3.1. Introduction:

Thermochemistry is the study of the transfer of heat (thermal energy) in chemical reactions.

3.2. Chemical reaction:

In a chemical reaction, reactants are converted into products. It is written in the following general form:

$\mathbf{a\,A_{(*)} + b\,B_{(*)} \rightarrow c\,C_{(*)} + d\,D_{(*)}}$

A and **B**: are the reactants

C and **D**: are the products

a, **b**, **c** and **d**: are the stoichiometric coefficients indicating the number of moles

(*) indicates the physical state (*solid* (**s**), *liquid* (**l**) or *gas* (**g**)).

Example: combustion of methane:

$CH_{4(gas)} + 2\ O_{2(gas)} \longrightarrow CO_{2(gas)} + 2\ H_2O(_{liquid)}$

Reactants Products

Initial state Final state

3.3. Heat of the chemical reaction:

Is the energy that is released or absorbed when chemicals are transformed.

*__Heat of chemical reaction at constant volume: $\Delta U = Q_v$__

***Heat of chemical reaction at constant pressure: $\Delta H = Q_P$**

Generally, chemical reactions are conducted at constant pressure ;

* **$\Delta H < 0$**: **exothermic** reaction (the reaction releases heat).

* **$\Delta H > 0$**: **endothermic** reaction (the reaction absorbs heat).

*Relationship between ΔH and ΔU (Q_p and Q_v) :

Consider a chemical reaction carried out in the gas phase at temperature T:

$\mathbf{a\,A_{(g)} + b\,B_{(g)} \rightarrow c\,C_{(g)} + d\,D_{(g)}}$

*** Reaction at constant volume: $\Delta U = Q_V$**

*** Reaction at constant pressure: $\Delta U = Q_P - P.(V_2 - V_1)$**

According to Joule's 1st law, the internal energy of an ideal gas depends only on the temperature. ΔU is therefore the same; for a transformation at V = constant and at P = constant, when these two reactions are carried out at the same temperature.

So we have :

$Q_V = Q_P - P(V_2 - V_1) \rightarrow Q_P = Q_V + (P.V_2 - P.V_1)$

And for an ideal gas : PV = nRT; that's to say :

$P.V_1 = n_{reactants}\ RT = (\mathbf{a} + \mathbf{b})RT$; and ; $P.V_2 = n_{products}\ RT = (\mathbf{c} + \mathbf{d})RT$

Hence : $\mathbf{Q_P = Q_V + \Delta ng.RT}$; and so; $\mathbf{\Delta H = \Delta U + \Delta ng.RT}$

With : $\mathbf{\Delta n = \Sigma\, n_{j(gaseous\ products)} - \Sigma\, n_{i(gaseous\ reactants)}}$

Example : $CO_{(g)} + ½\ O_{2(g)} \longrightarrow CO_{2(g)}$ T=25°C

ΔH = - 67.6 Kcal Δn = 1-1-1/2 = - 0.5

$\Delta U = -67.6 + 0.5*2*298*10^{-3} = -67.3$ Kcal

Example: The combustion of methane releases, at constant volume, 2000 KJ at 25°C. Deduce the enthalpy of reaction.

$CH_{4(gas)} + 2O_{2(gas)} \xrightarrow{T = 298K} CO_{2(gas)} + H_2O_{(liquid)}$

$\Delta U = - 2000$ KJ ; and ; $\Delta n = 1-1-2 = - 2$

Hence : $\Delta H = - 2.\ 10^6 - 2*8.314*298 = - 2004955.144$ J = -2004.95 KJ

3.4. Standard state – Standard enthalpy of formation:

3.4.1. Standard state:

The standard state of a substance is its most stable physical state at 25°C temperature and 1 atm pressure.

Examples: at T=298K and P=1atm

Carbon $\longrightarrow$ C (solid)

Hydrogen $\longrightarrow$ H_2 (gas)

3.4.2. Standard enthalpy of formation ($\Delta H°_f$):

Is the enthalpy change needed for the formation of 1 mole of a substance from its elements in their standard states.

Example :

$H_{2(g)} + 1/2O_{2(g)} \longrightarrow H_2O_{(g)}$ $\Delta H°_{f,298\ (H2O(g))} = - 242$ KJ/mol

Note:

By convention, standard enthalpy for formation ($\Delta H_f°$) of an ***element*** in standard state is taken as ***zero***.

Examples:$\Delta H°_{f(O2(g))}=0$KJ/mol,$\Delta H°_{f(H2(g))}=0$KJ/mol,$\Delta H°_{f(C(s))}=0$KJ/mol,$\Delta H°_{f(Fe(s))} = 0$ KJ/mol

3.5. Enthalpy of physical state change :

The enthalpy of state change at a temperature T is the enthalpy of the reaction:

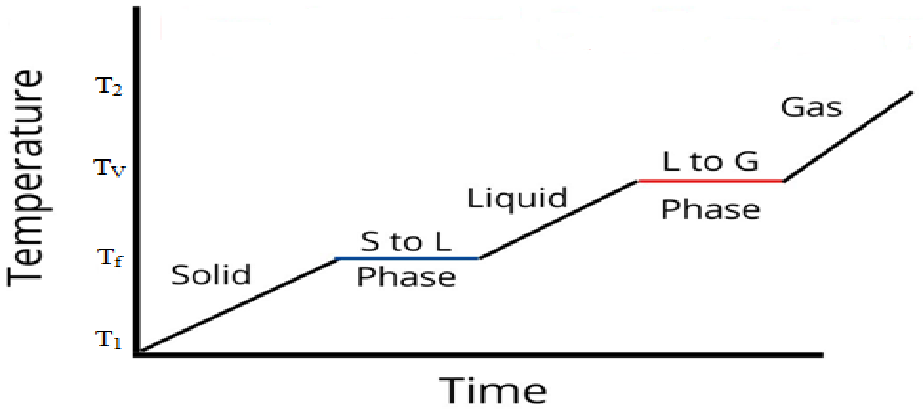
$A_{\ (state\ 1)} \rightarrow A_{\ (state\ 2)}$

ΔH° (change of state) = ***L*** (change of state) / L: is the latent heat

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

$\Delta H°_{vaporization} = \Delta H_f°_{\ (H2O(g))} - \Delta H_f°_{\ (H2O(l))} = - 241,83 + 285,84 = 44$ KJ/mol

*Calculating ΔH during the heating of a pure substance :



The enthalpy change of a mole of a pure substance passing from temperature T_1 to temperature T_2 while undergoing fusion and vaporization is written:

T_2

$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$

$$\Delta H = \int_{T_1}^{T_f} n.c_{P(solid)}.dT + n.\Delta H_f^{\circ} + \int_{T_f}^{T_v} n.c_{P(lquid)}.dT + n.\Delta H_v^{\circ} + \int_{T_v}^{T_2} n.c_{P(gas)}.dT$$

T_f: melting temperature. T_V: vaporization temperature.

3.6. Determination of the standard enthalpy of chemical reaction:

a) Use of reaction enthalpies (indirect method):

If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature

In general, if enthalpy of an overall reaction A→B along one route is $\Delta H°_R$ and $\Delta H°_{R1}$, $\Delta H°_{R2}$, $\Delta H°_{R3}$ ..... representing enthalpies of reactions leading to same product, B along another route, then we have : $\Delta H°_R = \Delta H°_{R1} + \Delta H°_{R2} + \Delta H°_{R3}$ ...

It can be represented as:

$$\begin{tikzcd}
\boxed{A} \arrow[r, "\Delta H_R"] \arrow[d, "\Delta H_{R1}"'] & \boxed{B} \\
\boxed{C} \arrow[r, "\Delta H_{R2}"] & \boxed{D} \arrow[u, "\Delta H_{R3}"']
\end{tikzcd}$$

Example :

$C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H°_{298}\,(1) = -\,393.5$ Kj

$CO_{(g)} + 1/2\ O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H°_{298}\,(2) = -\,283.0$ Kj

What is the standard enthalpy of reaction (3)?

$C_{(graphite)} + 1/2\ O_{2(g)} \longrightarrow CO_{(g)}$ $\Delta H°_{298}\,(3) = ?$

Note that by subtracting equation (1) from equation (2), we obtain equation (3),

So : $\Delta H°_{298}\,(1) - \Delta H°_{298}\,(2) = \Delta H°_{298}\,(3)$

Hence : $\Delta H°_{298}\,(3) = -\,393.5 + 283.0 = -\,110.5$ Kj $\Delta H°_{298}\,(3) = -\,110.5$ Kj

b) Use of the enthalpies of formation of compounds (HESS's law):

Consider the following reaction: $\mathbf{a\ A_{(*)} + b\ B_{(*)} \rightarrow c\ C_{(*)} + d\ D_{(*)}}$

The standard enthalpy change of a chemical reaction ($\Delta H°_R$) can be calculated from enthalpies of formation **($\Delta H°_f$)** of each reactant and product by HESS's law :

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

In the general case:

$\mathbf{\Delta H°_{R,\,298} = \Sigma\ (\nu_j.\ \Delta H°_{f,j})_{\ products} - \Sigma\ (\nu_i.\ \Delta H°_{f,i})_{\ reactants}}$

where $\boldsymbol{\nu_j}$ and $\boldsymbol{\nu_i}$ represent the stoichiometric coefficients of the products and reactants in the balanced equation, respectively.

Example:

$CH_3OH_{(l)} + 3/2\ O_{2(g)} \longrightarrow CO_{2(g)} + 2\ H_2O_{(l)}$ T = 298K

$\Delta H°_{298,f}\,(CH_3OH_{(l)}) = -57{,}04$ Kcal/mol ; $\Delta H°_{298,f}\,(H_2O_{(l)}) = -68{,}32$ Kcal/mol

$\Delta H°_{298,f}\,(CO_{2(g)}) = -94{,}05$ Kcal/mol ; $\Delta H°_{298,f}\,(O_{2(g)}) = 0$ Kcal/mol

According to Hess's law: $\mathbf{\Delta H°_{R,\,298} = \Sigma\ (\nu_j.\ \Delta H°_{f,j})_{\ products} - \Sigma\ (\nu_i.\ \Delta H°_{f,i})_{\ reactants}}$

$\Delta H°_{R,298} = \Delta H°_{298,f\ (CO2(g))} + 2.\ \Delta H°_{298,f\ (H2O(l))} - \Delta H°_{298,f\ (CH3OH(l))} - 3/2.\ \Delta H°_{298,f\ (O2(g))}$

$= -94{,}05 + 2.\,(-68{,}32) - (-57{,}04) - 3/2.\,(0) = \mathbf{-\ 173{,}65\ Kcal}$

c) Use of bond enthalpies:

* Enthalpy of bond formation (bond energy):

Is the energy released during the formation of a covalent bond between two atoms taken in the gaseous state. The bond formation reaction is written as follows:

Atom **A (g)** + Atom **B (g)** → Molecule **A – B (g)** $\Delta H^{\circ}_{f,\,A-B}$

It is always negative ($\Delta H^{\circ}_{f,A-B} < 0$).

*Enthalpy (energy) of dissociation:

It corresponds to the dissociation reaction of the covalent bond A-B

Molecule **A – B (g)** → Atom **A (g)** + Atom **B (g)** $\Delta H^{\circ}_{diss,\,A-B} = -\Delta H^{\circ}_{f,\,A-B}$

It is positive ($\Delta H^{\circ}_{diss,\,A-B} > 0$) because energy must be supplied to break the bond.

* Calculation of the reaction enthalpy from bond enthalpies:

Consider the following ***gas phase*** reaction: **a A(g) + b B(g) → c C(g) + d D(g)**

Hess's law allows the calculation of the standard enthalpy change of a chemical reaction from the bond enthalpies of the reactants and products in gas phase reactions as:

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

In the general case:

$\boldsymbol{\Delta H^{\circ}_{R,\,298} = \Sigma\ (\nu_j.\ \Delta H^{\circ}_{bonds})_{\ products} - \Sigma\ (\nu_i.\ \Delta H^{\circ}_{bonds})_{\ reactants}}$

Example :

$C_2H_{4(g)} + H_{2(g)} \longrightarrow C_2H_{6(g)}$

$\Delta H^{\circ}_{f,C-C} = -\ 83\text{Kcal/mol}$ $\Delta H^{\circ}_{f,C-H} = -\ 99\ \text{Kcal/mol}$

$\Delta H^{\circ}_{f,C=C} = -\ 147\ \text{Kcal/mol}$ $\Delta H^{\circ}_{f,H-H} = -\ 104\ \text{Kcal/mol}$

According to Hess's law: $\boldsymbol{\Delta H^{\circ}_{R,\,298} = \Sigma\ (\nu_j.\ \Delta H^{\circ}_{bonds})_{\ products} - \Sigma\ (\nu_i.\ \Delta H^{\circ}_{bonds})_{\ reactants}}$

$\Delta H^{\circ}_{R,298} = (1.\ \Delta H^{\circ}_{f,C-C} + 6.\ \Delta H^{\circ}_{f,C-H}) - (1.\ \Delta H^{\circ}_{f,C=C} + 4.\ \Delta H^{\circ}_{f,C-H} + 1.\Delta H^{\circ}_{f,H-H})$

$= \Delta H^{\circ}_{f,C-C} + 2.\ \Delta H^{\circ}_{f,C-H} - \Delta H^{\circ}_{f,C=C} - \Delta H^{\circ}_{f,H-H}$

$= (-\ 83) + 2\ (-\ 99) - (-147) - (-\ 104)$ $\boldsymbol{\Delta H^{\circ}_{R,\,298} = -31\ Kcal}$

*Calculation of bond enthalpies:

Determine the enthalpy of formation of the C-C bond in $C_2H_{6(g)}$.

Data: $\Delta H^{\circ}_{f,C2H6} = -319.46$kcal/mol; $\Delta H^{\circ}_{sublimation(C,s)} = 171{,}2$kcal/mol; $\Delta H^{\circ}_{(H-H)} = -104$ kcal/mol; $\Delta H^{\circ}_{(C-H)} = -99{,}5$ kcal/mol.

$$\begin{tikzcd}
2C_{(s)} \arrow[d, "2\Delta H^{\circ}_{sub\ (C)}"'] & + & 3H_{2(g)} \arrow[d, "-3\Delta H^{\circ}_{H-H}"'] \arrow[r, "\Delta H^{\circ}_{f,\ C2H6}"] & C_2H_{6(g)} \\
2C_{(g)} & + & 6H_{(g)} \arrow[ur, "\Delta H^{\circ}_{C-C} + 6\Delta H^{\circ}_{C-H}"'] &
\end{tikzcd}$$

$2\Delta H^{\circ}_{sub}(C) - 3\Delta H^{\circ}_{H-H} + \Delta H^{\circ}_{C-C} + 6\Delta H^{\circ}_{C-H} - \Delta H^{\circ}_{f,\ C2H6} = 0$

$\Delta H^{\circ}_{C-C} = \Delta H^{\circ}_{f,\ C2H6} - 2\Delta H^{\circ}_{sub}(C) + 3\Delta H^{\circ}_{H-H} - 6\Delta H^{\circ}_{C-H}$

$\Delta H^{\circ}_{C-C} = -319.46 - 2*171{,}2 + 3*(-104) - 6*(-99{,}5) = -376.9$ Kcal/mol

3.7. Effect of temperature on the reaction enthalpies (Kirchhoff's law):

Consider the following chemical reaction:

$a\,A_{(*)} + b\,B_{(*)} \rightarrow c\,C_{(*)} + d\,D_{(*)}$

Knowing the standard enthalpy of this reaction ($\Delta H^\circ_{R,298}$), we can determine the enthalpy of this reaction at temperature T ($\Delta H^\circ_{R,T}$).

$$\begin{tikzcd}
\mathbf{a\,A_{(*)}} \arrow[d, "\Delta H^\circ_1"'] & \mathbf{+\,b\,B_{(*)}} \arrow[d, "\Delta H^\circ_2"'] \arrow[r, "\Delta H^\circ_{R,T}"] & \mathbf{c\,C_{(*)}} & \mathbf{+\,d\,D_{(*)}} & \mathbf{T} \\
\mathbf{a\,A_{(*)}} & \mathbf{+\,b\,B_{(*)}} \arrow[r, "\Delta H^\circ_{R,T0}"] & \mathbf{c\,C_{(*)}} \arrow[u, "\Delta H^\circ_3"'] & \mathbf{+\,d\,D_{(*)}} \arrow[u, "\Delta H^\circ_4"'] & \mathbf{T_0 = 298K}
\end{tikzcd}$$

We will assume that the constituents do not undergo a change of state, therefore:

$\mathbf{\Sigma\,(\Delta H^\circ_i)_{cycle} = 0} \longrightarrow \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_{R,T0} + \Delta H^\circ_3 + \Delta H^\circ_4 - \Delta H^\circ_{R,T} = 0$

$\Delta H^\circ_{R,T} = \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_{R,T0} + \Delta H^\circ_3 + \Delta H^\circ_4$

$$\Delta H^\circ_{R,T} = \int_T^{T_0} a\,c_{P(A)}dT + \int_T^{T_0} b\,c_{P(B)}dT + \Delta H^\circ_{R,T_0} + \int_{T_0}^{T} c\,c_{P(C)}dT + \int_{T_0}^{T} d\,c_{P(D)}dT$$

$$\Delta H^\circ_{R,T} = \Delta H^\circ_{R,T_0} + \int_{T_0}^{T}[(c\,c_{P(C)} + d\,c_{P(D)}) - (a\,c_{P(A)} + b\,c_{P(B)})]dT$$

We assume: $\Delta c_P = [(c\,c_{P(C)} + d\,c_{P(D)}) - (a\,c_{P(A)} + b\,c_{P(B)})]$

$$\mathbf{\Delta c_P = \sum(\gamma_j . c_{P(j)})_{products} - \sum(\gamma_i . c_{P(i)})_{reactants}}$$

$$\mathbf{\Delta H^\circ_{R,T} = \Delta H^\circ_{R,T_0} + \int_{T_0}^{T} \Delta c_P . dT}$$ **1st law of KIRCHHOFF**

In the case of a chemical reaction carried out at constant volume. We have the following expressions:

$$\mathbf{\Delta c_V = \sum(\gamma_j . c_{V(j)})_{products} - \sum(\gamma_i . c_{V(i)})_{reactants}}$$

$$\mathbf{\Delta U^\circ_{R,T} = \Delta U^\circ_{R,T_0} + \int_{T_0}^{T} \Delta c_V . dT}$$ **2nd law of KIRCHHOFF**

Note: In the case where there is a phase change in the interval [T_0, T], the phase change enthalpies must be taken into account in the calculation.

Exercise :

The complete combustion of one mole of liquid methanol under standard pressure and temperature conditions releases 725.2 kJ according to the following reaction: $CH_3OH\,(l) + 3/2\,O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)$

Calculate the enthalpy of this reaction at 60°C.

Data :

compound	CH_3OH (l)	O_2 (g)	CO_2 (g)	H_2O (l)
c_p(J/mol.K)	81,6	34,7	36,4	75,2

Kirchhoff's law states:

$$\mathbf{\Delta H^\circ_{R,T} = \Delta H^\circ_{R,298} + \int_{298}^{T} \Delta c_P . dT} \longrightarrow \mathbf{\Delta H^\circ_{R,T} = \Delta H^\circ_{R,298} + \Delta c_P . (T - 298)}$$

$\Delta c_p = 2.c_p(H_2O) + c_p(CO_2) - c_p(CH_3OH) - 3/2.\,c_p(O_2) = 53{,}15$ j/mol K

$\mathbf{\Delta H^\circ_{R,T} = -723.34}$ Kj

3.8. Lattice energy :

The lattice energy of an ionic crystal is the energy required to form one mole of a crystal from its constituent ions in the gaseous state. This energy is the enthalpy of the reaction.

Example:

$Na^+_{(gas)} + Cl^-_{(gas)} \rightarrow NaCl_{(solid)}$ ($\Delta H°$: lattice energy)

knowing the enthalpy of formation of NaCl(s) from the elements Na(s) and Cl_2(g), according to the reaction:

$Na_{(s)} + ½\, Cl_{2(g)} \rightarrow NaCl_{(s)}$ ($\Delta H°_1 = -98$ Kcal)

And knowing the enthalpies of the following reactions:

1/ Sublimation of Na(s) and dissociation of Cl_2(g):

$Na_{(s)} \rightarrow Na_{(g)}$ ($\Delta H°_2 = 26$ Kcal)

$½\, Cl_{2(g)} \rightarrow Cl_{(g)}$ ($\Delta H°_3 = 29$ Kcal)

2/ Ionization of Na and Cl:

$Na_{(g)} \rightarrow Na^+_{(g)} + 1e^-$ ($\Delta H°_4 = 118$ Kcal)

$Cl_{(g)} + 1e^- \rightarrow Cl^-_{(g)}$ ($\Delta H°_5 = -86$ Kcal)

3/ Formation of the ionic crystal (NaCl) from the ions (Na^+) and (Cl^-) in the gaseous state:

$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)}$ ($\Delta H°$)

We represent these reactions by the following diagram (Born–Haber cycle):

$$\begin{tikzcd}
Na_{(s)} \arrow[d, "\Delta H°_2"'] & + & ½\, Cl_{2(g)} \arrow[d, "\Delta H°_3"'] \arrow[rr, "\Delta H°_1"] & & NaCl_{(s)} \\
Na_{(g)} \arrow[d, "\Delta H°_4"'] & + & Cl_{(g)} \arrow[d, "\Delta H°_5"'] & & \\
Na^+_{(g)} & + & Cl^-_{(g)} \arrow[uurr, "\Delta H°"'] & &
\end{tikzcd}$$

$\Delta H°_{cycle} = 0 \rightarrow \sum \Delta H°_i = 0 \rightarrow \Delta H°_2 + \Delta H°_3 + \Delta H°_4 + \Delta H°_5 + \Delta H° - \Delta H°_1 = 0$

So: $\Delta H° = \Delta H°_1 - \Delta H°_2 - \Delta H°_3 - \Delta H°_4 - \Delta H°_5 =$ **- 185 Kcal**