MANIPULATION N°04

Determination of Neutralisation Enthalpy (HESS law)

1- ***Introduction*** :

*Chemical reactions are generally accompanied by the **liberation** or **absorption** of heat. If heat is liberated, the reaction is said to be **exothermic**. If heat is absorbed, the reaction is said to be **endothermic**.*

*Many chemical reactions take place at **constant pressure**, usually atmospheric pressure. In this case, we define a state function, called **enthalpy** H, to study the heat of reactions at constant pressure.*

*For a reaction taking place at constant pressure and for which no work is exchanged (other than that of the pressure forces), the change in enthalpy **ΔH** is equal to the quantity of heat exchanged **Qp (ΔH = Qp)**.*

*By convention, **ΔH** and **Qp** are **negative** if the reaction is **exothermic** (energy is lost by the system). **ΔH** and **Qp** are **positive** if the reaction is **endothermic** (energy is gained by the system).*

2- ***Objective of the work*** :

1- *Determine the calorific capacity of the calorimeter.*
2- *Measure the heat of neutralisation of a strong acid by a strong base;*
3- *Check Hess's law.*

3- *Theoretical part:*

3-1 PRINCIPLE

When an acid is neutralized by a base, heat is liberated which varies with the strength of the acid.

*In dilute solution, strong acids and bases can be considered to be completely dissociated into their ions. The neutralisation of a strong **acid (HCl)** by a strong **base (NaOH)** is therefore limited to the **formation** of H_2O from these ions:*

$$(H^+ + Cl^-) + (Na^+ + OH^-) \longrightarrow H_2O + (Na^+ + Cl^-)$$

$\Delta H (H_2O) = -57.3\ kJ.mol^{-1}$ *(the (–) **sign** shows that the reaction is **exothermic**)*

*The calorific effect is therefore independent of the nature of the **anion** in the acid and the **cation** in the base.*

*The **heat of neutralisation** of a strong acid can be determined using a simple calorimeter. The experiments are carried out at **constant pressure**, and the heat of reaction is then related to the variation in the system by: **ΔH = Qp**.*

*The calorimeter and its contents are an isolated system; there is no exchange with the outside world **ΣQi = 0**.*

We have : $Q = m . c . (T_f - T_i)$

Knowing that : **m** *: the mass of the body in kg,*

c *: the mass heat of the body in kj.kg-1.°K-1.*

$(T_f - T_i)$ *: temperature difference between the initial and final states.*

Ou : $Q = C.(T_f - T_i)$ *Knowing that:* **C:** *the heat capacity of the body in* $j.°K^{-1}$.

- *Determine* **Qr***, the heat of reaction, knowing that:*

$$Q_r = Q_{Hcl} + Q_{NaOH} + Q_{cal}$$
$$Q_r = m_a.c_e. (T_f - T_a) + C (T_f - T_a) + m_b.c_e (T_f - T_b)$$

- $(\Delta_r H)$ *the enthalpy of the neutralization reaction*

knowing that : $\Delta_r H = Q_r / n_{H2O}$

The specific heat of water is **4.180** $J.K^{-1}.kg^{-1}$. *For a dilute solution of an acid and a base, the specific heats can be assumed to be equal to the specific heat of water.*
Note the specific heat of water.
Consequently, ***specific heat of acid = specific heat of base = specific heat of water = ce***

3-2 Verification of the HESS law:

Principle

The enthalpy variations of a system depend only on the initial and final states, if the transformation is effected at constant volume or constant pressure. It does not depend on the path taken from the initial to the final state.

Consider the following transformations:

(1) $NaOH_{(s)} + (H^+ + Cl^-) \longrightarrow (Na^+ + Cl^-) + H_2O$ $(\Delta_r H_1)$

(2) $NaOH_{(s)} \longrightarrow (Na^+ + OH^-)$ $(\Delta_r H_2)$

(3) $(Na^+ + OH^-) + (H^+ + Cl^-) \longrightarrow (Na^+ + Cl^-) + H_2O$ $(\Delta_r H_3)$

Note that reaction (1) is the sum of reactions (2) and (3). By measuring the heats of the different transformations separately using calorimetry, we can verify that :

$$\Delta_r H_1 = \Delta_r H_2 + \Delta_r H_3$$

4- *Experimental part:*

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

a) *Introduce a mass* m_1**=50 g** *of distilled water at* **room temperature** *into the calorimeter. Note the equilibrium temperature* T_1 *(Water + Calorimeter).*

b) *Add* m_2**=50 g** *of warm water at temperature* T_2 *(25°C <* T_2*< 40°C). Note* T_2

c) *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*).*

d) *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 ($J.K^{-1}$).
*c_e : the specific or mass heat of liquid water, equal to **4180** $J.\ K^{-1}.Kg^{-1}$.*
*μ : the water equivalent mass of the calorimeter in **kilograms** (kg).*

2- Determining the enthalpy of the neutralization reaction:

a) *Introduce* V_1**=50 ml** *of hydrochloric acid solution (**HCl**) (**1M**) into the calorimeter. Read the solution temperature* T_a*.*

b) *Pour into a beaker* V_2**=50 mL** *of the accurately measured sodium hydroxide solution (**NaOH**) (**1M**). Read the temperature of this solution (*T_b*). The temperature of the acid solution must not differ from that of the sodium hydroxide solution by more than **0.5°C**.*

c) *Pour all the soda solution into the calorimeter containing the acid. The orifice is immediately closed by the stopper containing the calorimeter. The mixture is stirred. Note the most stable temperature* T_f*.*

d) *Determine* Q_{r3}*, the heat of reaction, knowing that :*

$$Q_{r3} = -Q_{Hcl} - Q_{NaOH} - Q_{cal}$$

$$Q_{r3} = -\ (m_a.c_e.\ (T_f - T_a)) - (C\ (T_f - T_a)) - (m_b.\ c_e\ (T_f - T_b))$$

e) *Determine (*$\Delta_r H_3$*) the Enthalpy of the neutralisation reaction knowing that :*

- $\Delta_r H_3 = Q_{r3}\ /\ nH_2O$

la masse volumique of water $\rho = 1\ kg.l^{-1}$ **or 1g/ml**

3- Verification of HESS's law:

- **Reaction (1)**

a) *Pour* V_a **= 50 mL** *of the* **HCl (1M)** *solution into the calorimeter. Add exactly* **V=50mL** *of distilled water and note the temperature* T_1.

b) *Weigh out* m_b**=2g** *of solid* **NaOH***, place in the calorimeter and cover rapidly.*

c) *Stir and note the maximum temperature* T_2 *attained.*

d) *Determine* Q_{r1}*, the heat quantity of the neutralisation:*

$$Qr_1 = -(m_a.c_e.(T_2-T_1)) - (C(T_2-T_1)) - (m_b.ce.(T_2-T_1))$$

e) *Determine* ($\Delta_r H_1$) *the Enthalpy of neutralization:*

- $\Delta rH_1 = Q_{r1} / n_{H2O}$

- **Reaction (2)**

a) *Pour* V_1**=100 mL** *of* **distilled water** *into the calorimeter and note the temperature* T'_1. *Weigh out* m_2**=2g** *of solid* **NaOH***, place in the calorimeter and cover quickly.*

b) *Agitate and note the maximum temperature* T'_f *attained.*

c) *Determine* Q_{NaOH} (Qr_2) *the heat quantity of the NaOH, knowing that :*

$$Qr_2 = -(m_1.c_e.(T'_f-T'_1)) - (C(T'_f-T'_1))$$

d) *Determine* ($\Delta_r H_2$) *the Enthalpy of neutralization:*

$\Delta rH_2 = Q_{r2} / n_{NaOH}$, $n_{NaOH} = m_2/M$

$M_{NaOH} = 40\ g.mol^{-1}$

- **Reaction (3)**

Reaction (3) was studied in (Enthalpy of the neutralization reaction (ΔrH_3*))*

- ***Verification of HESS's law***

a- *Write the heat balance for reactions (1) and (2) and determine the values of* ΔrH_1, ΔrH_2 *and* ΔrH_3

b- *Check the validity of the relationship between* ΔrH_1, ΔrH_2 *and* ΔrH_3.