Introduction

Thermochemistry is a branch of thermodynamics that studies the thermal phenomena accompanying chemical reactions. Some reactions can release heat, making them exothermic, while others can absorb heat, making them endothermic.

3.1. Heat of reaction

The heat of reaction is defined as the amount of heat liberated or absorbed at a given temperature when the reactants are converted into products as represented by the balanced chemical equation.

Let's consider a closed system undergoing a chemical reaction assumed to be complete:

$$\mathbf{aA + bB \longrightarrow cC + dD}$$

At constant volume, the amount of heat is equal to the energy exchanged with the surroundings: $\mathbf{Q_v = \Delta U}$ (ΔU : internal energy)

Similarly, at constant pressure (P = constant), the heat of this reaction is equal to the energy exchanged with the surroundings: $Q_p = \Delta H$ (ΔH: enthalpy).

Generally, chemical reactions are carried out at constant pressure (p = constant).

If: $\mathbf{\Delta H} < 0 \longrightarrow$ The reaction is exothermic

If: $\mathbf{\Delta H} > 0 \longrightarrow$ The reaction is endothermic.

Relationship between ΔH et ΔU :

$H = U + PV \Longrightarrow \Delta H = \Delta U + \Delta(PV)$; For an ideal gas, $PV = nRT$, by replacing PV with its expression, we obtain. $\Delta H = \Delta U + \Delta(nRT) \Longrightarrow \Delta H = \Delta U + \Delta nRT$

The relationship between enthalpy and internal energy is expressed as:

$$\boxed{\mathbf{\Delta H = \Delta U + \Delta n_g RT \quad \text{with } \Delta n_g = \Sigma n_j \text{ (gaseous products)} - \Sigma n_i \text{ (gaseous reactants)}}}$$

In order to compare the heats of different reactions, it is necessary to specify the conditions under which these reactions are carried out. We then define the standard enthalpy of reaction ΔH°R for each reaction, which represents the change in enthalpy accompanying the reaction under standard conditions.

3.2. Définitions

1. Standard state: is the physical state under which a pure substance is most stable. A substance is in the standard state when it is taken at P° = 1 bar = 10^5 Pa = 0.9872 atm = 750 mmHg and at a temperature T (typically T = 25°C).

2. Internal energy and standard enthalpy: The internal energy ΔU and standard enthalpy ΔH characterize a substance in its standard state at P° = 1 bar, and they are denoted as ΔU° and ΔH°.

3. Standard enthalpy of formation: The standard enthalpy of formation of a compound is the enthalpy change accompanying the formation of one mole of the compound from its elements in their most stable state, all substances being in their standard state. The standard enthalpy of formation is denoted by $\Delta H_f°$

Example:

H_2 (g) + ½ O_2 (g) $\longrightarrow$ H_2O (g) $\Delta H^\circ_f = -57{,}88$ Kcal/mol

C(s) + 2 H_2 (g) $\longrightarrow$ CH_4 (g) $\Delta H^\circ_f = -17{,}89$ Kcal/mol

4. Standard enthalpy of formation of elemental substances: The standard enthalpy of formation of any element in its most stable form is zero. ΔH°_f (elemental substance) = 0

Example :

$\Delta H^\circ_f (O_2) = 0$; $\Delta H^\circ_f (Cl_2) = 0$; $\Delta H^\circ_f (C) = 0$

5. Enthalpy of phase change: It corresponds to the latent heat L of the phase change if the given temperature is the temperature of the phase change.

Example :

$H_2O_{(l)} \longrightarrow H_2O_{(g)}$ $\Delta H^\circ_{vap,\, H2O} = L_v = 40{,}7$ KJ/mol à T = 373 K

3.3. Calculation of Reaction Enthalpies: Hess's Law

a) Indirect method:

When a global reaction can be replaced by a series of reactions occurring at the same temperature, the overall enthalpy change is the sum of the enthalpy changes of the individual reactions.

$$\begin{tikzcd}
A \arrow[r, "\Delta H^\circ_R = ?"] \arrow[d, "\Delta H^\circ_1"'] & B \arrow[d, "\Delta H^\circ_3"] \\
C \arrow[r, "\Delta H^\circ_2"] & D
\end{tikzcd}$$

$$\boldsymbol{\Delta H^\circ_R = \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3 \qquad \Delta H^\circ_R = \; = \Sigma \Delta H^\circ_i}$$

Hess's law: "If a reaction is carried out in a series of steps, ΔH for the overall reaction will be equal to the sum of the enthalpy changes for the individual steps."

- Because ΔH is a state function, the total enthalpy change depends only on the initial state (reactants) and the final state (products) of the reaction. It doesn't matter how you get there.

Exercise :

Calculate the standard enthalpy ΔH°_R, 298K of the following reaction:

CO (g) + 3H_2(g) → CH_4(g) + H_2O (g)

a) Deduce the value of the internal energy $\Delta U^\circ_{R,298K}$ of the same reaction.

b) Is this reaction endothermic or exothermic?

The standard enthalpies of combustion reactions are given $\Delta H^\circ_{R,298K}$ of CO, H_2 and CH_4 :

CO (g) + ½ O_2 (g) → CO_2 (g) $\Delta H^\circ_{R,298K}$ (1) = -283 kJ

H_2 (g) + ½ O_2 (g) → H_2O (g) $\Delta H^\circ_{R,\, 298K}$ (2) = -241, 8 kJ

CH_4 (g) + 2 O_2 (g) → CO_2 (g) + 2H_2O (g) $\Delta H^\circ_{R,\, 298K}$ (3) = -803, 2 kJ

The standard enthalpy $\Delta H°_{R,298}$ of the reaction:
It is necessary to combine these reactions and their respective equations in order to obtain the desired reaction.

$CO(g) + 1/2O_2(g) \rightarrow CO_2(g)$ $\Delta H°_{R,298}(1) = -283$ kJ

(3) x $[H_2(g) + 1/2O_2(g) \rightarrow H_2O(g)]$ $3\Delta H°_{R,298}(2) = 3(-241{,}8)$ KJ

(-1) x $[CH4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)]$ $-1\Delta H°_{R,298}(3) = +803{,}2$ kJ

$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$ $\Delta H°_{R,298}(4)$

$\Delta H°_{R,298}(4) = \Delta H°_{R,298}(1) + 3\Delta H°_{R,298}(2) - \Delta H°_{R,298}(3)$
$\Delta H°_{R,298}(4) = -283 + 3(-241{,}8) + 803{,}2 = -206{,}23$ kJ
$\Delta H°_{R,298}(4) = -206{,}23$ KJ

a) The internal energy of the reaction $\Delta U°_{R,298}$:
$\Delta H°_{R,298} = \Delta U°_{R,298} + \Delta n_g RT$;
Δn_g is the change in the stoichiometric coefficients of the compounds in the products and the gaseous reactants.
$\Delta n_g = \sum n_j$ (gaseous products) - $\sum n_i$ (gaseous reactants)
$\Delta n_g = 2-4 = -2$
$\Delta U°_{R,298} = -206{,}23 - (8{,}31/1000).(298)(-2) = -201{,}28$ kJ
$\Delta U°_{R,298} = -201{,}28$ KJ

b) The reaction is exothermic because $\Delta H°_{R,298}(4) < 0$

b) <u>Direct method:</u>

• <u>Determination of reaction heats from the enthalpies of formation of compounds:</u>

Consider the following reaction: $aA + bB \longrightarrow cC + dD$. The knowledge of the enthalpies of formation of the products and reactants allows us to determine the enthalpy of the reaction**:**

$$\Delta H°_{R,298} = [(c\,\Delta H°_f(C) + d\,\Delta H°_f(D)) - (a\,\Delta H°_f(A) + b\,\Delta H°_f(B)]$$

In the general case,:

$$\boxed{\Delta H°_{R,298} = \sum \upsilon_j\, \Delta H°_{f,298K}\,(\text{products}) - \sum \upsilon_i\, \Delta H°_{f,298K}\,(\text{reactants})}$$

Where υ_i and υ_j are the stoichiometric coefficients of the reactants and products of the reaction.

<u>Exercise :</u>

Calculate the standard combustion heat $\Delta H°_{R,298K}$ of solid oxalic acid ($C_2H_2O_4$, s) at 25°C and atmospheric pressure, using the standard molar enthalpies of formation.
Knowing that: $\Delta H°_{f,298}(C_2H_2O_4, s) = -1822{,}2\ kJ.mol^{-1}$ $\Delta H°_{f,298}(CO_2, g) = -393\ kJ.mol^{-1}$ $\Delta H°_{f,298}(H_2O, l) = -285{,}2\ kJ.mol^{-1}$

The combustion reaction of oxalic acid:
$C_2H_2O_4(s) + 1/2\,O_2(g) \rightarrow 2\,CO_2(g) + H_2O(l)$ à 298K

To calculate the combustion heat of solid oxalic acid C2H2O4 (s), Hess's Law is applied.

$$\Delta H^\circ_{R,298} = \sum \upsilon_j \, \Delta H^\circ_{f,298K} \text{ (products)} - \sum \upsilon_i \, \Delta H^\circ_{f,298K} \text{ (reactants)}$$

$\Delta H^\circ_{R,298} = [(2\,\Delta H^\circ_{f,298}\,(CO_2) + \Delta H^\circ_{f,298}\,(H_2O)) - (\Delta H^\circ_{f,298}(C_2H_2O_4) + \frac{1}{2}\,\Delta H^\circ_{f,298}\,(O_2))]$

The standard enthalpy of formation of an elemental substance is zero => $\Delta H^\circ_{f,298}\,(O_2) = 0$

$\Delta H^\circ_{R,298} = 2\,(-392{,}9) + (-284{,}2) - (-1822{,}2) = 752{,}2$ kJ

• Determination of the enthalpy of the reaction from bond energies:

• Bond energy (Enthalpy of formation of a chemical bond):

It is the energy released (thus <0) during the formation of a covalent bond between two atoms in the gaseous state, under a pressure of 1 atm and at 25°C. It is denoted as ΔH°_L under standard conditions; ΔH°L is expressed in cal/mol or J/mol.

$$\textbf{Atom A}_{(g)} + \textbf{Atom B}_{(g)} \longrightarrow \textbf{Molecule AB}_{(g)}$$

Similarly, we define the dissociation energy, which corresponds to the energy required to break a covalent bond. It has the same absolute value as the bonding energy but with the opposite sign. $\Delta H^\circ_{diss} = -\Delta H^\circ_L$

• Calculation of bond energies:

Calculate the O-H bond energy (ΔH_L) in the H_2O molecule , given $\Delta H_f\,(H_2O)_l$

$$\begin{tikzcd}
H_2\,(g) + \frac{1}{2}\,O_2\,(g) \arrow[r, "\Delta H_f(H_2O)_l"] \arrow[d, shift right=4, "\Delta H_{diss}(H\text{-}H)"'] \arrow[d, shift left=4, "\frac{1}{2}\,\Delta H_{diss}(O{=}O)"] & H_2O\,(l) \\
2\,H\,(g) + O\,(g) \arrow[r, "2\Delta H_L(OH)"] & H_2O\,(g) \arrow[u, "-\Delta H_v"']
\end{tikzcd}$$

For a cycle $\Delta H_T = \sum \Delta H_i = 0$

$\Delta H_{diss}(H\text{-}H) + \frac{1}{2}\,\Delta H_{diss}(O{=}O) + 2\Delta H_L(OH) - \Delta H_v - \Delta H_f(H_2O)_l = 0$

$\Delta H_L(OH) = \frac{1}{2}\,[\Delta H_v + \Delta H_f(H_2O)_l - \Delta H_{diss}(H\text{-}H) - \frac{1}{2}\,\Delta H_{diss}(O{=}O)] = -110$ Kcal/mol

• Calculation of reaction enthalpy from bond energies:

By knowing the average values of bond energies, it is possible to determine the enthalpy of any chemical reaction; it is equal to the difference between the bond energies of the molecules in the products and the bond energies of the molecules in the reactants.

$$aA\,(g) + bB\,(g) \longrightarrow cC(g) + dD\,(g)$$

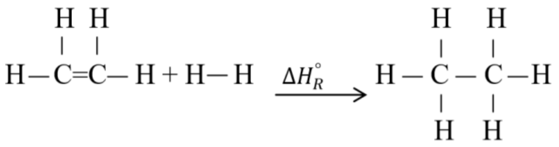
$$\Delta H^\circ_{R,298} = (c\,\Sigma\,\Delta H_L(C) + d\,\Sigma\,\Delta H_L(D)) - (a\,\Sigma\,\Delta H_L(A) + b\,\Sigma\,\Delta H_L(B))$$

In the general case:

$$\Delta H^\circ_{R,298} = \sum \upsilon_j \, \Delta H^\circ_{L,298K} \text{ (products)} - \sum \upsilon_i \, \Delta H^\circ_{L,298K} \text{ (reactants)}$$

Example:

$C_2H_4\,(g) + H_2 \longrightarrow C_2H_6\,(g)$



$$H_2C=CH_2 + H-H \xrightarrow{\Delta H_R^\circ} H_3C-CH_3$$

$\Delta H°_{R,298}$ = $[\Delta H°_L(C\text{-}C) + 6\ \Delta H°_L(C\text{-}H) – (\Delta H°_L(C{=}C) + 4\ \Delta H°_L(C\text{-}H) + \Delta H°_L(H\text{-}H)]$

3.4. Effect of temperature on reaction enthalpies: Kirchhoff's Law

Consider the following reaction for the oxidation of ammonia:

$4NH_3\ (g) + 3\ O_2\ (g) \longrightarrow 2\ N_2\ (g) + 6\ H_20\ (l)$

Knowing the reaction enthalpy at T_1 = 25°C, let's calculate the enthalpy of this reaction at another temperature T_2.

$$\begin{tikzcd}
4NH_3\ (g) + \arrow[d, "\Delta H°_1"] & 3\ O_2\ (g) \arrow[d, "\Delta H°_2"] \arrow[r, "\Delta H°_R(T_1)"] & 2\ N_2\ (g) + \arrow[d, "\Delta H°_3"] & 6\ H_20\ (l) \arrow[d, "\Delta H°_4"] & T_1 \\
4NH_3\ (g) + & 3\ O_2\ (g) \arrow[r, "\Delta H°_R(T_2)"] & 2\ N_2\ (g) + & 6\ H_20\ (l) & T_2
\end{tikzcd}$$

For a cycle $\sum \Delta H_i = 0$

$\Delta H°_R(T_1) + \Delta H°_3 + \Delta H°_4 - \Delta H°_1 - \Delta H°_2 - \Delta H°_R(T_2) = 0$

$\Delta H°_R(T_2) = \Delta H°_R(T_1) + (\Delta H°_3 + \Delta H°_4) – (\Delta H°_1 + \Delta H°_2)$

$\Delta H°_1 = \int_{T_1}^{T_2} n_{NH_3} c_{p_{NH_3}}\, dT$ $\qquad \Delta H°_2 = \int_{T_1}^{T_2} n_{O_2} c_{p_{O_2}}\, dT$

$\Delta H°_3 = \int_{T_1}^{T_2} n_{N_2} c_{p_{N_2}}\, dT$ $\qquad \Delta H°_4 = \int_{T_1}^{T_2} n_{H_2O} c_{p_{H_2O}}\, dT$

$\Delta H°_R(T_2) = \Delta H°_R(T_1) + \int_{T_1}^{T_2} [(n_{N_2} c_{p_{N_2}} + n_{H_2O} c_{p_{H_2O}}) - (n_{NH_3} c_{p_{NH_3}} + n_{O_2} c_{p_{O_2}})]dT$

$$\boxed{\begin{array}{c} \mathbf{\Delta H°_R(T_2) = \Delta H°_R(T_1) + \int_{T_1}^{T_2} \Delta c_p\, dT} \\[1em] \textbf{avec } \mathbf{\Delta c_p = \sum \upsilon_j\, c_{p,j}} \textbf{ (products) - } \mathbf{\sum \upsilon_i\, c_{p,i}} \textbf{ (reactants)} \end{array}}$$

For reactions carried out at constant volume (V), we have:

$$\boxed{\begin{array}{c} \mathbf{\Delta U°_R(T_2) = \Delta U°_R(T_1) + \int_{T_1}^{T_2} \Delta c_v\, dT} \\[1em] \textbf{avec } \mathbf{\Delta c_v = \sum \upsilon_j\, c_{v,j}} \textbf{ (products) - } \mathbf{\sum \upsilon_i\, c_{v,i}} \textbf{ (reactants)} \end{array}}$$

Exercice :

Consider the following reaction be carried out at T = 298 K and P= 1atm

$CH_4\ (g) + 4Cl_2\ (g) \longrightarrow CCl_4\ (g) + 4\ HCl\ (g)$ $\quad \Delta H°_R = -\ 401{,}1$ KJ/mol

Calculate the enthalpy of the reaction at T = 650 K

Data at T = 298 K.

	CH_4 (g)	Cl_2 (g)	HCl (g)	CCl_4 (g)
C_p (J/K.mol)	35,71	33,93	22,12	83,50

$$\mathbf{\Delta H^\circ_R(650\ K) = \Delta H^\circ_R(298\ K) + \int_{T_{298}}^{T_{650}} \Delta c_p\, dT}$$

$\Delta c_p = c_p(CCl_4) + 4\, c_p(HCl) - c_p(CH_4) - 4\, c_p(Cl_2) = 191{,}69$ J/K.mol

ΔH°_R (398 K) = - 333,61 KJ/mol

3.5. Standard ionization enthalpy:

The standard ionization enthalpy of an atom M is the standard enthalpy change of the reaction producing one mole of gaseous M+ ion from one mole of gaseous M atom.

$M(g) \longrightarrow M^+(g) + 1\, e^-$

3.6. Standard electron attachment enthalpy:

It is the standard enthalpy change of the reaction producing one mole of M- ion from one mole of gaseous M atom.

$M(g) + 1\, e^- \longrightarrow M^-(g)$

3.7. Lattice energy: Born-Haber cycle

The lattice energy ΔHr is the energy required to decompose one mole of a crystalline solid into its constituent gaseous components. The larger ΔHr, the more stable the solid is. The most common technique for calculating lattice energy is to perform a so-called Born-Haber cycle.

$$\begin{tikzcd}
Na(s) \arrow[d, "\Delta H_1"'] & + \frac{1}{2} Cl_2 \arrow[r, "\Delta H_f(NaCl)"] \arrow[d, "1/2\Delta H_2"'] & NaCl(s) \arrow[ddl, "\Delta H_r"] \\
Na(g) \arrow[d, "\Delta H_3"'] & + Cl(g) \arrow[d, "\Delta H_4"'] & \\
Na^+(g) & + Cl^-(g) &
\end{tikzcd}$$

ΔH_r : lattice energy

ΔH_1: enthalpy of sublimation of Na

ΔH_2: energy of dissociation of one mole of Cl_2 = - negative bond energy

ΔH_3: ionization energy, providing energy to remove an electron from the sodium atom

ΔH_4: electron affinity enthalpy

For a cycle $\Delta H_T = \sum \Delta H_i = 0$

$\Delta H_f(NaCl) + \Delta H_r - \Delta H_3 - \Delta H_4 - \Delta H_1 - \frac{1}{2}\Delta H_2 = 0$

$\Delta H_r = \Delta H_1 + \frac{1}{2}\Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_f(NaCl) = 768$ KJ/mol

Exercise :

The combustion reaction of gaseous benzene (C_6H_6) releases 330 KJ/mol at 298 K.

- **a)** Write the combustion reaction.
- **b)** Calculate the enthalpy of formation of (g) at 298 K.
- **c)** Calculate of C_6H_6 using bond energies.

Data at 298 K.: ΔH°_f (CO_2 (g)) = -393,5 KJ/mol ; ΔH°_f (H_2O(l)) = -285,2 KJ/mol ; ΔH°_{sub} (C) = 716 KJ/mol

a) The combustion reaction:

$$C_6H_6 \text{ (g)} + 15/2\ O_2 \text{ (g)} \longrightarrow 6\ CO_2 \text{ (g)} + 3\ H_2O \text{ (l)}$$

b) Calculation of the enthalpy of formation of C_6H_6 (g) at 298 K :

$\Delta H^\circ_R = 6\ \Delta H^\circ_f\ (CO_2) + 3\ \Delta H^\circ_f\ (H_2O(l)) - \Delta H^\circ_f\ (C_6H_6\ (g)) - 15/2\ \Delta H^\circ_f\ (O_2)$

$\Delta H^\circ_f\ (C_6H_6\ (g)) = 6\ \Delta H^\circ_f\ (CO_2) + 3\ \Delta H^\circ_f\ (H_2O(l)) - \Delta H^\circ_R = 83{,}4$ KJ/mol

c) Calculation of ΔH°_f of C_6H_6 using bond energies:

$$\begin{tikzcd}
6\,C(s) + 3\,H_2(g) \arrow[r, "\Delta H^\circ_f\,(C_6H_6)"] \arrow[d, "6\,\Delta H^\circ_{sub}"', "3\,\Delta H^\circ_{diss}\,(H\text{-}H)"] & C_6H_6\ (g) \\
6\,C\ (g) + 6\,H\ (g) \arrow[ur, "3\,\Delta H^\circ_{C=C} + 3\,\Delta H^\circ_{C\text{-}C} + 6\,\Delta H^\circ_{C\text{-}H}"'] &
\end{tikzcd}$$

$6\ \Delta H^\circ_{sub} + 3\ \Delta H^\circ_{diss}\ (H\text{-}H) + 3\ \Delta H^\circ_{C=C} + 3\ \Delta H^\circ_{C\text{-}C} + 6\ \Delta H^\circ_{C\text{-}H} - \Delta H^\circ_f\ (C_6H_6) = 0$

$\Delta H^\circ_f\ (C_6H_6) = 6\ \Delta H^\circ_{sub} + 3\ \Delta H^\circ_{diss}\ (H\text{-}H) + 3\ \Delta H^\circ_{C=C} + 3\ \Delta H^\circ_{C\text{-}C} + 6\ \Delta H^\circ_{C\text{-}H}$

$\Delta H^\circ_f\ (C_6H_6) = 237$ KJ/mol.