_{(g)}$$
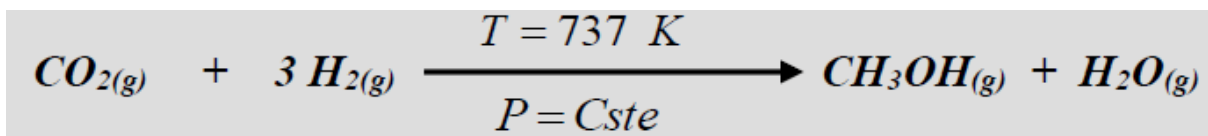
It is assumed that the heat released is attributed to the gases formed:

$$-\Delta H^0_{773} = \int_{773}^{Tflamm} \left(C_{P,CH3OH(g)} + C_{P,H2O(g)}\right) dT$$

First determine $\Delta H_{773}{}^0$ by applying Kirchhoff's law:

Avec :
$$\Delta H^0_T = \Delta H^0_{298} + \int_{298}^{T} \Delta C_P.dT$$

$$\Delta C_P = \sum_i \theta_i C_P(produits) - \sum_i \theta_i C_P(réactifs)$$

$$\Delta C_P = C_{P,CH3OH(g)} + C_{P,H2O(g)} - C_{P,CO2(g)} - 3\times C_{P,H2(g)}$$

$$\Delta C_P = 19,15 + 8,025 - 8,87 - 3\times 6,89$$

$$\Delta C_P = -2,365 \ cal/K = -9,88 \ J/K$$

$$\Delta H^0_{733} = -49,5 - 9,88.10^{-3} \times (733 - 298) = -54,193 \ kJ$$

$$-\Delta H^0_{733} = \int_{733K}^{Tflam} \left[\left(C_{P,CH3OH(g)}\right) + C_{P,H2O,(g)} \right] dT \Rightarrow 54,193 = (10,49 + 8,025) \times 4,18.10^{-3} \left(T_{flam} - 733\right)$$

$$T_{flam} = 1472,97 \ K$$