CHAPTER II :

Heat, Work and Calorimetry

Introduction :

The aim of thermodynamics is to study the properties of systems and their evolution as a function of exchanges between two forms of energy with the external environment (mechanical work and heat). The latter is linked to the notion of temperature, a macroscopic parameter with which we are all familiar. At our scale, work and heat are two different manifestations of energy. So, when we lift a suitcase, we're doing work, whereas if we heat water in a saucepan, we're giving heat to the fluid in the container.

It wasn't until the 17th^{ème} century that serious research began on this subject. At first, the focus was on temperature, which is more easily understood than heat. The design of the thermometer raised a number of engineering and physical problems: how could the idea of "temperature" be linked to a directly observable, predictable and reproducible phenomenon?

Notion of temperature

Temperature is an intensive, measurable quantity. It characterizes the state of a body (cold - hot), and therefore the degree of molecular agitation of matter. If speed v_i of molecules and therefore their kinetic E_C are increasing, then the degree energy thermal agitation of the medium is greater.

This agitation is linked to kinetic energy according to Maxwell's law of velocity distribution. Indicates that the higher the temperature of the gas, the greater the velocity (kinetic energy):

$$\frac{1}{2} m_i v_i^2 = \frac{1}{2} k_B T \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (II.1)$$

- m: the mass of the molecules.
- T: temperature.
- K: Boltzmann's constant, $k \approx 1.380\ 648\ 52 \times 10^{-23}\ J.K^{-1}$.
- v : particle velocity.

Thermometry

Thermometry is the field of physics concerned with temperature measurement. A thermometer (from the Greek thermós ("hot") and métron ("measure")) is a device for measuring and displaying temperature values.

Example:

Gas thermometer used to determine fixed points. There are many corrections to be made.

Gases used :

He (from -270°C) H_2 (from -250°C to 300°C)

N_2 (for high temperatures)

The zero principle of thermodynamics

Consider two systems A and B separated by a diathermic wall. Set A+B is adiabatically isolated from the outside environment.

If the initial states of the two systems in contact were different, heat would be exchanged between them. After a certain time, there is no longer any heat exchange between the two systems: they are said to be in thermal equilibrium.

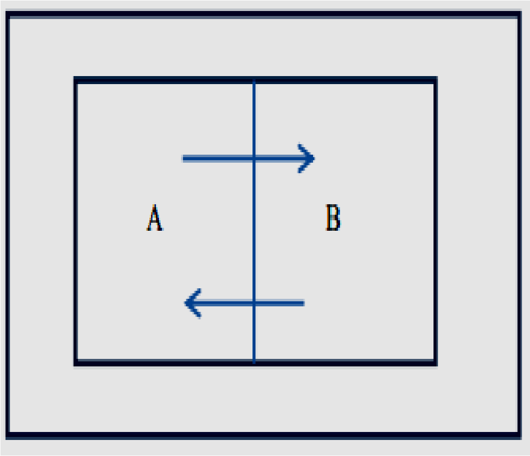


Fig.II.1: Thermodynamics zero principle [7].

This allows us to postulate the existence of an intensive state parameter called temperature. This takes the same value for both systems when thermal equilibrium is reached.

Temperature scales: centesimal, absolute and Fahrenheit

Different scales are used to measure temperature: the Newton scale (established around 1700), Rømer (1701), Fahrenheit (1724), Réaumur (1731), Delisle (1738), centigrade (Celsius) (1742), Rankine (1859), kelvin (1848), Leyden (ca. 1894), Celsius (1948).

Centesimals

In the centesimal scale, since the two phenomena are 100 apart on this scale, 1°C represents one hundredth of the reference range. The scale is therefore centesimal.

θ	**0°C melting ice; 100°C boiling water**
	unit the (°C) , degree Celsius

Absolutes

Absolute temperature expresses the energy intensity of matter. It is zero when matter contains no energy or heat.

T	**273.15 K melting ice; triple point of water 273.16 K**
	unit the kelvin (K)
Relationship between θ and T	**T = θ + 273,15**

Fahrenheit

0 on the Fahrenheit scale is the solidification temperature of an equal mixture of water and ammonium chloride. The scale chosen is a subdivision of the interval into 12 units, themselves subdivided into 8 degrees, giving an amplitude of 96 degrees - the degree Fahrenheit.

t	**32°F melting ice; 212°F boiling water**
	unit the (°F) , degree Fahrenheit
Relationship between θ and T	**T = 32+1.**8∗θ

Example:

The thermometric degree is the hundredth part of the distance between the ice termand boiling water under normal atmospheric pressure.

2 fixed points: 0°C melting ice 100°C boiling water linear relationship

$\theta = ax + b$, we can write: For $\theta = 0$; $x_0 + b = 0$

For $\theta = 100$; $_{ax100} + b = 100$

$a = \frac{100}{\xi 100 - x0}$ $b = \frac{100x0}{x100 - x0}$. We then have: $\frac{x - x0}{x100 - x0}$

There are as many centesimal scales as there are thermometric phenomena.

Mercury thermometer design

The mercury thermometer was invented by Gabriel Fahrenheit in 1724. Its operation relies onmercury contained in a glass tube. The volume of the mercury, i.e. the length of the column in the tube, is a function of its temperature. The temperature can be read from marks along the length of the tube. To increase the thermometer's sensitivity, a bulb wider than the tube is formed at one end and filled with mercury; small changes in the volume of the mercury are then reflected in large displacements of the end of the column. The other end of the tube is filled with nitrogen, at apressure lower than atmospheric.

Thermometer types

These are the most common types of thermometer:

Gas thermometer :

Based on the principle of gas volume change at constant pressure and mass, or pressure change at constant volume and mass, thanks to its sensitivity to temperature variation it is used as a regulator that controls the others.

Dial and pointer thermometer :

Also known as a Bilame, this thermometer consists of a pair of blades with different coefficients of expansion.

Liquid crystal thermometer :

Using the change in color of the liquid crystals as a function of temperature, you can define a temperature range (but not a precise value), and this type of thermometer is often used in aquariums.

Liquid thermometers :

The liquids inside a thermometer are numerous, but the most common are as followsfrequent :

- *Alcohol thermometer:* thanks to its very low melting point, from

From -130°C to 78°C, it is used in the medical field to measure body and air temperature, and a t very lowfreezing temperatures.

- *Mercury thermometer:* often used in wall-mounted thermometers formeasure air temperature.

Electronic thermometer :

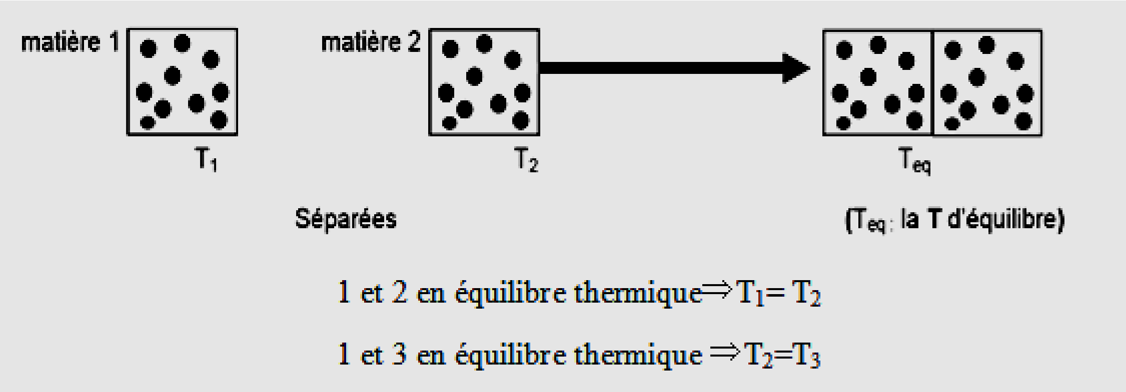
This type of thermometer remains the most accurate and efficient, and can be used in all conditions, measuringbody temperature, air temperature, room temperature, room temperature, etc. liquid...etc., and it's extremely easy to use: a simple click and in a few moments it displays the exact value on itsscreen.

Notion of heat or quantity of heat *Q*

Heat is a form of energy, just like work, which passes through the wall separating the system from theoutside environment. It is therefore a heat transfer (transfer of energy in the form of heat). This transfer isgenerally the result of a temperature difference between the system and the external environment (***Q a*** ΔT). [Q]: cal or joules 1 cal = 4.185 joules

Example:

If two bodies are initially of different temperatures, thermal equilibrium is reached after a certain time (see diagram below).



Two bodies are said to be in thermal equilibrium if they have the same temperature.

General expression for the heat quantity Q

Heat quantity formula :

$$Q = m \times C_p \times \Delta T \quad \text{.........} \quad (II.2)$$

With :

- *Q: in J.*
- *m : in kg.*
- C_p *: in* $J.kg^{-1}.K^{-1}$.

- ΔT: (T_{final} - $T_{initial}$) in K or °C.

We can define two types of heat: sensible heat and latent heat.

Sensitive heat:

(Heat exchanged without changing the state of the system) This is the heat consumed or produced by asystem as its temperature varies. At constant pressure,

$$Q = m \times C_P \times \Delta T = n \times C_P \times \Delta T \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (II.3)$$

Latent heat :

(When a body's physical state changes).

$$Q = m \times L = n \times L \quad (II.4)$$

With : *L:* latent heat by mass in j/kg , *L:* latent heat by mole in *J/mol.*

Heat capacity C (J/K or cal/K)

By definition, the heat capacity is the quantity of heat required to raise the temperature of 1 g of a body by 1 K. It is expressed in joules per kelvin ($J.K^{-1}$). It is *an extensive quantity:* the greater the quantity of material, the greater the heat capacity.

The different types of heat capacity II.3.3.1. Mass heat capacity (J/Kg.K)

Corresponds to a system defined by the mass unit (kg or g) of a compound. (The expression 'mass heat' is sometimes used).

Example:

The heat capacity of water is *4185 J/(kg. K).*

So we need *4185 J* to increase the mass of one kg of water by 1 Kelvin. The mass heat capacity of aluminium C_{Al} *=900 J/ (kg. K)*

Molar heat capacity (J/mol.K)

Corresponds to a system defined as a mole of a compound (the expression `specific heat` is sometimes used).

Example:

Water has a molar specific heat capacity of *75.32 J / mol. K*

Copper has a molar specific heat capacity of *24.78 J / mol. K*

Molar or isobaric mass heat capacity

The ratio of the amount of energy transmitted by heat Qp required to raise the temperature of one mole of pure substance by a small amount (T'-T) to this small amount (T'-T) is known as the isobaric molar heat capacity, where pressure P is constant, i.e. :

$$Cp = \frac{\partial Q}{\partial P}\, en.J.mol / K \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (II.5)$$

A latent heat of compression coefficient h is then introduced:

With $h = -V.T.\alpha$

With Clapeyron formula:

$$\partial Q = Cp.dT + h.dP \quad (II.6)$$

Example:

A lead block with mass $m1=280g$ is removed from an oven at temperature $T1=98°C$. It is immersed in a calorimeter with a heat capacity $C=209\ J/K$ containing a mass $m_2=350\ g$ *of* water. The initial temperature is $T2=16°C$.

ermal equilibrium temperature $Te=17°C$ is measured. Determine the mass heat of lead. Data: $ce=4185\ j/kg/K$; density of water $\mu=1000 kg.m^{-3}$.

Solution:

Hot system S1: {lead block}.θ_1 = 98 °C ; m_1 = 280 g. Final temperature :

$\theta e = 17{,}7°C$. C_{Pb} = ? ; $Q_1 < 0$. Let $Q1$ be the amount of heat released by the lead block:

$Q_1=m_1.c_{Pb}.\ (\theta_e - \theta_1)$.

System 2 cold S2: {calorimeter + cold water}$\theta 2\ = 16\ °C\ ;\ m2water\ = 350\ g$. Final temperature:

$\theta e = 17{,}7°C$. $Q_2 > 0$.

Let $Q2$ be the amount of heat captured by the cold water and the calorimeter:

$Q_2= (m_2.ce + C).(\theta_e - \theta_2)$.

The {water + calorimeter + lead} system is isolated: $Q1+Q2=0$

$m_1.c_{pb}.(\theta_e - \theta_1) + (m_2.c_e + C).(\theta_e - \theta_2) = 0$. we pull c_{pb} :

$$\Rightarrow m_1.c_{pb}.(\theta_e-\theta_1)=-(m_2.c_e+C).(\theta_e-\theta_2)\Rightarrow c_{pb}=\frac{(m_2c_e+C).(\theta_e-\theta_2)}{m_1.(\theta_1-\theta_e)}$$

Molar or isochoric mass heat capacity

The molar heat capacity at constant volume C_{vm} $(V.T)$, is the ratio of the amount of energy transmitted by heat Qv required to raise the temperature of one mole of pure substanceby a small amount ***(T'-T)*** by this small amount ***(T'-T)***, i.e. :

$$C_v m=\frac{\partial Q}{\partial T}..enJ.mol/K...(II.7)$$

It should always be pointed out that when a small change occurs from one state A(V .T) to another nearby state another neighbouring state $A'(V+dV,T+dT)$, there's another very important coefficient, called the latent heat of expansion coefficient :

$$l=T.\left(\frac{\partial P}{\partial T}\right)_V$$

in pascal (worth P.T.B Clapeyron's formula):

The thermal energy exchanged during a transformation is therefore :

$$\partial Q=Cv.dT+l.dV...(II.8)$$

Thermal heat capacity for perfect gases II.3.4.1. monoatomic perfect gases

A monoatomic gas is a gas whose constituents are isolated atoms. Statistical thermodynamics can be used todetermine the molar heat capacities of monoatomic gases.

$$C_P=\frac{5}{2}\times R=20.785\ kJ/kmol...(II.9)$$

$$C_v=\frac{3}{2}\times R=12.471\ kJ/kmol\ ....\ (II.10)$$

diatomic perfect gases

The molar heat capacities of diatomic gases are defined as follows:

$$C_P=\frac{7}{2}\times R=29.1\ kJ/kmol\ ....\ (II\ .11)$$

$$C_v=\frac{5}{2}\times R=20.785\ kJ/kmol$$

Example:

At low pressures, the constant volume heat capacity o f a gas (carbon monoxide) is a function of absolute temperature T :
$c_v = \; A - A\big)_0 \quad T + A_2 \, |T^2\big)$ or $A0= 1.41\ J.K^{-1}\ .g^{-1}$; $A1=492\ J.K^{-1}\ .g^{-1}$ and $A2=16.104\ J.K^{-1}\ .g^{-1}$
for c_v in $J.K^{-1}\ .g^{-1}$.
1. Calculate the heat transfer for one mole of carbon monoxide when the gas is heated from 27°C to 127°C at constant volume.
We give ($MC=12\ g.mol^{-1}$ and $O=16\ g.mol\ ).^{-1}$
Deduce the average mass heat capacity relative to one mole of gas.

Solution :

$$Q_v = \left(M_C + M_0\right)\left[A_0\left(T_f - T_i\right) - A_1 \ln\frac{T_f}{T_i} - A_2\left(\frac{1}{T_f} - \frac{1}{T_i}\right)\right] = 3{,}72.10^3.J$$

$$C_v = \frac{Q_v}{\left(M_C + M_0\right)\left(T_f - T_i\right)} = 1{,}33.J.K^{-1}.g^{-1}$$

Relationship between Cp and CV for a perfect gas, Mayer relationship

In physics, and more specifically in thermodynamics, the Mayer relation, established in the XXIX^{ème} centuryby Julius Robert von Mayer, is a formula linking the heat capacities at constant pressure ***Cp*** and constant volume ***Cv*** of a perfect gas according to: Mayer relation :

With :

$$C_P - C_V = nR \text{ ....} (II.12)$$

- n: the quantity of matter (number of moles).
- R: the universal constant for perfect gases.

$$\gamma = \frac{C_P}{C_v} \text{ ....} (II.13)$$

Example:

The following table gives γ values for a number of gases. Note that, for monoatomic gases, γ = 1.67 and for diatomic gases γ = 1.4 , in accordance with the predictions of classical theory (Boltzmann's law).

Gas	**T (K)**	**C_{pm} (J.K^{-1} .mol)$^{-1}$**	γ
Helium	288	20,9	1,66
Argon	288	20,8	1,66

Dihydrogen	288	28,7	1,41
Air	288	29,1	1,40
Carbon dioxide	288	37,0	1,30
Water vapor	373	36,3	1,32

Cp and CV for a mixture of perfect gases

We consider a mixture of chemically inert gases (a mixture that does not give rise to a chemical reaction).For a mixture of perfect gases, we have Dalton's law:

$$P=\sum P_i \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (II.14)$$

Where ***Pi*** denotes the partial pressure of gas ***i***, i .e. the pressure that thegas ***i*** if it occupied the entire volume on its own.

In molar notation :

$$C_p=\sum x_i C_{pi} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (II.12)$$

$$C_v=\sum x_i C_{vi} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (II.13)$$

Example:

In a mixture w it h air, what will be the partial pressure of oxygen and nitrogen at 40m ?

Solution:

PpO_2 = 5 x 0.2 = 1 bar

PpN_2 = 5 x 0.8 = 4 bar

(Verification 1+4 = 5)

Heat capacity for liquids

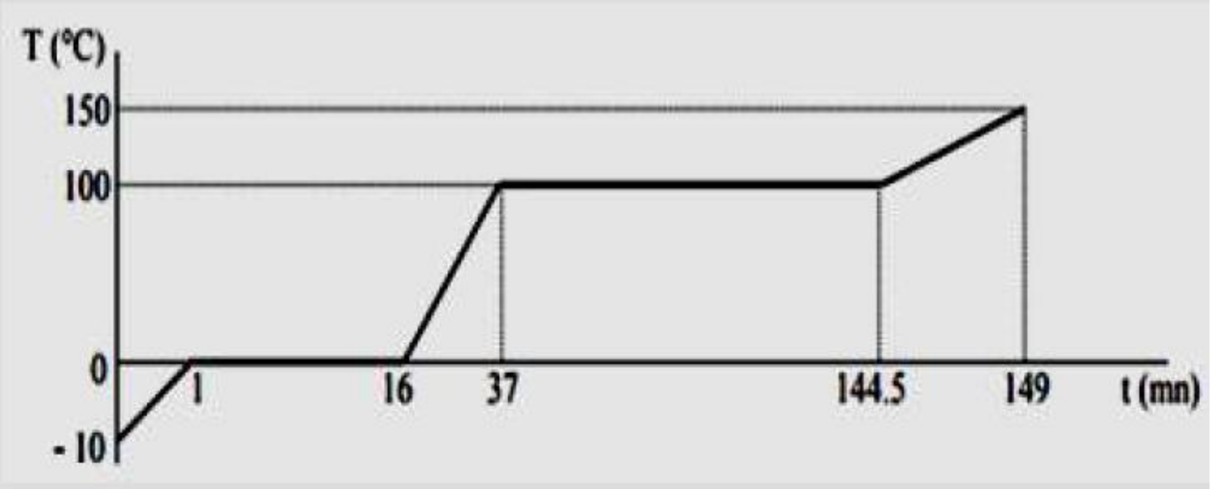
For solids and liquids, no distinction is made between constant-pressure and constant-volume values. In fact we have :

$$C_p=\lim_{\Delta T\to 0}\left(\Delta Q/M.\Delta T\right)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (II.14)$$

The specific heat of water is C_{peau} ***= 4186 Joule/kg K*** (at 0° C and normal pressure conditions).

Example:

Evaluate the heats of mass of each phase for a piece of ice of mass M=500g. Taken at -10°C, receives a heat quantity *p=175 J/ s*, according to the diagram in the figure.



Solution:

The heats of mass of each phase : $p \times \Delta t = MC_p \Delta T \Rightarrow C_p = \dfrac{p \times \Delta t}{M \times \Delta T}$

a) The warm-up phase, $t \in [0,\ 1\ \text{mn}]:\ C_p = 2.1\ kJ/kg.K$

b) The warm-up phase, $t \in [16,\ 37\ \text{mn}]:\ C_p = 4410\ kJ/kg.K$

c) The warm-up phase, $t \in [149,\ 144.5\ \text{mn}]:\ C_p = 1890\ kJ/kg.K$

Thermal heat capacity for solids

To determine ***Cp***, we use an adiabatic calorimeter (glass or stainless steel dewar) containing a mass ***m*** ofwater at temperature ***t***. A mass ***M*** of the body to be studied at temperature ***T*** > t, then immerse the body in the calorimeter and wait for thetemperature to stabilize at T_f.

In the initial state, we have :

$$Q_1 = (m + m_{ca}) \times C_{Peau}.t + M \times C_p.T \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (II.14)$$

In the final state, we have:

$$Q_2 = (m + m_{cal}) \times C_{Peau}.T_f + M \times C_p.T_f \ldots\ldots\ldots\ldots\ldots\ldots\ldots (II.15)$$

If the calorimeter is adiabatic, ***Q1* = *Q2***. From the measurement of Tf, we can deduce ***Cp***.

Example:

A beaker containing 800g of water is heated on a hot plate.
If the water temperature rises from 20°C to 85°C, how much energy has the water absorbed?

Solution:

Data: $Q=x; m=800g; c=4.19J/(g\cdot{}^\circ C)$;$\Delta T=85°C-20°C=65°C$.

Energy calculation: $Q=m\cdot c\cdot \Delta T$

$Q=800g\cdot 4.19\ J/(g\cdot °C)\cdot 65°C\ Q=217880\ J$.

The energy absorbed by the water is 217,880 J.

Calculating the heat quantity for different transformations

Consider a pure substance of mass ***m*** in the solid state at temperature T_1. This body receives a quantity of heat ***Q*** leading it to the gaseous state at temperature T_2. We have recorded the evolution of temperature as a function of time. The result is shown in the graph below:

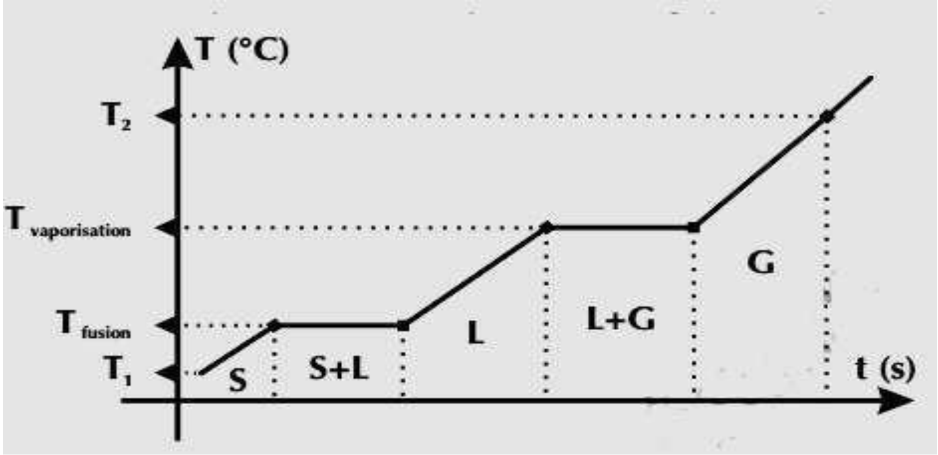


Fig. II.2: Temperature vs. time for different transformations

The amount of heat required by this mass to move from ***T1*** to ***T2*** is :

$$Q = Q_1 + Q_2 + Q_3 + Q_4 + Q_5 \ldots\ldots (II.16)$$

With :

$$Q_1 = \int_{T1}^{T2} m \times C_{P \to solide} dT = m \times C_{P \to solid}(T_f - T_1) \ldots\ldots\ldots\ldots (II.17)$$

$$Q_2 = m \times L_f \ldots\ldots\ldots\ldots (II.18)$$

$$Q_3 = \int_{Tf}^{Tv} m \times C_{p \to liquide} dT = m \times C_{P \to liquide}(T_v - T_f) \ldots\ldots\ldots\ldots (II.19)$$

$$Q_4 = m \times L_v \ldots\ldots\ldots\ldots (II.20)$$

$$Q_5 = \int_{Tv}^{T2} m \times C_{P \to gaz} dT = m \times C_{P \to gaz}(T_2 - T_v) \ldots\ldots\ldots\ldots (II.21)$$

Example:

An explorer puts 500g of ice at -50°C into a pan and places it on a stove. After a while, he realizes that all the water in the pan has evaporated.

Calculate the minimum energy required for this operation.

Solution:

Calculation of minimum vaporization energy: Three calculation steps are required:

a. Heat ingot to melting temperature

Q1 = m. cpb. ΔT = 2.5.129.(327.5 - 24) ≈ 9.79.104 Joules

b. Melt the ingot

Q2 = m . Lf = 2.5. 0.25.105 = 6.25.10 4 Joules

c. Heating liquid lead

Q3 = m.cpb liquid . ΔT = 2.5. 140. (370 - 327.5) ≈ 1.49.104 Joules

Qtot = Q1 + Q2+ Q3 = 1.68.105 = 1.8.105 Joules

He thus obtains the minimum amount of vaporization energy :

ΔEconsumed ≈ Qtot / 0.73 ≈ 2.4.10 5 Joules.

Calorimetry

The calorimeter

A calorimeter is an instrument for measuring the amount of heat exchanged between two bodies A and Bwhich are in contact with each other, where the properties of the two bodies are different.

of body A are known (calorimeter body). A calorimeter contains a calorimeter vessel where the heat to bemeasured appears (calorimeter vessel), and a protective jacket to minimize heat loss to the outside.

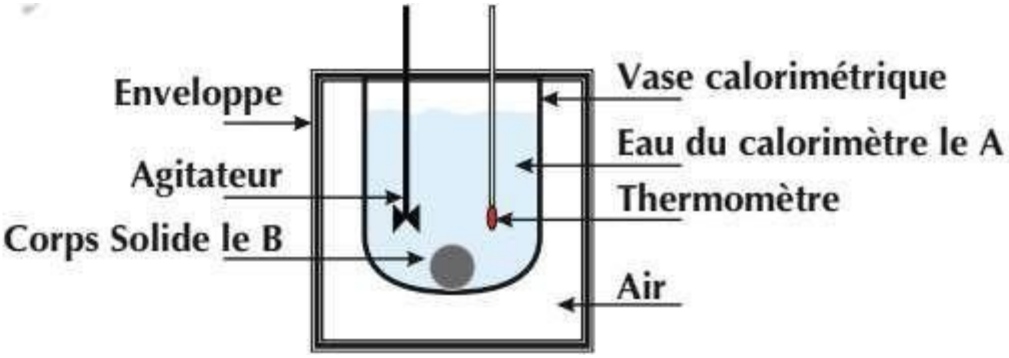


Fig.II.3: *Bertelot calorimeter (water heating)* **[5].**

The different types of calorimeters

Depending on the nature of the compounds and transformations being studied, these devices are mainlyadapted to :

- For transformations involving condensed phases only ***(liquids or solids)***, a constant-pressure calorimeter (in contact with atmospheric pressure) is used. The heats exchanged within the calorimeter between the various subsystems are then equal to the variation in the enthalpy state function

$$\Delta H = Q_P \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (II.22)$$

- For chemical reactions ***involving gases***, a constant-volume calorimeter bomb is used to prevent material (in the form of gas) leaving the calorimeter.
- In this case, the heat exchanged within the bomb is equal to the variation in the internal energy state function

$$\Delta U = Q_v \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (II.23)$$

The value or water mass of the calorimeter μ

This is the body of water that removes the same amount of heat as the calorimeter and its accessories(thermometer, stirrer, etc.) when subjected to the same temperature variation.

$$\mu = \frac{C_{Cal}}{C_{eau}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (II.24)$$

C_{cal}: calorific capacity of the calorimeter and

C_{eau}: mass heat of water) $C_{eau} = 4.18\ J.\ g^{-1}.K^{-1} = 1\ cal.\ g^{-1}.K^{-1}$.

Example:

Consider an adiabatic calorimeter, with a mass of water one to be determined, containing *0.200 kg* of water at *15°C*. To this is added *0.2 kg* of water at *45.9°C*. The final temperature is *30°C*.

Calculate the water mass m of the calorimeter.

The heat of water $c=4185\ J/kg.\ °C$

Solution:

- $M = 0.200\ kg$ of "hot" water ($\theta i = 45.9°C$) is mixed with a "cold" system, at a temperature of: $\theta' i = 15°C$, comprising a mass $M' = 0.200\ kg$ of water and a calorimeter whose "mass in water" is μ. The final temperature is $\theta f = 30°C$.
- Mixing principle: the heat received and given off by the hot and cold systems is equalized.
- Heat released Qc: $Qc = M'\,c\,(\theta i - \theta f)$; c mass heat of water.
- Heat received Qr : $Qr = (M + \mu)\,c\,(\theta f - \theta' i)$
- Equality : $Qc = Qr \Longrightarrow M'c(\theta i - \theta f) = (M+\mu)c(\theta f - \theta' i)$

  or: $\mu = M'(\theta i - \theta f)/(\theta f - \theta' i) - M$
- A.N : $\mu = 0.200(45.9 - 30)/(30 - 15) - 0.200 = 0.012\ kg = 12\ g$

Calculation of equilibrium temperature

The temperature of thermal equilibrium is reached when a body with a higher temperature transfers thermal energy to another body with a lower temperature, according to the zero principle of thermodynamics. This transfer takes place until both bodies are at the same temperature.

Let's assume an evolution in which a **body 1**, with a high temperature, transmits thermal energy to a **body2**, with a low temperature.

$$-C_{P1}\times m_1\left(T_{eq}-T_1\right)=C_{P2}\times m_2\left(T_{eq}-T_2\right)\ldots\ldots\ldots\ldots\ldots\ldots\ldots(II.23)$$

In the absence of any other energy exchange, the energy released by **body 1** is fully recovered by **body 2**, which can be translated as :

$$T_{eq}=\frac{T_1\times C_{P1}\times m_1+T_2\times C_{P2}\times m_2}{C_{P1}\times m_1+C_{P2}\times m_2}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(II.24)$$

Example:

A calorimeter initially contains *1 kg* of water at *T1= 20 °C, 0.5 kg* of water is added at *T2= 60 °C*.

If we neglect the influence of the calorimeter on the heat, calculate T_{eq}?

Given: *cm= 4185 J / kg.K.*

Solution :

$$\sum Q=0\Rightarrow Q_1+Q_2=0$$

$$Q_1=m_1C_m\left(T_{eq}-T_1\right)$$
$$Q_2=m_2C_m\left(T_{eq}-T_2\right)$$

$$\Rightarrow m_1C_m(T_{eq}-T_1)+m_2C_m\left(T_{eq}-T_2\right)=0\Rightarrow T_{eq}=\frac{m_1T_1+m_2T_2}{m_1+m_2}$$

$$\begin{cases} m_1=1kg\ ;\ T_1=20°C \\ m_2=0.5kg\ ;\ T_2=60°C \end{cases}$$

A.N :

$$T_{eq}=\frac{1\times(20+273)+0.5\times(60+273)}{1+0.5}=306K=43.33°C$$

Calculation of heat of combustion at constant pressure

For reactions other than combustions (i.e., endothermic reactions)or less exothermic) we have :

$$Q_{réaction}=-(Q_{eau}+Q_{calorimètre})\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(II.25)$$

where ***Qcalorimeter*** has been determined in advance - because we are at constant pressure

$$Q_{réaction}=\Delta H\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(II.26)$$

Example:

Calculate the heat exchanged at $P=Cste$ when reacting 4 moles $H2$ and 2 moles of $O2$ gas to give $H2O\ (l)$, using either of the two ways of writing the reaction

$$2H_{(g)} + _{O2(g)} \rightarrow 2H\,2O_{(l)} \qquad \Delta_r H1 = \quad 570{,}4\ kJ/mol$$

$$H_{2(g)} + 12|_{O2} \rightarrow H\,2O_{(l)} \qquad \Delta_r H2 = \quad 285{,}2\ kJ/mol$$

Corrected:

First, we calculate the advance rates of the two reactions:

Réaction 1 : $\xi_{\max 1} = 2\ \ mol$

Réaction 1 : $\xi_{\max 2} = 4\ \ mol$

The amount of heat released is :

Reaction 1 : $Q_P = \xi_1.\Delta_r H_1 = (2).(-570{,}4) = -1140{,}8\ \ kJ$

Reaction 1 : $Q_P = \xi_2.\Delta_r H_2 = (4).(-285{,}2) = --1140{,}8\ \ kJ$

Calculation of heat of combustion at constant volume

The heat of combustion is measured in a constant-volume calorimeter bomb - the bomb is insulated, sothere is no heat transfer to the outside world:

$$Q_{système} = 0 \ldots\ldots\ldots\ldots (II.27)$$

$$Q_{eau} + Q_{bombe} + Q_{réaction} = 0 \ldots\ldots\ldots\ldots (II.28)$$

$$Q_{réaction} = -(Q_{eau} + Q_{bombe}) \ldots\ldots\ldots\ldots (II.29)$$

Exemple :

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \quad ; \qquad Q_P = -285{,}941\ \ kJ \quad (P = Cste \quad ,T = 25°C)$$

$Q_v = ?.$ **So** $Q_v = Q_P - \Delta nRT$ With $n_{H_2O_{(l)}} = 0$.

$$Q_v = -285{,}941 - (0-1-1/2).8{,}31 \times 298 \Rightarrow Q_v = -2822{,}56\ \ J$$

$$\frac{|Q_P| - |Q_v|}{|Q_P|} = \frac{285{,}941 - 2822{,}86}{285{,}941} = 1{,}3\%$$

In all that follows we will consider $Q_v = Q_P$ and instead of heat of reaction, the enthalpy of reaction.

Latent heat of physical state change

Latent heat changes the physical state of a material. As opposed to sensible heat, which changes thetemperature of a material. Whatever the material, we speak of :

- heat of liquefaction: heat required to transform a solid into a liquid.
- heat of vaporization: heat required to transform a liquid into a gas.

Example:

Vaporization-condensation

At atmospheric pressure at sea level, at 100°C, the latent heat of vaporization-condensation is commonly taken to be equal to : $L_v = 2250\ kJ/kg$.

Solidification-melting

At atmospheric pressure at sea level, at 0°C, the latent heat of solidification-condensation is commonly taken to be equal to : $L_f = 334\ kJ/kg$.

The work

For mechanical systems, work is defined as the action of an external force on an object over a distance. It is equal to the product of the force (F) times the displacement (d).

In thermodynamics, it's important to distinguish between the work done by the system on its external environment and the work done on the system by the external environment. In other words, there is work received by the system, as in the case of turning a turbine to produce electricity in a generator. And there is work supplied by the system, as in an internal combustion engine. A positive value for work indicates that work is received by the system, while a negative value indicates that work is supplied by the system to the external environment.

A cylinder containing a gas at pressure P pressure P; the piston has a cross-section S. See (Figure II.4.).

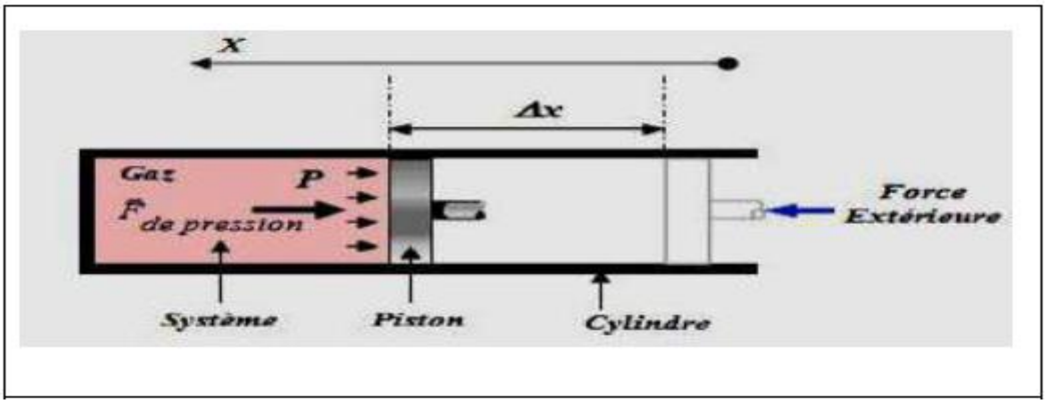


Fig. II.4: The work of a pressure force[11].

When an external operator exerts force on the piston, it moves to the left.

$$F = P.S \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (II.30)$$

The gas then exerts a pressing force F.
The elementary work resulting from this pressure force during displacement (*dx*) is then :

$$dW = \vec{F} \times \vec{dx} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (II.31)$$

<u>General expression of the work of pressure forces</u>

The pressure force *F* exerted by the gas is parallel to the displacement *dx* and it is in the opposite direction to this displacement, so the work done by the force is negative.
(resistive work). The force *F* is decomposed into its two plane components and is therefore written as :

$$dW = \vec{F} \times \vec{dx} = F.dx.\cos(180°) = -F.dx = -P.S.dx \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (II.32)$$

With :
$dV = S.dx$ change in volume as the piston moves. This gives :

$$dW = -P.dV \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (II.33)$$

Remarks :

1°/ In the case of compression: $dV \langle 0$; the volume decreases and $dV \rangle 0$; *the* receives work from the outside world.

2°/ In the case of expansion: $dV \rangle 0$; the volume increases and $dW \langle 0$ the gas supplies of work to the outside environment.

Example:

One (01) m^3 of air, assimilated to a perfect gas at a pressure $P_1 = 10\ bar$, undergoes expansion at constant temperature. The final pressure is $P2=1\ bar$.

1°/ Determine the work involved in expanding the air.

2°/ Determine the amount of heat exchanged by the air during its evolution.

Solution:

Since the transformation of the air under consideration is isothermal: at constant n and T, we write :

P1V1 = nRT1

P2V2 = nRT2

With $T1=T2$ (isothermal expansion), therefore : P1V1 = P2V2

Hence :

$$V_2 = \frac{P_1V_1}{P_2} = \frac{10\times10^5\times1}{1\times10^5} = 10m^3$$

1- Work from air relaxation:

$$W_{1\to2} = -\int_1^2 PdV = -nRT\int_1^2 \frac{dV}{V} = -nRT\int_1^2 d(\ln V) = -nRT\ln\left(\frac{V_2}{V_1}\right)$$

With: $nRT = P_1V_1 = P_2V_2$ et $P_1=10^6\ Pa\ ;\ V_1=1m^3$

Hence: $W_{1\to2} = -10^6\ln 10 = -2{,}3.10^6\ J$

1- The amount of heat exchanged by the air :

$$Q_{1\to2} = \int_1^2 m.c.dT = m.c\int_1^2 dT = m.c(T_2 - T_1) = 0\,.$$

Knowing that: $T2=T1$ (isothermal transfer)