MANIPULATION N°01

Thermodynamics
Calorific Capacity & Specific Heat

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1 - Introduction :

Thermodynamics is the science of energy exchange. It is used as much in physics as in chemistry and biology, relying in particular on mathematical tools. It enables us to understand and predict variations in energy between different interacting systems, based on fundamental principles. Thermodynamics has many applications. These include thermal machines (car engines, refrigerators, heat pumps).

2- Objective of the work :

1- Determine the calorific capacity of the calorimeter.
2- Determining the specific heat of a liquid (ethanol).
3- Determining the specific heat of a metal.

3- Theoretical Part : :

3-1 . Thermodynamic System : This is the name given to the part of space we are studying. It is separated from the outside by an imaginary wall, through which exchanges take place between the **system** and the **outside environment**. The system as a whole and the outside environment constitute the **universe**.

3-2 . Description of the system :

a) **State Variables (parameters)** : The state of a system is described by knowledge of a small number of macroscopic quantities called state parameters (Density (ρ), Energy (E), Enthalpy (H), Internal energy (U), Mass (m), Pressure (p), Entropy (S), Temperature (T), Volume (V)).

b) **Intensive and extensive parameters :**

• **An extensive parameter** is proportional to the quantity of matter (Example: Volume, Mass, Nbr mole, Electric charge).
• **An intensive parameter** is defined at each point of a system and is independent of the quantity of matter (Example: Temperature, Pressure).

c) **Phase of a system:** A system whose aspect is the same at all points. There are three phases: liquid (L), gas (G) and solid (S).

d) **Possible transformations between the system and the external environment:**

• Different types of transfer : **Energy transfer** in the form of heat (**Q**) or mechanical work (**W**), expressed in joules (J) and **transfer of matter**.

- **Different types of system:** Depending on the nature of the frontier between the system and the external environment, a distinction is made between different systems:

System	Nature of transformation		Example
	Energy	Matter	
closed system	Yes	No	lamp
isolated system	No	No	thermos
open system	Yes	Yes	living cell

3-3 . Adiabatic transformation :

The word adiabatic comes from the Greek (adiabatos: which cannot be passed through). A transformation is said to be adiabatic if it takes place without any heat transfer between the system and the outside environment ($\delta Q=0$), bearing in mind that according to the first principle of thermodynamics :

$$dU=\delta Q+\delta W……………………………(1)$$

dU : represents the change in internal energy.
δQ : the elementary heat transfer over the transformation.
δW : the elementary work of the forces acting on the system during the transformation.

3-4 . Calorific capacity of a calorimeter (C) :

The study instrument used is a calorimeter. Calorimetric measurements are based on heat exchanges between sub-systems in the calorimeter; we will also take into account heat exchanges between what is contained in the calorimeter and the calorimeter (this is the role of m); but we will neglect parasitic exchanges between the calorimeter and the outside environment.
We therefore consider the assembly {calorimeter + its contents} to be **isolated**.
We reduce the calorimeter and its accessories to a (thermal) equivalent of a certain mass m of water.
The **calorific capacity of the calorimeter (C)** is therefore written as :

$$C = m.c_e$$

With : m : the **water value** of the calorimeter. C : expressed in $J.K^{-1}$; m en kg.
            c_e :   the specific or mass heat of liquid water: $c_e = 4180\ J.kg^{-1}.K^{-1}$.

3-5 . Quantity of Heat :

- Heat is a transfer of energy due to a difference in temperature between two objects. The heat **Q** required to change the temperature of a mass **m** by **ΔT**.
- The specific or mass heat of a object « **c** » ($J.kg^{-1}.K^{-1}$) or (($Cal.\ kg^{-1}.K^{-1}$) is the quantity of heat that must be given to (or taken from) the unit mass of this object for its temperature to change by **1 °C**.

$$Q= m.c.\Delta T = C.\Delta T…………………………(2)\qquad (\Delta T=T_f-T_i)$$

C : calorific capacity of the object (J/K) ou (cal/K).
m : object mass.
c : specific heat.

3-6 . The adiabatic calorimeter:

The calorimeter is like a bottle of "Thermos". The calorimeter is an isolated thermodynamic system that exchanges no energy with the outside environment (neither work nor heat). Its wall is undeformable and adiabatic. So **W=0** and **Q=0**.
However, heat is transferred between the various parts of the calorimeter: components under study, accessories, wall…. As there is no heat exchange with the outside, this implies that the sum of heat exchanged **Qi** within the calorimeter is **zero**: $\sum Qi = 0$.

thermomètre

couvercle en liège

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mélange

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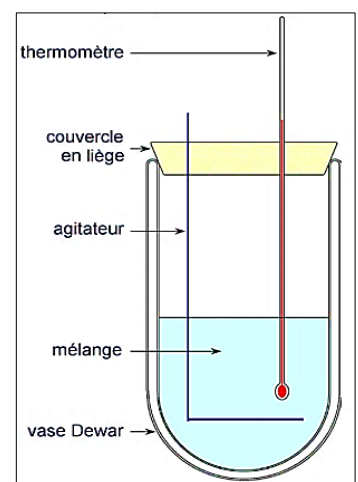
Example of Comprehension :

Determining the equilibrium temperature of a mixture of components introduced at different temperatures.
Consider a calorimetric system consisting of *i* elements defined by their mass **mi**, their calorific capacity **Ci** and their initial temperature before mixing **Ti**. The heat required by each element to reach equilibrium temperature **Te**, if there is no change of state or chemical reaction, is given by the equation :

$$Q = m \cdot c \cdot \Delta T = C \cdot \Delta T$$

Let's apply the relation of calorimetry $\sum Q_i = 0$.

3-7 Heat in water:

Calorimetric measurements are based on heat exchanges between sub-systems in the calorimeter, so we also need to take into account heat exchanges between the contents of the calorimeter and the calorimeter itself.
This is the role of « μ », known as the water value of the calorimeter. In terms of heat exchange, the calorimeter and its accessories are considered to be equivalent to a mass of water « μ »
The calorific capacity of the calorimeter can therefore be written as: $C_{cal} = \mu \times c_e$

$$Q_{cal} = C_{cal} \cdot \Delta T = \mu \cdot c_e \cdot \Delta T.$$

C_{cal} : the calorific capacity of the calorimeter ($J.K^{-1}$).
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).

So, the quantity of heat (calorimeter system + m_{water}):

$$Q = Q_{eau} + Q_{cal} = m \cdot c \cdot \Delta T + \mu \cdot c_e \cdot \Delta T = (m + \mu) \cdot c_e \cdot \Delta T.$$

4- Experimental part:

1- Determining the calorific capacity of the calorimeter (C) :

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.

$$Q_{cal} + Q_1 = \mu \, c_{cal} (T_f - T_1) + m_1 \, c_{eau} (T_f - T_1) = (\mu + m_1) \, c_{eau} (T_f - T_1).$$

- And the isolated system can be written as: **($\Sigma Q_i = 0$)** $\Longrightarrow$ $Q_1 + Q_{cal} + Q_2 = 0$

e. Determination of μ (the water equivalent mass of the calorimeter).

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- Determination of the specific heat of ethanol (c$_{ethanol}$) :

a. Cool the calorimeter, the calorific capacity of which is known, and introduce a volume V_1=50mL of **ethanol**. Wait for thermal equilibrium and note the temperature (T_1), which is the initial temperature of the ethanol.

b. Heat a mass m_2= **50 g** of **distilled water** in a beaker, then measure its temperature (T_2) (Note: 65 °C < T_2 < 70 °C).

c. Pour the hot water into the calorimeter (this step must be carried out quickly to avoid cooling the water).

d. Stir and note the final temperature of the mixture at thermal equilibrium (T_f = T_{eq}).

e. Calculate the heat of mass of the ethanol (c$_{ethanol}$) given that :
- The quantity of heat Q_{EtOH} **received** by the ethanol, Q_{Cal} **received** by the calorimeter.
- The quantity of heat Q_{Water} **ceded** by the hot water.
- Applying the principle of heat conservation in an adiabatic system: (ΣQi =0)

f. Compare the experimental value of the mass heat of ethanol with the theoretical value.

ρ $_{ethanol}$: Volumic mass of **ethanol**:   ρ =0,79 g.cm^{-3}
c$_{ethanol}$: the heat mass of the **ethanol** c = 2438 J/Kg.K.
c$_e$: the mass heat of the **water**:   c$_e$ = 4180 J/kg.K.

3- Determining the heat mass of a metal (c$_{copper}$) :

a. Cool the calorimeter, the calorific capacity of which is known, and introduce a mass m_1=50g of distilled water at **room temperature**. Note the temperature (T_1), this will be the initial temperature of the water and the calorimeter.

b. Weigh a m_2 ≈ **20 g** piece of **copper**, note m_2.

c. Heat the metal by placing it in a **boiling** water bath (≈ **80°C**).

d. After about **2 minutes** in the bath of boiling water, note the temperature of this water (T_2), this will be the initial temperature of the **copper**.

e. Quickly immerse the piece of **copper** in the water in the calorimeter.

f. Shake the calorimeter carefully and record the final temperature (T_f = T_{eq}) of the mixture at thermal equilibrium.

g. the heat mass of the metal (c$_{copper}$) given that :
- The quantity of heat Q_{water} **received** by the water, Q_{Cal} **received** by the calorimeter.
- The quantity of heat Q_{copper} **ceded** by the metal.
- Applying the principle of heat conservation in an adiabatic system: (ΣQi =0)

h. Compare the **experimental** value of the heat mass of the copper with the **theoretical** value.

c$_{cuivre}$: the specific heat or heat mass of **copper** c = 385 J/Kg.K.
c$_e$: the specific heat or heat mass of the **water** c$_e$ = 4180 J/Kg.