



MANIPULATION N°03

Determining Enthalpies of Reaction

1- Introduction :

In any chemical reaction, heat is either **absorbed** or **liberated**. This exchange of heat between a chemical reaction and its immediate environment is known as the **enthalpy** of reaction or "**H**". This enthalpy cannot be measured directly, so scientists use the "**variation**" in **temperature** between the **start** and **end** of the reaction, which can then be used to calculate the "**variation**" in **enthalpy** over the same lapse of time (variation noted as ΔH). Using the ΔH , scientists are able to tell whether a reaction has been "**exothermic**" (losing or liberating heat during the reaction) or "**endothermic**" (absorbing heat). In general, a **Constant Pressure** ($\Delta H = Q = m.c.\Delta T$), with **m** representing the mass of the components, **c** the specific heat of the product and ΔT being the temperature variation during the reaction.

2- Objective of the work:

- 1- Determine the **calorific capacity** of the calorimeter.
- 2- Measuring the enthalpy of dissolving **KCl** salt in water.
- 3- Measuring the enthalpy of diluting an **HCl** solution.

3- Theoretical part :

3-1 . Enthalpy :

According to the first principle of thermodynamics, the elementary variation in internal energy **dU** of a system is equal to the sum of the quantities of heat and work that this system has exchanged with the external environment. We can therefore write $dU = dW + dQ$.

In the particular case of a fluid at uniform pressure **P**, the elementary work **dW** is expressed by the relation: $dW = -PdV$. So we can write: $dU = -PdV + dQ$.

- If the transformation takes place at constant volume (**isochore**), then $dV = 0$ and therefore $dU = dQ$.
- If the transformation is at constant pressure (**isobaric** transformation), then $dP = 0$.

In this case, we introduce the greatness **H**, which is the enthalpy of the system.

Enthalpy is a **state function** used in the first principle of thermodynamics. It is defined by the expression: $H = U + PV$. The expression of enthalpy is also frequently used in its differential form: $dH = dU + PdV + VdP$. The result is: $dH = dQ + VdP$.

so, if we change the volume of the system while imposing a constant pressure (isobaric transformation, $dP = 0$), the difference in enthalpy between the final state of the system and the initial state is equal to the heat exchanged, i.e. $\Delta H = Q$.

It is found that this principle gives a precise definition of heat. When a hot element comes into contact with a colder one, the temperatures of the two elements are equalized. For an isolated system (the case in a calorimeter), we deduce the following relationship: $\sum Q_i = 0$.

❖ We have: $Q = m \cdot c \cdot (T_f - T_i)$

Knowing that: m : the mass of the element in Kg,
 c : specific heat of the element in $J.Kg^{-1} \cdot ^\circ K^{-1}$.
 $(T_f - T_i)$: temperature difference between initial and final state.

❖ Or: $Q = C \cdot (T_f - T_i)$ Knowing that : C : calorific capacity of the element in $J \cdot ^\circ K^{-1}$.

3-2 . Enthalpy of dissolution :

The dissolution of one mole of substance in a given quantity of solvent is accompanied by a quantity of heat (either absorbed or ceded). This heat is called the Enthalpy of dissolution.

$$\Delta H_d = \frac{Q}{n} \quad , n = m / M$$

This Enthalpy is the sum of two Enthalpies :

- One corresponds to the decomposition of the cell network - accompanied by the **Endothermic** effect.
- The other corresponds to the interaction between free solute ions and solvent molecules - accompanied by the **Exothermic** effect.

4- Experimental part :

1- Determining the calorific capacity of the calorimeter (C_{cal}) :

- Introduce a mass $m_1=50$ g of distilled water at **room temperature** into the calorimeter. Note the equilibrium temperature T_1 (Water + Calorimeter).
 - Add $m_2=50$ g of warm water at temperature T_2 ($25^\circ C < T_2 < 40^\circ C$). Note T_2
 - Record the new temperature ($T_f = T_{eq}$) (minimum temperature reached in the calorimeter) (Water at Temperature T_1 + Calorimeter + Water at Temperature T_2).
 - Determine (C) the Calorific Capacity of a Calorimeter knowing that :
 - the quantity of heat Q_2 **ceded** by the hot water is $Q_2 = m_2 c_{eau} (T_f - T_2)$.
 - the quantity of heat Q_{cal} **received** by the calorimeter + Q_1 **received** by the cold water.
- $$Q_{cal} + Q_1 = \mu c_{al} (T_f - T_1) + m_1 c_{eau} (T_f - T_1) = (\mu + m_1) c_{eau} (T_f - T_1).$$
- And the isolated system can be written as: ($\Sigma Qi = 0$) $\Rightarrow Q_1 + Q_{cal} + Q_2 = 0$

C_{cal} the calorific capacity of the calorimeter in Joule per Kelvin ($J \cdot K^{-1}$).
 c_e : the specific or mass heat of liquid water, equal to $4180 J \cdot K^{-1} \cdot Kg^{-1}$.
 μ : the water equivalent mass of the calorimeter in **kilograms** (kg).

2- Determination of the enthalpy of dissolution of KCl salt in water

- a. Introduce $m_1=50\text{g}$ of water at **room temperature** into the calorimeter.
- b. Using thermometer, note equilibrium temperature T_1 .
- c. Place a mass $m_2 = 4\text{g}$ of salt (**KCl**) in the calorimeter.
- d. After dissolving the salt, note the temperature T_f .
- e. Determine Q_{KCl} the quantity of heat dissolved by the **KCl** salt, given that :
 - the quantity of heat Q_{Eau} **ceded** by the water.
 - the quantity of heat Q_{Cal} **ceded** by the calorimeter.
 - the quantity of heat Q_{KCl} **received** by the KCl.
- f. Determine (ΔH_{KCl}) the Enthalpy of dissolution of **KCl** knowing that :
 - $\Delta H_{\text{KCl}} = Q_{\text{KCl}} / n_{\text{KCl}}$

M_{KCl} : molar mass of KCl = **74,55 g.mole⁻¹**.

3- Determination of the enthalpy of dilution of an HCl solution :

- a. Introduce $m_1=50\text{g}$ of water at **room temperature** into the previous calorimeter.
- b. Using the thermometer, note the temperature (T_1), which will be the initial temperature of the water and the calorimeter.
- c. We have added **10 mL** of HCl solution (**C% or P = 37.5%**) into the calorimeter.
- d. Note the new temperature of the mixture at thermal equilibrium ($T_f = T_{\text{eq}}$).
- e. Determine Q_{HCl} the heat quantity of **HCl**, given that :
 - the quantity of heat Q_{Eau} **received** by the water.
 - the quantity of heat Q_{Cal} **received** by the calorimeter.
 - the quantity of heat Q_{HCl} **ceded** by the HCl.
- f. Calculate the mass m_2 of **HCl** contained in **10 ml** of the solution, knowing that :
 - $m_2 = m_{\text{HCl}} = \text{C\%} \cdot m_{\text{solution}}$ et $m_{\text{solution}} = \rho \cdot V_{\text{solution}}$
- g. Determine (ΔH_{HCl}) the Enthalpy of the **HCl** dilution knowing that :

Molar mass $M_{\text{HCl}} = 36.5 \text{ g. mole}^{-1}$.

The density $d = 1.19$.

Degree of purity **P** ou **C%** = 37.5 %.

