People's Democratic Republic of Algeria
Ministry of Higher Education and Scientific Research

MUSTAPHA STAMBOULI UNIVERSITY, MASCARA
FACULTY OF SCIENCE AND TECHNOLOGY

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Chemicals II (THERMODYNAMICS) Course and corrected application exercises

Presented by:

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For students: 1st year Common Base Licences (L1) (ST)

Algeria
2024

Educational content

First year

Semester 2

Fundamental Teaching Unit 2

Thermodynamics

Thermodynamics programme (2 courses + 1 TD) / week:

Chapter 1: Fundamental concepts of thermodynamics (3 weeks)

1- Fundamental properties of state functions.

2- Definitions of thermodynamic systems and the external environment.

3- Thermodynamic system description.

4- Evolution and thermodynamic equilibrium states of a system.

5- Possible transfers between the system and the external environment.

6- Transformations in the state of a system (operation, evolution).

7- Reminder of the laws of perfect gases.

Chapter 2: The 1st principle of thermodynamics (3 weeks)

1. Work, heat, internal energy, conservation of energy.
2. The 1st principle of thermodynamics: statement, concept of the internal energy of a system, application to the perfect gas, the enthalpy function, heat capacity, reversible transformations (isochore, isobaric, isothermal, adiabatic).

Chapter 3: Applications of the first principle of thermodynamics to thermochemistry (3 weeks)

Heat of reaction, standard state, standard enthalpy of formation, enthalpy of dissociation, enthalpy of change of physical state, enthalpy of a chemical reaction, Hess's law, Kirchhoff's law.

Chapter 4: The 2nd principle of thermodynamics (3 weeks)

1- 2nd principle for a closed system.

2. Statement of the 2nd principle: Entropy of a closed isolated system.

3. Calculating the change in entropy: reversible isothermal transformation, reversible isochoric transformation, reversible isobaric transformation, adiabatic transformation, during a change of state, during a chemical reaction.

Chapter 5: The 3rd Principle and absolute entropy (3 weeks)

Chapter 6: Free energy and enthalpy - Criteria for the evolution of a system

(3 weeks)

1 -Introduction .

2 -Energy and free enthalpy .

3- Chemical equilibrium

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Foreword

In line with the LMD (Licence-Master-Doctorat) programmes defined by ministerial decree of the Ministry of Higher Education and Scientific Research, this booklet is aimed at first-year university undergraduate students in the field of Material Sciences (SM) and Sciences and Techniques (ST). It is designed to smooth out the difficulties inherent in scientific discourse while maintaining the necessary rigour.

This book presents all the fundamental concepts in thermodynamics. Corrected application exercises are provided at the end of each chapter, enabling students to test their knowledge**.**

This handout is divided into four chapters

- The first chapter provides a general introduction to thermodynamics, including a mathematical review, some definitions of heat and work, and a statement of the zero principle.
- The second chapter describes the different forms of energy, their transfer and the first principle of thermodynamics.
- Le troisième chapitre est consacré à la thermochimie et montre les applications du premier principe en thermochimie.
- The fourth and final chapter illustrates the fundamentals of the second principle of thermodynamics, the concepts and the different expressions of entropy.

The course presented in this handout is the result of several years of teaching given to students in the first year of the Licence Sciences et Techniques (ST) at the Mustapha Stambouli University in Mascara. It is a "thermodynamics 2" course.

CHAPTER I :

Fundamental concepts of thermodynamics

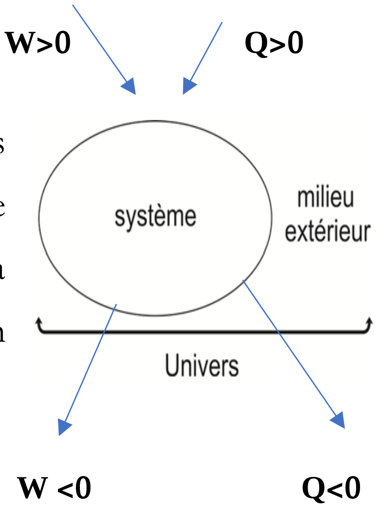
CHAPTER I: Fundamental concepts of thermodynamics

I.1 Introduction

Thermodynamics is the science which studies the exchange of energy between a system and the external environment. A number of terms need to be defined in order to complete the concepts taught in secondary school about the heat of combustion, dissolution or change of state. Thermodynamics is used in many fields: chemistry, chemical engineering, biology, etc. It can be approached from two angles: macroscopic and microscopic. Classical (or microscopic) thermodynamics, which is the subject of this course, involves only macroscopic quantities that can be measured experimentally, such as temperature, pressure, volume, composition, etc.

I.2 Basic definitions

I-2.1. A system: This is an object or a set of objects under study, which belong to a domain of space and are transformed either by a physical phenomenon or by a chemical reaction. Everything that surrounds the system is called the external environment.



I-2.1.1. Convention

Energies exchanged with the external environment are given a positive sign when they are received by the system, and a negative sign when they are not. The system and the external environment together constitute the universe.

I-2.2 External environment

This is the rest of the universe (universe = system + external environment).

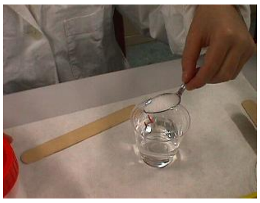
I.3 System classification

There are two types of system classification:

I.3.1. From the point of view of the matter contained in the system

There are two types of system;

- **Homogeneous system** containing a single phase (gas, miscible liquids, solid)



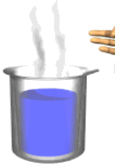
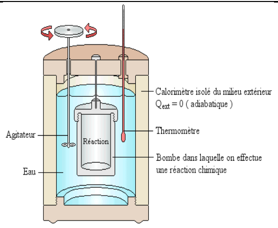
- **Heterogeneous system** containing several phases (immiscible liquids, several Solids)

I.3.2. From the point of view of exchanges between the system and the external environment

Depending on the nature of the boundary between the system and the external environment, a distinction is made between different systems:

- **Open system:** it exchanges matter and energy with the outside world; example: a living cell.

- **Closed system:** no exchange of matter with the outside world; example: closed reactor.
- **Isolated system:** no exchange with the outside world (neither of energy in the form of work or heat, nor of matter). The universe is an example of an isolated system.
- **Adiabatic system:** no heat transfer with the outside; example: system in a dewar.

Système	Echange de matière	Echange d'énergie	Exemple
Ouvert	Oui	Oui	
Fermé	Non	Oui	
Isolé	Non	Non	
Adiabatique	Non	Non	 Calorimètre

I.4 State of a system and state quantities

The thermodynamic state of a system is represented by macroscopic quantities relating to the microscopic state of the matter making up the system. All macroscopic quantities, whether directly measurable or not, that can be used to describe the state of a system are called state quantities. For example: volume (V), pressure (P), temperature (T), mass (m), etc.

I.4.1. State of a system:

The state of a system is defined at a given moment; it is conceivable that this state could be fixed by an instantaneous photograph. It is described macroscopically using physical quantities such as: T, P, n quantities of matter, V, etc. All these quantities are state variables. Some of them are not independent of each other but can be linked by one or more equations of state.

Example: the equation of state for perfect gases: $PV = n\,RT$ where

R: Cst of perfect gases = 8.314 JK-1mol-1.

P: Pressure inside the system in Pascal (Pa).

V: Volume of the system in m.

T: Temperature of the system in Kelvin (K).

n: Number of moles of gas in the system in (moles).

In this equation, known as the equation of state for perfect gases, each state variable (pressure, volume or temperature) depends on the other two variables

Hence : $p = f\,(V.$

$T) \quad ou\ V = f\,(P.T) \quad ou\ T = f\,(P.V)$

Application:

Given that one mole of gas occupies a volume of 22.4 l under standard conditions (T = 0°C and P = 1atm), calculate the value of the perfect gas constant R:

1 (When the pressure is measured in (atm) and the volume in (L)

2 (When the pressure is measured in (cm Hg) and the volume in (L).

3 (When the pressure is measured in (atm) and the volume in (cm^3).

4 (When the pressure is measured in (dyne/ cm 2) and the volume in (cm^3).

5) In the international system.

Solution :

1) Pressure is measured in (atm) and volume in (L):

PV=nRT. (n=1) ⇒ R=PV/T= 1×22.4/273=0.082L.atm/K.mole.

2) The pressure is measured in (cm Hg) and the volume in (L):

1 atm = 760 mm Hg =76 cm Hg. ⇒ R =PV/T=22×10^3 /273=82 atm.cm^3 /K. mole

3) The pressure is measured in (atm) and the volume in (cm^3):

R=PV/T=$10^3\times22.4$ /273=82atm.cm^3 /K. mole

4) The pressure is measured in (dyne/ cm2) and the volume in (cm^3):

1atm=760mmHg =$1.013*10^6$ dyne/cm^2 ⇒ R = $1.013\times10^6 \times22.4\times10^3$ /273

R = 8.314×10^7 dyne.cm/K.mole

5) In international system: 1dyne.cm= erg; R = $8,314*10^7$ erg/K.mole

1 Joule = 10^7 erg ; *1 cal = 4,18 J donc ;* R =*8.14/ 4.18=1.92 ≈ 2K/mole. K*

I.4.2. State quantities:

These are state variables, such as temperature (T), pressure (p), quantity of matter (n(B)), volume (V) and mass (m). Some of these variables are not independent of each .other, but can be represented by one or more equations of state

pV = nRT equation for a perfect gas

P (Pa), V (m^3), T (K), n (mol), R = 8.31441±0.00026 $JK^{-1}mol^{-1}$ constant of the perfect gas. Each system is characterised by exactly defined properties, which can be divided into two groups: intensive and extensive properties

.

Physical quantities

Extensive quantities:

Proportional to the quantity of the material. Defined for the system as a whole.

If a system is divided into i subsystems, the extensive magnitude is the sum of the magnitudes of its subsystems: $X = \sum x_i$

m, V, n, U (internal energy),
F (Helmholtz energy),
H (Enthalpy), G (Gibbs energy),
S (entropy)
$m = \sum mi$; $V = \sum vi$; $n = \sum ni$

m, V, n, U (internal energy),
F (Helmholtz energy),
H (enthalpie), G (Gibbs energy), S
(entropy)
$m = \sum mi$; $V = \sum vi$; $n = \sum ni$

Intensive quantities:

Not dependent on quantity of matter : ≠ f(n). Defined at every point of a system

T, p, p_i, x_i (molar fraction), ρ, μ (chemical potential)

Molar quantities :

$$M = \frac{m}{\sum n_i}$$ *Molar mass*

$$V = \frac{V}{\sum n_i}$$ *Molar volume*

Application exercise : Intensive and extensive quantities.

One mole of a gas occupying a volume V_m at pressure *P* and temperature *T*.

1)- It is assumed that these quantities are linked by the equation:

$$\left(P+\frac{a}{V_m^2}\right)(V_m-b)=RT$$

where a, b and R are constants. Use the properties of intensivity or extensivity of quantities to establish the corresponding equation relating to n moles.

2) The same question applies to equation:

$$\left(P+\frac{a}{V_m^2}\right)exp\left(\frac{a}{RTV_m}\right)=RT$$

Corrected:

1)- as $V_m=\frac{V}{n}$: on a

$$\left(P+\frac{a}{V_m^2}\right)(V_m-b)=RT \leftrightarrow \left(P+\frac{an^2}{V^2}\right)\left(\frac{V}{n}-b\right)=RT \leftrightarrow \left(P+\frac{an^2}{V^2}\right)(V-nb)=RT$$

N.B.: the equation of state can be written as

$$\left(P+\frac{a}{V_m^2}\right)(V_m-b)=nRT$$

Posing: $B=nb$ et $A=an^2$

B is an extensive quantity since it is additive, if $n=n_1\ +\ n_2$

$$B=nb=n_1\,n+\ n_2\,b=B_1\ +\ B_2$$

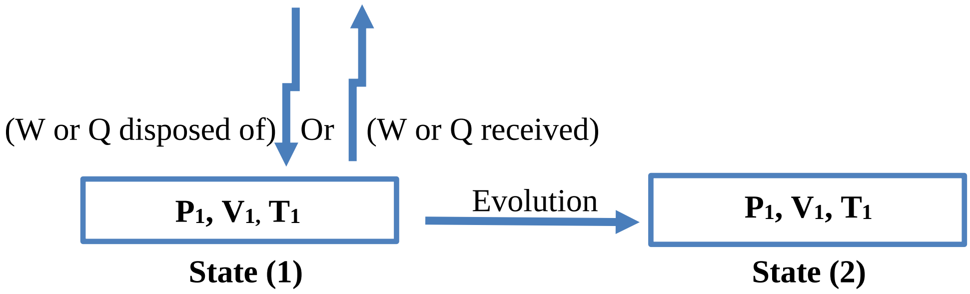
A is also an extensive quantity, but it is not additive because if

$$an^2\ \ n_1^2a+n_2^2a$$

2: $(P)(V-nb)\ exp\left(\frac{na}{RTV}\right)=nRT$

I.5. Transformation of the system by exchange of energy (Q or W) with the external environment

Under the influence of exchanges or transfers of energy between the system and the external environment, the system evolves and the variables of state of the system are modified. The system is said to transform or change state by moving from an initial state of equilibrium (1) to another final state of equilibrium (2). Any finite transformation can be obtained by summing an infinite number of infinitesimal transformations (integration):



- **Isochoric transformations:** V= constant, ΔV=0; transformation with constant volume throughout the path followed.
- **Isobaric transformations:** P= constant, ΔP=0; transformation at constant pressure throughout the path followed. - Isothermal transformations: T= constant, ΔT=0; transformations during which the temperature remains constant.
- **Adiabatic transformations:** Q=0, transformations during which there is no exchange of heat with the external environment.

I.5.1. Open transformations

An open transformation is a transformation where the final state of the system is different from the Initial state (Figure 1).

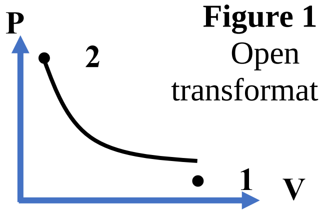


Figure 1: Open transformation

I.5.2. Closed transformations

A closed transformation is one where the final state of the system is identical to (Figure 2). the initial state

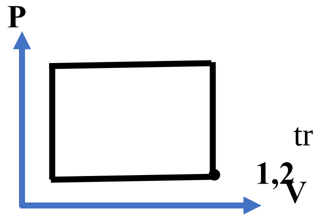
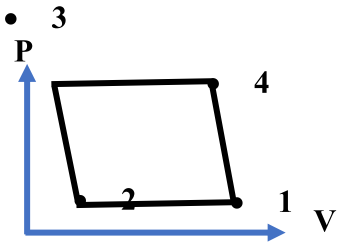


Figure 2: Closed transformation.

I.5.3. Notion of thermodynamic cycle

A thermodynamic cycle is a sequence of open transformation. Either the system undergoes, a series of transformations, which returns it to its initial state (Figure 3).



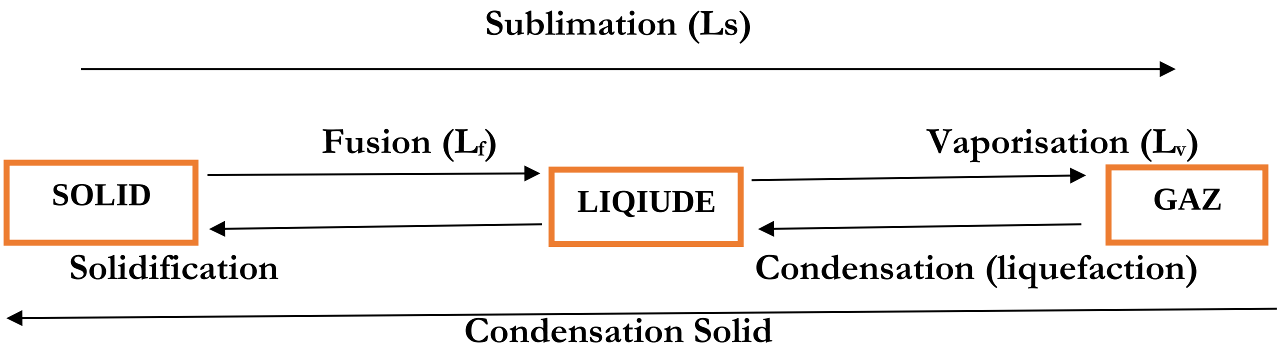
I.5.4. Reversible or (ideal) transformations: these are infinitely slow transformations of a succession of equilibrium states.

I.5.5. Irreversible (real) transformations: these are rapid and brutal transformations outside equilibrium.

I.5.6. Reversible transformation: A system is made to undergo a transformation between the initial state and a final state, and the reverse transformation can be carried out by reversing the direction of the variations in stresses.

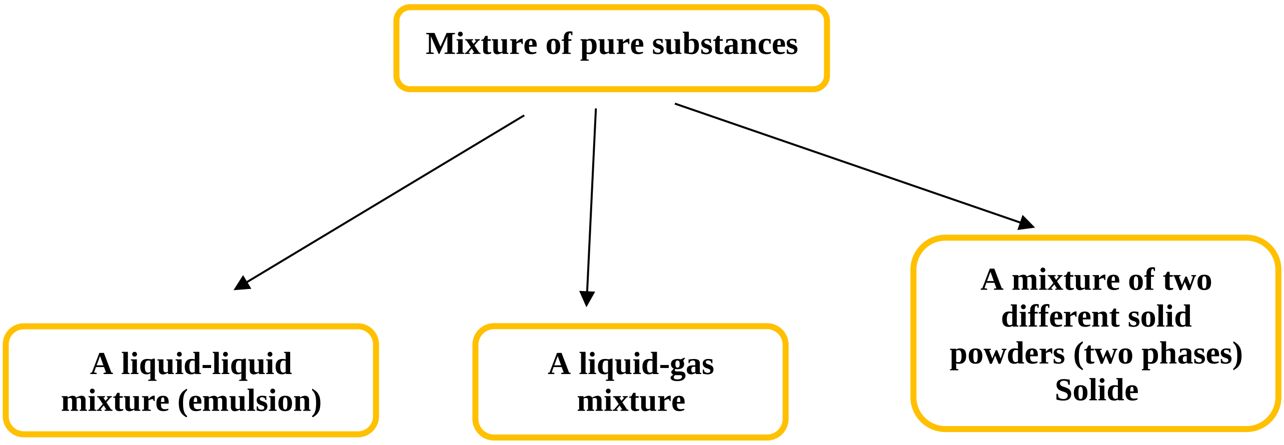
I.6. State of matter

Depending on temperature and pressure conditions, all substances can be in one of three states: solid, liquid or gas. The transition from one state to another constitutes a change of physical state or phase change.



<u>Different types of transformation of physical states of matter</u>

At equilibrium, a pure body can only be in a given phase.



A "map" of the phases, i.e. the phase in which the system is for given conditions (pressure, temperature, composition).

I.7. Energy exchange in a thermomechanical system between the system and the external environment

- **Different types of transfer:** When a system undergoes thermomechanical transformations, energy can be transferred in the form of heat (Q), mechanical work (W) or electrical work (W'). Q, W and W' are exchange quantities. They are expressed in joules (J). Matter can also be transferred.
- **Convention**

Quantities (energy, matter) received by the system are counted

positively

Quantities released to the outside environment are counted as negative.

Figure I-2 shows the conventional direction of the energy received or given off by a given system.

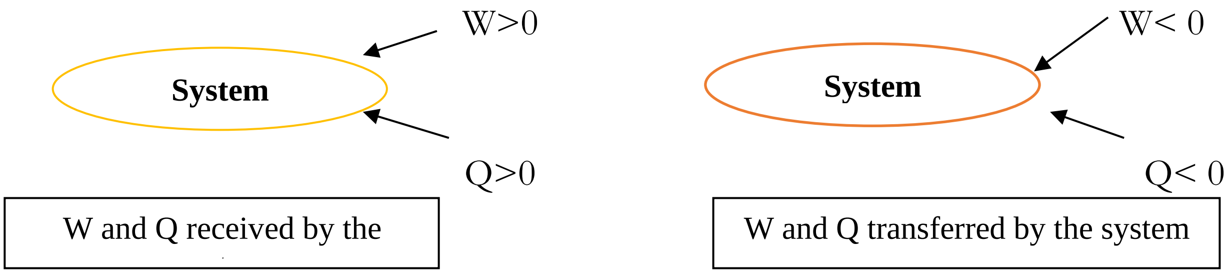


Figure I-2: Conventional directions of energy exchanged with a system.

I.8. Definition of a chemical reaction:

A chemical reaction is a chemical transformation in which a certain number of initial constituents called reactants give rise to products in the final state. Interatomic bonds are broken in the reactants, while new bonds are formed in the products. If a transformation takes place without any exchange of heat with the outside environment, it is adiabatic (for example if the system is a perfectly insulated calorimeter). If the transformation takes place at

- T = constant, so it is isothermal.
- V = constant, so it is isochoric.
- P = constant, so it is isobaric.

A succession of transformations at the end of which the final state is identical to the initial state is a cycle.

B. Equation - bilan.

General rating: $\sum \nu_i A_i \rightarrow \sum \nu_k A_k$

Reactive **products**

A balance equation expresses the qualitative and quantitative conservation of chemical elements.

The numbers ν_i and ν_k are the stoichiometric coefficients. If the proportions of the reactants correspond to the coefficients ν_i, the reaction is said to be in stoichiometric proportions.

It is advisable to specify the physical state of the species involved: solid (s), liquid (l), gas (g), aqueous solution (aq).

C. Rate of progress of the reaction.

This is calculated in relation to the limiting reagent. By definition, the rate of reaction, τ, is equal to the ratio of the quantity of the limiting reagent reacted to its initial quantity.

$$\tau = n(\xi)/n(0)$$

$\tau = 0$ at the start of the reaction

$\tau = 1$ at the end of a total reaction

$\tau < 1$ at the end of a limited reaction

τ

I.9. Energy aspect of chemical reactions

During a chemical reaction, heat can be released or absorbed, electrical energy created, etc. Thermodynamics studies this energy aspect of reactions. This science enables us to predict the evolution of chemical systems, and is based on three fundamental principles. A principle cannot be demonstrated, but experience shows that its consequences are always verified. Energy can neither be created nor destroyed. Energy can only be transformed from one kind into another. Work and heat are the most common forms of energy.

I.9.1. Heat exchanged by a system

Heat expresses the variation in the kinetic energy of molecules. A heat transfer between the system and the external environment is characterised either by:

- A heat input results in heating (a rise in temperature) or a change in physical state: fusion, vaporisation, sublimation.
- Heat subtraction results in cooling (lowering of temperature) or a change in physical state: solidification, liquefaction, condensation, etc.

I.9.1.1. Variation in temperature

Heat is a special form of energy:

- It is an energy expressed in [J] or [k cal].
- It is exchanged on a microscopic scale in a disordered form by molecular agitation (i.e. by shock between moving molecules). Elle s'écoule toujours d'une source chaude vers une source froide.
- Heat is not a state function, i.e. it depends on the path followed.

There are two distinct types of heat: **Sensible** heat and **latent** heat

A. Sensible Heat

For a small transformation δQ quantity of heat received by the system, whether heating or cooling. It is proportional to the quantity of matter (mass or number of moles) and the temperature difference (ΔT).

- For infinitesimal transformation:

$$\delta Q = C.\, dT$$

Where:

$$\boxed{dQ = n.c.dT \quad \text{ou} \quad dQ = m.c.dT} \qquad \textbf{(I.1)}$$

Q: quantity of heat received by the system - elementary heat.

C: heat capacity, JK^{-1}.

m: The mass of the matter in the system.

n: Number of moles in the system.

c: The mass or molar heat capacity of the material expressed in [J. Kg -1. K-1] or [J. mol -1. K-1] respectively. It can be expressed at constant pressure (Cp) or constant volume (Cv).

dT: the temperature rise.

Example 1: Mass heat capacity (J/Kg.K)

The mass 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)

Example 2: Molar heat capacity (J/mol. K)

Water has a specific molar heat capacity of 75.32 J / mol. K Copper has a specific molar heat capacity of 24.78 J / mol. K

Sign of Q

$\delta Q < 0$ the system releases heat; the reaction is exothermic (e.g. NaOH in water).

$\delta Q > 0$ the system gains heat; the reaction is endothermic (e.g. 3 KNO in water).

$\delta Q = 0$ no exchange with the outside; the reaction is athermic (esterification equilibrium).

I.9.1.2. Change of state of matter

B. Latent heat

In this case, the latent heat of change of state is defined as the amount of heat required for a quantity of matter to change its physical state at a constant temperature. It is proportional to the quantity of matter (mass or number of moles) and the value of the latent heat associated with this change of physical state.

$$\boxed{\boldsymbol{Q = nL \ \ ou \ \ Q = mL}}$$

(I .2)

Where L is the heat of change of state in J.mol-1 and n is the number of moles transformed.

For each type of substance, there are three types of latent heat associated with the six physical changes of state **(Ls, Lv and Lf)**. Where Ls, Lv or Lf: is the mass or molar heat associated with sublimation, vaporisation or fusion respectively.

Exercise 1:

A block of lead of mass m_1=280g is removed from an oven at temperature T_1=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 T_2=16°C. The thermal equilibrium temperature Te=17°C is measured. Determine the mass heat of the lead.

Data: c_e=4185 j/kg/K; density of water μ=1000kg.m^{-3}.

Solution:

The hot system S_1: {lead block}. $\theta_1 = 98$ °C; $m_1 = 280$ final temperature: $\theta_e = 17{,}7$°C. c_{Pb} =? $Q_1 < 0$.

Let Q_1 be the amount of heat given up by the lead block: $Q_1 = m_1.cPb. (\theta_e - \theta_1)$.

System 2 cold S_2: {calorimeter + cold water} $\theta_2 = 16$ °C; m_2 water = 350 g. Final temperature: Qe = 17.7°C. Q2 > 0.

Let Q2 be the quantity of heat captured by the cold water and the calorimeter: $Q_2 = (m_2.c_e + C). (\theta_e - \theta_2)$.

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

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

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

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

Exercise 2:

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

Solution :

Données : Q=x ; m=800g ; c=4,19J/(g·∘C) ; ΔT=85°C−20°C=65°C.

Calcul de l'énergie : Q=mC·ΔT Q=800g·4,19 J/(g·°C) ·65°C Q=217880 J. L'énergie absorbée par l'eau est de 217 880 J.

Solution: Data: Q=x; m=800g; c=4.19J/(g·∘C); ΔT=85°C-20°C=65°C.

Calculation of the energy: Q= mC ·ΔT

Q=800g·4,19 J/(g·°C) ·65°C

Q=217880 J. The energy absorbed by the water is 217,880 J.

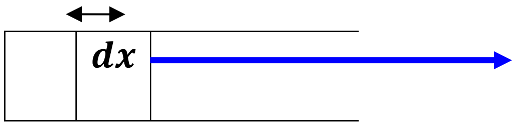
I.9.2 Energy exchange in a thermomechanical system (The mechanical work of external pressure)

A system that undergoes thermomechanical transformations exchanges heat and mechanical energy (work of pressure forces) with the external environment, while work is another form of energy (mechanical energy):

.· It is energy expressed in [J] or [cal]

· On a microscopic scale, it is energy that is exchanged in an orderly fashion (thanks to the movement of a piston, for example, which imparts a certain direction to the atoms).

· It is not a state function



Work resulting from a piston displacement

The pressure exerted by a force (F) on the surface (S) of the piston is defined by:

$$\boldsymbol{P = F/S}$$

So the work done on this piston is the force (F) per displacement (dx):

$$\boxed{\boldsymbol{W = Fdx = PSdx = PdV}} \qquad \textbf{(I .3)}$$

Hence the elementary work is defined by the relation:

$\boxed{\delta W = -\boldsymbol{P}_{\mathbf{ext}} dv}$ in Joule, if P_{ext} is in Pa et dv en m^3, δW is called the elementary work

Note :

- The (-) sign is imposed by the energy sign convention.
- If the piston moves to the right ($dV > 0$) and the work is transferred or supplied by the system to the external environment, then the work ($dV < 0$) is negative. If the piston moves to the left ($dV < 0$) and the work is received by the system from the external medium, then the work > 0 (positive).

- - For a finite transformation between the initial state (1) and the final state ;(2) the variation in work is

$$\boxed{W_{12} = -\int_1^2 PdV} \qquad \textbf{(I .4)}$$

Calculation examples

We calculate the work received by a system between an initial state ($\boldsymbol{P_i}$, $\boldsymbol{V_i}$) and a final state ($\boldsymbol{P_f}$, $\boldsymbol{V_f}$) $\boldsymbol{P_{syst} = P_{ext} = Cst}$.

We talk about an isobaric transformation if at each instant, $\boldsymbol{P = P_{ext} = Cst}$

We speak of a monobaric transformation if final pressure = initial pressure = external pressure. If a transformation takes place at constant external pressure, the work is expressed by:

$$\boxed{\boldsymbol{W = -P_{ext}\,(V_f - V_i)}} \qquad \textbf{(I .5)}$$

General case of any transformation: $\boldsymbol{W = -\int_1^2 PdV}$ The result depends on the variation in pressure.

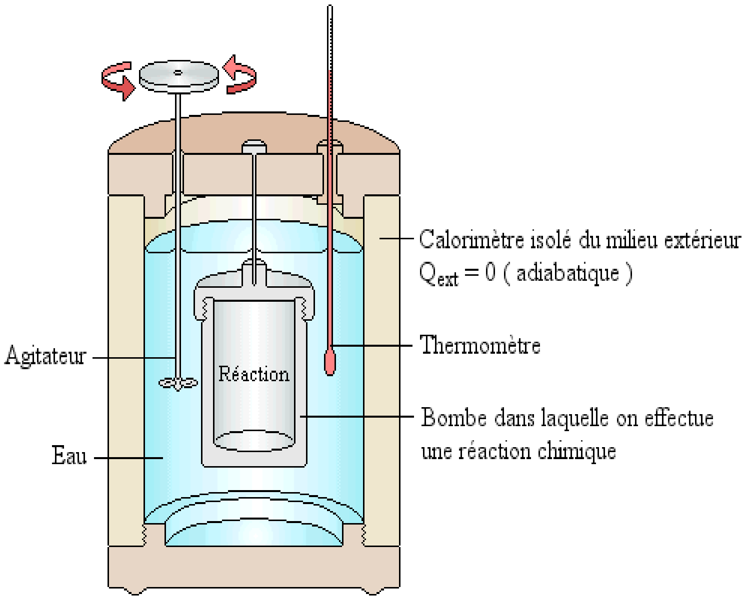
$\boldsymbol{\delta W}$ - Elementary work, Joule

$\boldsymbol{dV}$ - Change in system volume, m3

$\boldsymbol{P}$ - External pressure, Pa

I.10.Calorimetry: Measurement of heat quantity

I.10.1. Device



I.10.2. Principle of calorimetry

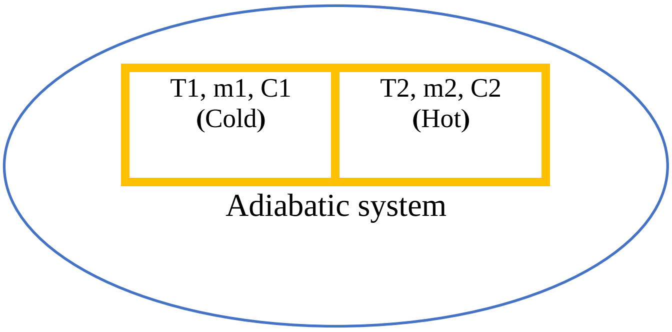
Bring the system to be studied (body, reaction) into contact with the water in the calorimeter. On met un réactif dans le calorimètre ; on attend l'équilibre thermique ; on note T_1

- The second reagent is brought to temperature T2, thermal equilibrium is reached and T3 is recorded.

may be heat absorbed or given off, depending on whether the system under study releases or absorbs heat. We will always have: $Q_{Cédée} = -Q_{Absorbée} \Rightarrow Q_{Cédée} + Q_{Absorbée} = 0$

Adiabatic conditions: $\sum$quantities of heat exchanged = 0. The heat capacity of the calorimeter, or its equivalent mass in water, can be calculated from this.

Example 1: If the system is adiabatically isolated from the external environment, we have:



A system isolated adiabatically from the external environment: $\Sigma Q = 0$

$$\Rightarrow Q_1+Q_2=0$$

$$\Rightarrow m_1C_1\int_{T1}^{Tf} dT + m_2C_2\int_{T2}^{Tf} dT = 0$$

$$\Rightarrow m_1C_1(Tf - T1) + m_2C_2(Tf - T2)$$

$$Tf = Teq = \frac{m1C1T1 + m2C2T2}{m1C1 + m2C2}$$

$$\boxed{Tf = Teq = \frac{m1C1T1 + m2C2T2}{m1C1 + m2C2}} \qquad \textbf{(I .6)}$$

Example 2:

Consider an adiabatic calorimeter, with a mass of water to be determined, containing 0.200 kg of water at a temperature of 15°C. Add 0.2 kg of water at 45.9°C. The final temperature is 30°C. Calculate the mass of water m in the calorimeter. Give the mass heat

of water c=4185 J/kg. °C

Solution:

- M = 0.200 kg of "hot" water ($Q_i =$ 45,9°C) is mixed with a "cold" system, at a temperature of: Q_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 Q_f = 30°C.
- The principle of mixing is to equalise the heat received and given off by the hot and cold systems.
- Heat transferred Q_c : Q_c = M'c (Q_i- Q_f); c mass heat of water.
- Heat received Q_r : Q_r = (M + μ) c (Q_f- Q_i)
- Equality: Q_c =Q_r ===>M'c (Q_i- Q_f) = (M+μ) c (Q_f- Q_i)
- or: μ = M' (Q_i- Q_f)/ (Q_f- Q_i) – M
- A.N : μ = 0,200(45,9 - 30) / (30 - 15) - 0,200 = 0,012 kg = 12 g

I.10.3 Objectives

Enthalpies of reaction can sometimes be measured directly by calorimetry, by carrying out the reaction in a device that is thermally isolated from the outside world, called a calorimeter. The calorimeter is also used to determine the heat capacity of a substance.

I.10.4. Definition of heat capacity

The heat capacity is the quantity of heat required to raise the temperature of a substance by one (01) degree.

Application: Mix 20 g of water at 20°C and 40 g of water at 60°C. Calculate the equilibrium temperature if the mixture is considered to be an adiabatic system.

$$Tf = Teq = \frac{m1C1T1 + m2C2T2}{m1C1 + m2C2}$$

C1=C2

$$Tf = Teq = \frac{m1T1 + m2T2}{m1 + m2}$$

$$\boxed{Tf = Teq = \frac{20 \times 20 + 40 \times 40}{20 + 40}}$$

I.11. Graphical representations of system changes

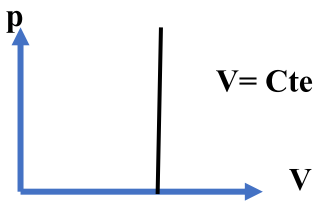
Variations in the state of a system following a transformation are represented in various diagrams, enabling the evolution of the system to be followed. The following diagrams are used: Clapeyron diagram (P, V).

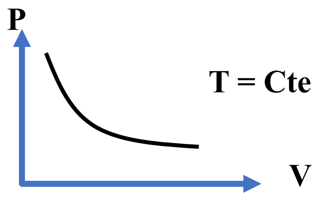
The figures below show the most commonly used Clapeyron diagram. There are different types of transformations or changes following an exchange of energy between the system and the external environment. These changes are easily represented in these diagrams by vertical or horizontal lines:

- Isochore transformation **(V = constant)**
- Isobaric transformation **(P = constant)**
- Isothermal transformation **(T = constant)**
- An isentropic (adiabatic) transformation **(S = constant)** or **(Q = constant)**

1) V = Cte, isochore process

$W_{12} = 0$



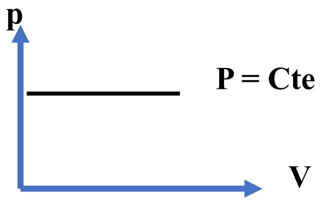


2)P = Cte, isobaric process

$W_{12} = -\int_1^2 PdV = P(V_1 - V_2)$

3)T = Cte : isothermal process

$W_{12} = -\int_1^2 PdV$



$P \neq$ constante ; gaz parfait

$PV = \frac{nRT}{V} \Rightarrow W_{12} = -nRT \int_1^2 \frac{dV}{V}$

$$W_{12} = -nRT \ln \frac{V_2}{V_1}$$

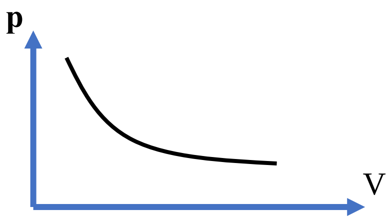
On a: $P_1V_1 = nRT_1$; $P_2V_2 = nRT_2$

$\frac{P_1}{P_2} = \frac{V_2}{V_1} \Rightarrow W_{12} = -nRT \ln \frac{V_2}{V_1}$

4) dQ = 0 : adiabatic process

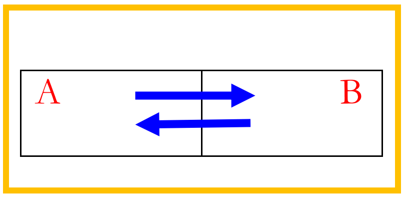
$$\Delta U = Cv(T_1 - T_2)$$

$$Q = 0$$



I.12. Zero principle (thermal equilibrium)

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 brought into contact were different, heat would be exchanged between them. After a certain time, no heat exchange is observed between the two systems: they are said to be in thermal equilibrium. 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. The zero principle can therefore be stated as follows :

« Two systems in thermal equilibrium with a third are in equilibrium with each other ».

I.13.Perfect gas model

The perfect gas is a theoretical model based on the following assumptions:

- There is no interaction between molecules (distant molecules).
- The molecules are treated as point masses.
- Shocks between molecules or against the walls of the container are perfectly elastic.

The behaviour of a perfect gas is described by the relationship: PV=nRT;

P: pressure of the gas

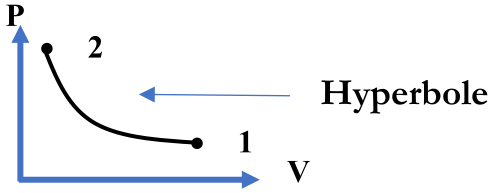
V: volume occupied by the gas; n: number of moles of gas; T: temperature in Kelvin

R: constant=0.082 l.atm.mol^{-1}K^{-1}=8.314 J.mol^{-1}K^{-1}=1.987 cal.mol$_{-1}$K^{-1}.

I.13.1. Boyle Mariote's law

In 1662, Robert Boyle and Edme Mariotte showed that the product of the pressure P of a gas and its volume V depends only on temperature. It was stated as follows;

At constant temperature (T=constant) pressure (P) and volume (V) are inversely proportional: $P = A(const)\frac{1}{V}$

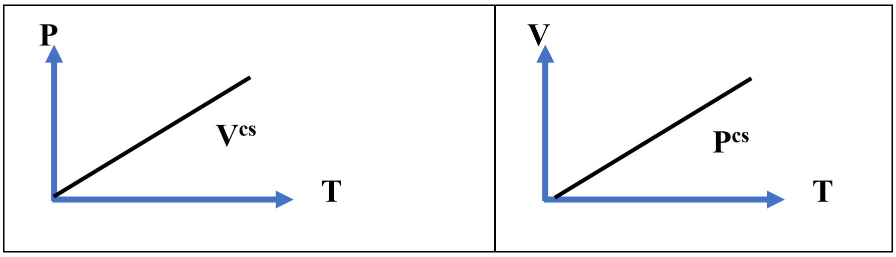


For one mass of a gas and for different pressures (P1 and P2) and volumes (V1 and V2) and at constant temperature, we have:

$$\boxed{P_1V_1 = P_2V_2 = K_1} \quad \textbf{(I.7)}$$

I.13.2. Gay-Lussac and Charles law

In 1800, Louis Joseph Gay-Lussac and Charle proved that; At constant volume (V=constant), the pressure of a gas is proportional to temperature and at constant pressure (P=constant) the volume of a gas is proportional to temperature.



For a mass of a gas at different temperatures $(T_1 et T_2)$ and volumes $(V_1 et\ V_2)$,

we have:

$$\boxed{\frac{V_1}{T_1} = \frac{V_2}{T_2} = K_2\ at\ P\ and\ n} \qquad \textbf{(I.8)}$$

A consequence of the Gay-Lussac-Charles law is that for a given mass of gas at constant volume, the pressure P of the gas is directly proportional to its absolute temperature T we have :

$$\boxed{\frac{P_1}{T_1} = \frac{P_2}{T_2} = K_3\ \ with\ V\ and\ n\ constant} \qquad \textbf{(I.9)}$$

I.13.2. Dalton's law; partial pressures: Pi = x_i .P_T

In a mixture of gases, partial pressure of the gas is the pressure at which is

$$P_{tot} + P_{gaz1} + P_{gaz2} + P_{gaz3} + \ldots\ldots\ldots \Rightarrow \sum P_T = P_I \qquad \textbf{(I.10)}$$

Submits each gas separately.

Dalton's law using the mole fraction of gas: x_i

$$x_i = \frac{n_i}{P_{Tot}} \Rightarrow P_i = P_T \,.\, x_i \qquad \textbf{(I.11)}$$

$$x_i = \frac{P_i}{P_T}$$

With:

$$\sum x_i = 1 \qquad \textbf{(I.12)}$$

Example:

A mixture of three gases: O_2 ; N_2 ; CO_2 :

What is the partial pressure of O_2 à P=1atm and T=273,15 K? If (N_2) =0,1 mole, (CO_2) =0,4 mole, n_T=2mole.

Calculate P(O_2) = ?

Solution:

$P_{(O2)} = x_{(O2)}$. P

We have: $n_T = n_{(n2)} + n_{(O2)} + n_{(CO2)} \rightarrow n_{(O2)} = n_T - n_{(n2)} - n_{(CO2)})$

$n_{(O2)} = 2 - (0.1 + 0.4) = 1.5$ mole

$x_{(O2)} = \frac{n_{(O2)}}{n} = 1.5 / 2 = 0.75$

$P_{(O2)} = x_{(O2)}$. P ==0.75atm

Corrected exercises

Exercise 01:

A gas obeys the perfect gas equation. From a state of equilibrium, the pressure of the gas increases by 1% and the temperature by 2%. Determine the relative change in volume?

Answers:

The gas equation is $PV = nRT$. Taking the differential of this expression, we obtain:

Dividing each member by the product PV gives:

$$\frac{VPdV + VdP}{PV} = \frac{nR}{PV}\,dT \leftrightarrow \frac{dV}{V} + \frac{dP}{P} = \frac{dT}{T}$$

Hence: $\frac{dV}{V} + \frac{dP}{P} = \frac{dT}{T} = 2\% - 1\% = 1\%$

Exercise 02 :

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 P_2=1 bar. Determine the work resulting from the expansion of the air.

Answers:

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

$P_1 V_1 = n_1 RT$

$P_2 V_2 = n_2 RT$

With, $T_1 = T_2$ (isothermal expansion), therefore: $P_1 V_1 = P_2 V_2$

Hence: $V_2 = \frac{P_1 V_1}{P_2} = \frac{10*10^5}{10^5} = 10m^3$

1-Work resulting from air expansion:

$\Rightarrow W_{12} = -P \int_1^2 dV = -nRT \int_1^2 d(ln V) = -nRTln\frac{V_2}{V_1}$

With: $nRT = P_2 V_2 = P_1 V_1$: and P_1 =106 Pa; V_1 =1m^3

Hence: $W_{12} = -10^6$ln 10 =-2.3.10^6 j

CHAPTER 2 :

First Principle of Thermodynamics

CHAPTER 2: First Principle of Thermodynamics

II.1 The 1st principle of thermodynamics

The first principle of thermodynamics, also known as the principle of conservation of energy, states that:

- The energy of the system is conserved during transformations of the system (i.e. does not degrade).
- The system's energy is only transformed from one form of energy to another (equivalence of energy forms).
- The change in the internal energy of a system during a transformation is equal to the algebraic sum of the energies exchanged. ΔU =W + Q.
- The internal energy of the system therefore varies during the transformation between state (1) and state (2): $\Delta U = (U_2 - U_1)$
- The energy of an isolated system remains constant $\Delta U = (0)$

If the change is elementary (infinitesimal): $dU = (\delta w + \delta Q)$

dU **:** is an exact total differential, whereas δw and δQ generally are not (in which case δ is used instead of d)

II.1.1. Statement of the 1st principle of thermodynamics

«The variation in the internal energy of a closed system during a transformation is equal to the algebraic sum of the work W and the quantity of heat exchanged Q with the external environment».

- The variation ΔU of this function to go from state A to state B depends only on the initial and final states of the system and not on the path travelled (Figure 1).
- The first principle of thermodynamics expresses the conservation of the system's energy.
- In other words, the internal energy is a state function, and its variation does not depend on the path followed by the transformation.

II.1.2. Mathematical expression of the 1st Principle

$\Delta U = (U_2 - U_1) = W + Q$ U : is a state function, whereas W and Q are not, in general. The first principle states that the sum [W(work) + Q(heat)] depends only on the initial and final states. W and Q are transfer functions between states 1 and 2. Let: W12 and Q12.

The first principle expresses the conservation of energy during a transformation. Thus, the sum (W+Q) is constant whatever the nature of the transformation:

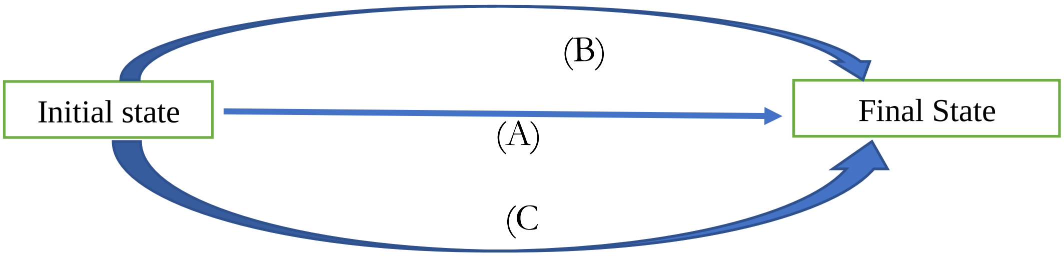


Figure 1: Typical path taken during a transformation.

On a: $W_A + Q_A$ = $W_B + Q_B$ = $W_C + Q_C$ = Cst = $U_2 - U_1 = \Delta U$

Sign convention:

If ΔU > 0: the system receives energy, and if ΔU <0 the system gives up energy. The same applies to W and Q. Cas particuliers:

- **Isolated system:** the system does not exchange work or heat with the external environment, hence: Q =0 and W =0, so $\Delta U = W + Q = 0$. The internal energy of an isolated system is constant (conservation principle) and W and Q are two quantities of the same nature, in other words they have the same unit : the joule or the calorie.
- **Cyclic transformation:** the system undergoes a series of transformations which return it to its initial state: $U_2 = U_1$ So; $\Delta U = U_1 - U_1 = 0$

  $\Rightarrow \Delta U = W + Q \; et \; W = -Q$ (equivalence principle)

II.2 Application of the first principle to chemical reactions

II.2.1 Constant volume reaction

A reaction takes place at constant volume if:

- It is carried out in a closed enclosure (closed reactor);
- The volume of the products is the same as that of the reactants (reactions between solids and/or liquids).

If, moreover, the transformation is reversible, we have at all times: $P_{ext} = P_{int} = P$ (P_{int} : internal pressure, i.e. that of the gas), so $\delta w = -PdV$

In the case of an isochoric transformation (dV=0):

$$\boxed{\delta w = -PdV = 0 \text{ et } dU = \delta Q} \qquad \textbf{(II. 1)}$$

As a result, the variation in the system's internal energy: $\Delta U = U_1 - U_1 = Q$; in this case Q is a state function, depending only on the initial and final states.

Sign convention :

- **Q<0:** exothermic reaction (the system releases heat) .
- **Q>0:** endothermic reaction (the system absorbs heat) .
- **Q=0:** athermic reaction (no absorption or release of heat).

Note: In this case, the heat exchanged is constant volume heat (Q_V), equal to the variation in the internal energy of the system: $\Delta U = Q_V$.

II.2.2. Reaction at constant pressure "Enthalpy of reaction

A reaction takes place at constant pressure if

- It takes place under constant external pressure (e.g. atmospheric pressure in free air). In this case, the heat exchanged is heat at constant pressure Q_P .

For an isobaric transformation from state 1 to state 2, the total work:

$$W_{12} = -\int_1^2 PdV = P(V_2 - V_1)$$

$$\Delta U = U_2 - U_1 = W + Q = -P(V_2 - V_1) + Q_P$$

$$Q_P = \Delta U + P(V_2 - V_1) = U_2 - U_1 + P(V_2 - V_1) = U_2 - U_1 + PV_2 - PV_1$$

$$\Rightarrow \quad Q_P = (U_2 + PV_2) - (U_1 + PV_1) \ \dots\dots\dots\dots\dots \ (1)$$

In this case Qp depends only on the initial state and the final state. Q_p is equal to the sum of a state function. $H = U + PV$; called Enthalpy either:

$$\boxed{(1) \quad \Rightarrow \quad \boldsymbol{Q_p = (H_2 - H_1) = \Delta H} \text{ (with } \Delta\text{H enthalpy of reaction)}} \qquad \textbf{(II2)}$$

- Energy expressed in [Joules] or [calories].
- It is also a state function, like internal energy.

Sign convention:

• Q < 0: exothermic reaction (system gives off heat);

• Q > 0: endothermic reaction (system absorbs heat);

• Q = 0: athermal reaction (no absorption or release of heat).

II.2.3. Relationship between Q_V et Q_p

Let us consider a chemical reaction between perfect gases, assumed to be total, carried out at temperature T and symbolized by:

$$(aA + bB)\text{Reactants} \rightarrow (cC + dD) \text{ Products}$$

Where (a, b, c, d) are the stoichiometric coefficients $(A, B, C\ D)$ are the gas compositions

Initial state: a Number of mole of **A** **Final state**: c Number of mole of **C**

b Number of mole of ***B*** d Number of mole of **D**

- **Reaction at constant volume:** $\Delta U = Q_v = mC_v\Delta T$
- **Reaction Under constant pressure :** $\Delta U = -P(V_2 - V_1) + Q_p \; ou\ bien \quad \Rightarrow$

  $\boldsymbol{Q_p = \Delta H}$

According to Joule's law, the internal energy of a perfect gas depends only on temperature, so:

$$\boxed{\boldsymbol{Q_v = -P\Delta V + Q_P}} \qquad \textbf{(II3)}$$

and for a perfect gas $PV = nRT$ d'out $P\Delta V = RT\Delta n$

$$\Delta n = \sum(a + b) - \sum(c + d)$$

$$\boxed{\Rightarrow \; Q_v \; = -RT\Delta n + Q_P} \qquad \textbf{(II. 3)}$$

$$\boxed{\Rightarrow \Delta H = \Delta U + RT\Delta n} \qquad \textbf{(II. 4)}$$

R: constant of perfect gases equal to 8.34 $J.mol^{-1}. K^{-1}$=1.987 $Cal.mol^{-1}. K^{-1}$=0.082l. atm. $mol^{-1.} K^{-1}$.

Note: If both solid and liquid components are involved in the reaction

$$\boxed{\Delta n = \Delta V_{gaz}}$$

Example:

Combustion of methane gives off 2000 Kj at constant volume at 25°C. Deduct the enthalpy of reaction .

We have: $CH_{4\,gaz} + 2O_{2\,gaz} \quad \rightarrow \quad CO_{2\,gaz} + 2H_2O_{\,liquid}$

$$\boxed{= -RT\Delta n + Q_P \Rightarrow \; Q_P = RT\Delta n + Q_v = \Delta \mathbf{H} Q_v}$$

$$Q_v = -2000Kj \; ; \; \Delta n = 1 - 3 = -2$$

$$\boxed{Q_P = \; -2 \times 106 \; + \; (-2) \; \times \; 8.314 \times 298 = -1995044{,}856 \text{ joule}}$$

Sign convention :

- If the reaction produces heat, it is **exothermic:** $Q_v < 0$
- If the reaction absorbs heat, it is **endothermic**: $Q_v > 0$

II.2.4. Relationship between Cp and Cv (MAYER relationship):

Knowing that: $H = U + PV \Rightarrow dH = dU + d(PV)$ et $\mathrm{PV} = \mathrm{nRT}$

So, we have: $dH = dU + nRTdT$

Hence: $nc_P dT = nc_V dT + nRdT$ Therefore : We have the MAYER relation:

C_P et C_V : molar heat) $\boxed{c_P - c_V = nR}$ **(II. 5)**

We define the ratio as: $\boxed{\frac{c_P}{c_V} = \gamma}$ known as the desormes coefficient

Note :

Consider n moles (or m grams) of a substance. Depending on the units of heat capacity, we can define:

- C_P : Total calorific capacity (J.K^{-1});
- c_P : Molar calorific capacity (J.mol^{-1}. K^{-1});
- $\grave{c}_P$: Mass calorific capacity (J.g^{-1}. K^{-1});

They are linked by the following relationship: $C_P = nc_P = m\grave{c}_P$, same for Cv.

Example:

The following table gives the values of γ 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).

Gaz	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 vapour	373	36,3	1,32

Remarque

Cp and C_V 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:

$P = \sum P_i$

Where Pi is the partial pressure of gas i, i.e. the pressure that gas i would have if it occupied the entire volume on its own. In molar notation:

$c_P = \sum x_i . c_{Pti}$

$c_v = \sum x_i . c_{vi}$

Example:

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

Solution :

p_{PO2} = 5 x 0,2 = 1 bars

p_{pN2} = 5 x 0,8 = 4 bars

(Vérification 1+4 = 5)

II.3. Application of the 1st principle to perfect gases

II.3.1. Application to basic transformations

According to Joule's law for a perfect gas, $U = f(T)$, so if T = constant ⇒ U =constant; hence: $\Delta U = 0$. First principle: $W + Q = \Delta U = 0 \Rightarrow Q = -W$.

II.3.1.1. Isochore transformation

For an isochoric transformation: $\delta w = 0$, where: $dU = \delta Q_v$, Q_v : heat (calorific) at constant volume. Now we have $\delta Q_v = nC_V dT$, C_V : molar heat of the gas. ⇒ $dU = nC_V dT$, d'où :

$\Delta U = nC_V dT = nC_V\ (T_2 - T_1)$

Since ΔU does not depend on the nature of the transformation, The previous expression ($\Delta U = nC_V\ (T_2 - T_1)$ is then valid for any type of perfect gas transformation.

II.3.1.2. Isobaric transformation

In this case: P=constant ⇒ $W = -P(V_2 - V_1)$), where ($\Delta U - P(V_2 - V_1) + Q_P$

⇒ $Q_P = (U_2 - U_1) + P(V_2 - V_1) \Rightarrow Q_P = (U_2 + PV_2) - (U_1 + PV_1)$.

Q_P is written as the difference of a state function (U + PV). This function is called the Enthalpy H.

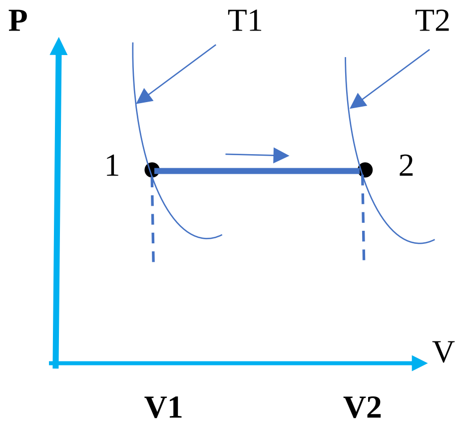
II.4. Isobaric, isochoric, isothermal and adiabatic transformations Representation in a CLAPEYRON diagram (P, V) and calculation of W, Q, ΔU and ΔH.

II.4.1 Isobaric transformation (P = cste)

If a gas is assumed to be perfect and enclosed in a deformable volume enclosure, it undergoes a transformation at constant pressure

Initial state $(T_1, V_1, P_1) \rightarrow P_1V_1 = \mathrm{nR}T_1$ **Final state** $(T_2, V_2, P_2 \rightarrow P_2V_2 = \mathrm{nR}T_2$

Since: P = cst; so dP = 0 et $P_1 = P_2$, we have: $\frac{V1}{V2} = \frac{T1}{T2}$



Isobaric transformation

- **Calculating the work (W) :**

$$W_{12} = -\int_1^2 PdV = -P\int_1^2 dV = -P\,(V_2 - V_1)$$

$$W_{12} = -P(V_2 - V_1) = -(PV_2 - PV_1) = -(nRT_2 - nRT_1)$$

$$\boxed{W_{12} = -nR(T_2 - T_1)} \qquad \textbf{(II. 6)}$$

- **Calculating heat quantity (Q) :**

$$Q_{12} = \Delta\mathrm{H} = Q_P = nc_P(T_2 - T_1)$$

- **Calculating internal energy and enthalpy:**

$$\Delta\mathrm{U} = U_2 - U_1 = W_{12} + Q_{12}$$

$$\boxed{= Q_V = nc_V(T2 - T1) \qquad et \qquad \Delta H = Q_P = nc_P(T_2 - T_1)\Delta U}$$

(II. 6)

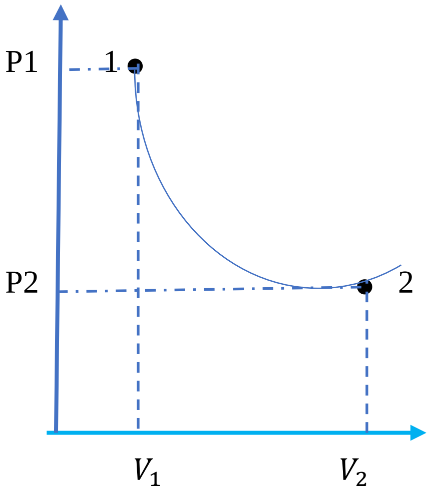
$$\boxed{W_{12} = nRTln\frac{V_1}{V_2} = nRTln\frac{P_2}{P_1}} \qquad \textbf{(II. 7)}$$

II.4.2. Isothermal transformation (T= cste)

Consider a gas, assumed to be perfect, undergoing a transformation at constant temperature.

Initial state (T_1, V_1, P_1) **Final state** (T_2, V_2, P_2)

With : $T_1 = T_2$; so : $P_1V_1 = P_2V_2 = \cdots P_nV_n = PV = cste$



Isothermal transformation

- **Calculating the work (W) :**

$$\boxed{W_{12} = -\int_1^2 PdV = -\int_1^2 nRT\frac{dV}{V} = -nRT\int_1^2 \frac{dV}{V}} \qquad \textbf{(II. 8)}$$

- **Calculating heat quantity :**

T = cste ; $\boldsymbol{U = f(T)}$; donc $\Delta U = 0$

$$\Delta U = W_{12} + Q_{12} = 0$$

$$\boxed{\Rightarrow Q_{12} = -W_{12} = +nRTln\frac{V_2}{V_1} = -nRTln\frac{P_2}{P_1} = -nRTln\frac{V_2}{V_1}}$$ **(II.9)**

- **Calculating internal energy and enthalpy**

$\Delta U = 0 \longrightarrow \Delta U = f(T)$

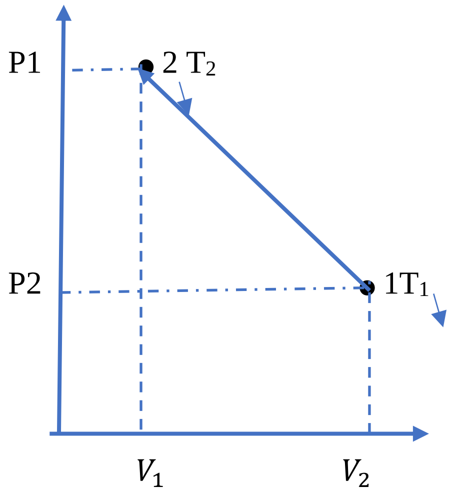
$\Delta H = 0 \longrightarrow \Delta H = f(T)$

II.4.3 Transformation isochore (V= cste)

Assume a perfect gas enclosed in a rigid non-deformable enclosure (dV =0). The equation of state for a perfect gas: $PV = nRT$; therefore

Initial state $\rightarrow P_1V_1 = \text{n}RT_1$ **Final state** $\rightarrow P_2V_2 = \text{n}RT_2$

Since (V= cste) then $dV = 0\,;(V_1 = V_2)$ we have : $P_1T_2 = P_2T_1$



Transformation isotherme

- **Calculating the work (W) :**
- $dw = -PdV \Rightarrow W_{12} = -\int_1^2 PdV = 0 \Rightarrow$ $\boxed{W_{12} = 0}$ **(II.10)**
- **Calculating heat quantity:**

$$\boxed{Q_{12} = mC_V\Delta T = Q_v}$$ **(II.11)**

$$dU = dQ + dW$$

$$\Delta U = W_{12} + Q_{12} = U_2 - U_1 = mC_V(T2 - T1)$$

- **Calculating the internal energy and enthalpy:**

$$\boxed{\Delta U = W_{12} + Q_{12} = mc_V(T2 - T1) = Q_v}$$ **(II.12)**

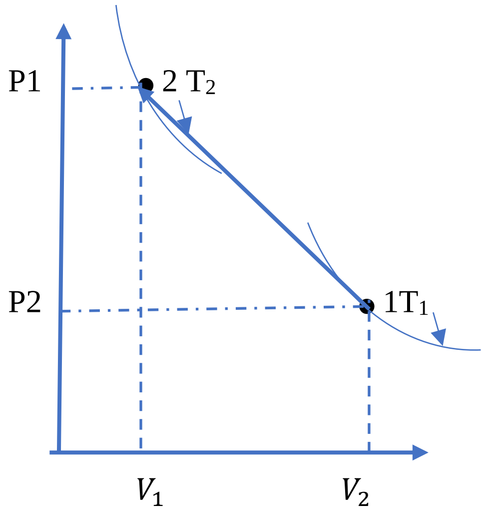
(II.13)

$$\boxed{\Delta H = \Delta U + \Delta(PV) = mc_p(T2 - T1) = Q_p}$$

II. 4.4. Reversible adiabatic transformation (dQ = 0)

Consider a gas, assumed to be perfect, undergoing an adiabatic (isentropic) transformation, i.e. with no change in the quantity of heat.

Initial state (T_1, V_1, P_1) → **Final state** (T_2, V_2, P_2)



Transformation isotherme

Adiabatic transformation is characterised by: $dQ = 0$ the result is $dU = -PdV$

$\Rightarrow nC_V dT = -PdV \Leftrightarrow nC_V dT + PdV = 0$ …………… (1)

We also have $C_P - C_V = R$ et $\frac{C_P}{C_V} = \gamma$, we pull $C_P = R + C_V$

and we replace in the expression of gamma: $\gamma = \frac{R+C_V}{C_V} \Rightarrow \gamma = \frac{R}{C_V} + 1$

$$\Rightarrow C_V = \frac{R}{\gamma-1} \text{ ……………… (2)}$$

As a result (1) et (2) $\Rightarrow$ $n\frac{R}{\gamma-1}dT + PdV = 0$ ……………. **(3)**

and for a perfect gas: $PV = nRT$ d'où:

$d(PV) = nRdT \Leftrightarrow PdV + VdP = nRdT$ ……. **(4)**

(3) et (4) $\Rightarrow \frac{1}{\gamma-1}(PdV + VdP) + PdV = 0 \Rightarrow PdV + VdP + \gamma PdV - PdV = 0$

$\Rightarrow VdP + \gamma PdV = 0 \quad \Rightarrow \frac{dP}{P} + \gamma\frac{dV}{V} = 0$ This is the logarithmic differential of the relationship $PV^{\gamma} = \text{Cst}$

This formula describes the adiabatic equation of state, also known as the LAPLACE formula: $\boxed{P_1V_1^{\gamma} = P_2V_2^{\gamma} = \text{Cst}}$ **(II.14)**

- The equation of state for adiabatic gases can also be described as a function of temperature and volume, and temperature as a function of pressure.:

We have: $PV = nRT \Rightarrow = P = \frac{nRT}{V}$

We have also: $\frac{P_2}{P_1} = \frac{V_1^{\gamma}}{V_2^{\gamma}} \Leftrightarrow \frac{nRT_2}{V_2}V_2^{\gamma} = \frac{nRT_1}{V_1}V_1^{\gamma}$

So: $\boxed{T_2V_2^{\gamma-1} = T_1V_1^{\gamma-1} = Cst}$ **(II.15)**

Or else: $PV = nRT \Rightarrow = V = \frac{nRT}{P}$ and : $\frac{P_2}{P_1} = \frac{V_1^{\gamma}}{V_2^{\gamma}}$

$P_2(nR)^\gamma \frac{T_2^\gamma}{P_2^\gamma} = P_1(nR)^\gamma \frac{T_1^\gamma}{P_1^\gamma}$ So: $\boxed{P_2^{1-\gamma}\, T_2^\gamma = P_1^{1-\gamma}\, T_1^\gamma = \text{Cst}}$ **(II.16)**

- **Calculation of work :**

1. **From the expression of the first principle**

2. $W_{12} = -\int_1^2 PdV$ then we have: $dU = dQ + dW$; $dQ = 0$

So: $dW = dU = nc_V dT$

$$\Rightarrow W_{12} = \int_1^2 dU = \int_1^2 nc_V dT = nc_V \int_1^2 dT = nc_V\, \Delta T$$

We have: $c_P - c_V = R$ et $\frac{c_P}{c_V} = \gamma$ and secondly $C_V = \frac{R}{\gamma-1}$

$$\Rightarrow W_{12} = n\frac{R}{\gamma-1}(T_2 - T_1) = \frac{1}{\gamma-1}(nRT_2 - nRT_1) \text{ et } PV = nRT$$

So: $\boxed{W_{12} = \frac{1}{\gamma-1}(P_2V_2 - P_1V_1)}$ **(II.17)**

3. **From the integral expression**

$W_{12} = -\int_1^2 PdV$ et $PV^\gamma = \text{Cst} = \text{A} \Rightarrow P = \frac{A}{V^\gamma} \Rightarrow W_{12} = -\int_1^2 \frac{A}{V^\gamma} dV$

$= A\int_1^2 \frac{dv}{V^\gamma}$

$= -A\left[\frac{1}{\gamma-1} V^{1-\gamma}\right] = -\frac{A}{\gamma-1}\left[V_2^{1-\gamma} - V_1^{1-\gamma}\right] = \frac{1}{\gamma-1}\left[AV_1^{1-\gamma} - AV_2^{1-\gamma}\right]$

$= \frac{1}{\gamma-1}\left[P_1V_1^\gamma V_1^{1-\gamma} - P_2V_2^\gamma V_2^{1-\gamma}\right] = \frac{1}{\gamma-1}\left[P_1V_1 - P_2V_2\right]$

so: $\boxed{W_{12} = \frac{P_2V_2 - P_1V_1}{1-\gamma}}$ **(II.18)**

- **Calculating the amount of heat:**

The transformation is adiabatic, so there is no variation in the quantity of heat.

$\boxed{Q_{12} = 0}$ **(II.19)**

- **Calculating internal energy and enthalpy:**

$\Delta U = W_{12} = nC_V(T_2 - T_1)$

$\Delta H = Q_p = nC_p(T_2 - T_1)$

We have: $\frac{c_P}{c_V} = \gamma$; Then $c_P = \gamma c_V$

So: $\Delta H = Q_p = n\gamma c_V\,(T_2 - T_1)$ $\boxed{\Rightarrow \quad \Delta H = \gamma \Delta U}$ **(II.21)**

Notes:

1.The change in internal energy and enthalpy is zero in three special cases:

- for an isolated system (W=0 and Q=0)

- for a cycle

- for an isothermal transformation.

2. The heat capacity at constant pressure (c_P) and constant volume (c_V) generally depend on temperature: $c_P = c_P\,(T)$ et $c_V = c_V(T)$, hence the expressions for ΔU and ΔH for a perfect gas: $\Delta U = \int_{T_1}^{T_2} c_V dT$ and $\Delta H = \int_{T_1}^{T_2} c_P dT$.

3. for the 1st principle: $dU = \delta Q + \delta W$; $\Delta U = W + Q$

4. $W_{12} = -\int_1^2 PdV$ (Reversible)

5. Perfect Gas: $U = f(T)$; $dU = nc_V dT$; $dH = nc_P dT$

Application:

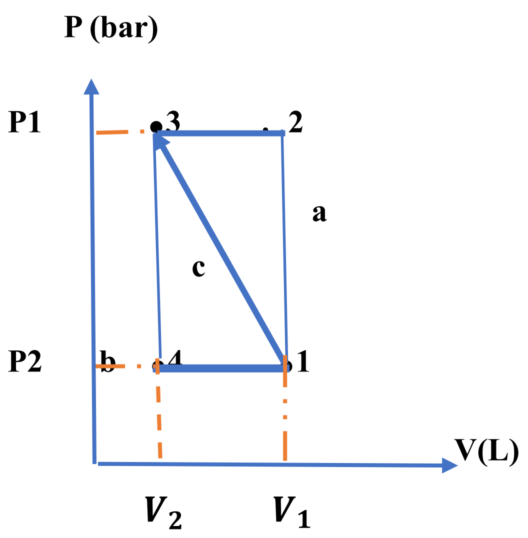
A mixture (air-gasoline) undergoes a transformation from state (1) to state (2) following three different paths (a, b and c) with: The 1st transformation is isochoric then isobaric (path a), the 2nd is isobaric then isochoric (path b) and the 3rd is such that PV =cst (path c). State (1): P_1= 1 bar; V_1= = 3 l State (2): P_1 = 3 bars; V_1= = 1 L

1 -Show the three transformations in Clapeyron coordinates.

2 -Calculate between state (1) and state.(2)

3- Calculate the work in the three cases and deduce the heat exchanged; is it received or given up by the system?

The solution :



2- ΔU :

ΔU : does not depend on the path taken because it is a state function;

So: $\Delta U = \Delta Q = nc_P\Delta T = 0j$

3- Calculation of work on the three routes (a, b and c)

- **For path (a) :**

$$W_a = W_{1-2} + W_{2-3} = -P_2(V_2 - V_1)$$

W_{1-2} (Isochore) et W_{2-3} (isobare)

So : $W_a = -P_2(V_2 - V_1)$ = 3.10^5 (3-1) 10^{-3}

$$\boxed{W_a = 600\, joul}$$

- **For path (b) :**

$$W_b = W_{1-4} + W_{4-3} = -P_1(V_2 - V_1)$$

So : $W_b = W_{1-4} = -P_1(V_2 - V_1) = P_1(V_1 - V_2) =$ 10^5 (3-1) 10^{-3}

$$\boxed{W_b = 200\ joul}$$

- **For path (c) :**

$$W_C = -\int_1^2 PdV = -\int_1^2 nRT\frac{dV}{V} = -nRT\int_1^2 \frac{dV}{V} = nRTln\frac{V_1}{V_2} == P_1V_1ln\frac{V_1}{V_2}$$

$$\boxed{W_C = 10^5.3 10^{-3} \ln 3 = 227\ joul}$$

<u>4-The heat quantities for paths a, b and c:</u>

Since : $\Delta U = 0$ donc ; $W = -Q$

$$\boxed{Q_a = -600\ joul < 0 \quad ; Q_b = -200\ joul < 0 \quad ; Q_C = -227\ joul < 0}$$

Notes :

This exercise shows that the variation in internal energy is indeed a state function that depends only on the initial and final states, whereas work and the quantity of heat are not state functions that really depend on the path followed.

Chapter III:

Thermochemistry Application of the 1st principle to chemistry

Chapter III: Thermochemistry Application of the 1st principle to chemistry

III.1 Introduction

Thermochemistry is the application of the first principle to isothermal and isobaric chemical reactions. The basis of thermochemistry is the equation $Q_p = \Delta H$, which provides an experimentally measurable state function related to the energy of the system. It studies the ability of molecules to store energy and exchange it with other molecules in physical processes, as well as the production or absorption of energy during physical and chemical reactions. Since, H depends only on the initial and final states, it will be possible to calculate ΔH for any reaction, simply by constructing a path from the initial state to the final state made up of elementary steps for which the enthalpy change is known.

For exemple :

$\Delta U = W + Q$

$\Delta U = -P(V_2 - V_1) + Q_P \; (U_2 - U_1) = -P(V_2 - V_1) + Q$

$$\boxed{\Rightarrow Q_P = (U_2 + PV_2) - (U_1 + PV_1).} \qquad \textbf{(III.1)}$$

Q_P is written as the difference of a state function $(U + PV)$.This function is called the Enthalpy H.

(Variation in enthalpy). $\boxed{Q_P = H_2 - H_1 = \Delta H}$ **(III.2)**

This function is used to describe the thermal effects that occur in chemical reactions taking place at constant pressure. The unit of enthalpy is the unit of energy symbolised by "ue" 1 ue = 1cal

Other units such as the joule and multiples are used from time to time (1J = 10-3 KJ, 1cal = 4.18 J).

Reaction in the liquid or solid phase, $\Delta V \approx 0$; So: $\Delta H = \Delta U + P\Delta V \Rightarrow \Delta H = \Delta U$

Reaction in the gas phase, $\Delta V \neq 0$; So: $\Delta H = \Delta U + RT\Delta n$ gases taken to be perfect.

- When will $\Delta H < 0$, the reaction absorbs heat. In this case, it is **exothermic.**
- When will $\Delta H > 0$, However, the reaction gives off heat and is therefore **endothermic**.

Thermochemistry is the study of the thermal effects that accompany chemical reactions.

Example1

The oxidation of carbon-to-carbon monoxide at 298K and 1atm is -26.416 cal.

$$C + \frac{1}{2} O_2 = CO$$

Discuss the values of ΔH et ΔU

Solution:

$Q_P = \Delta H = -26{,}416$ cal

$P\Delta V = \Delta nRT = \frac{1}{2} \times 1{,}987 \times 298 = 296{,}063$ cal

$\Delta U = \Delta H - RT\Delta n = -26{,}416 - 296{,}063 = -322{,}479$ cal.

III.2 Thermodynamic definition of a chemical reaction

From a thermodynamic point of view, a chemical reaction is the transformation of a system from an initial state with a given chemical composition (reactants) to a final state formed by new chemical compounds (products). A chemical reaction can be written in the following general form:

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

- (A, B, C, D) - is a chemical compound.
- (a, b, c, d) - are the stoichiometric coefficients indicating the required number of molecules (moles)
- $_{(*)}$ the required number of molecules (moles) and (*) indicates whether it is a solid (S), liquid (l) or gas (g).

Example: combustion of methane:

$$2C_2H_{6\,(g)} + 7O_{2\,(g)} \rightarrow 4CO_{2\,(g)} + 6H_2O_{\,(L)}$$

Product Reactive

III.3 Calculation of reaction enthalpy

- Applications : Calculation of industrial installations, etc.
- Exothermic reaction: the reaction medium may need to be cooled to prevent an explosion or damage to the equipment.
- Endothermic reaction: the reactor must be heated to maintain a reaction at a sufficiently high speed.
- By using, we can introduce another function which allows us to predict the direction of the reaction.

The enthalpy of a reaction can be determined experimentally, using calorimetry (direct method), by measuring the effect that accompanies the reaction. Secondly, by calculation (indirect method), based on quantities that are already known (thermodynamic tables). In particular; formation, combustion, bonding, etc.

III.3.1. Standard state - Standard enthalpy of formation

III.3.1.1. Standard or reference state

A substance is in the standard state (reference state) if it is in its pure state, taken in its most stable physical state under a pressure of 1 atm and a given temperature, generally 298K. The standard state is denoted by the symbol "°" when a reaction takes place under these conditions (reactants and products are in the standard state), and is referred to as the "standard enthalpy of reaction", denoted by ΔH_R^0. The standard enthalpy of a reaction is written as: ΔH_T^0 si T=298K, on écrit ΔH_{298}^0

Example: ΔH_{298}^0 represents the enthalpy variation of a reaction at T=298 K and P=1atm (105Pa), with the products and reactants in their standard state at 298 K.

III.3.1.2. Standard enthalpy of formation ΔH_f^0 (kJ.mol^{-1})

The standard enthalpy of formation ΔH_f^0 of a compound A is the enthalpy variation of the reaction of formation under standard conditions: at P = 1atm, of this compound from its simple body elements taken in their most stable states, the temperature generally being 298 K.

Example 1:

$6\,C_{(s)} + 3\,H_{2\,(g)} \rightarrow C_6H_{6\,(L)}$,

$\Delta H_R^0(298°K) = \Delta H_f^0(298°, C6H6, L)$

N.B: N.B: The enthalpy of formation of simple bodies is conventionally assumed to be zero.

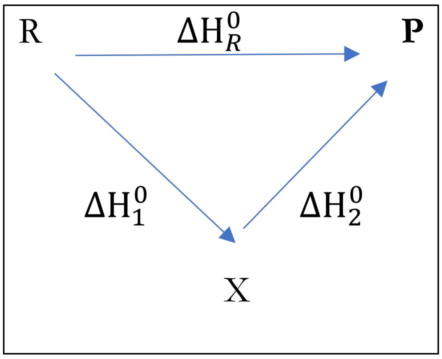
Example 2: ΔH_f^0 (O_2) g = 0; ΔH_f^0(H_2) g = 0; $\Delta H_f^{0\,0}$ (N_2) g = 0; ΔH_f^0(Fe)s = 0)

$$H_{2\,(g)} + \frac{1}{2}\,O_{2\,(g)} \xrightarrow{\Delta H_R^0} 2H_2O_{\,(L)} \qquad \Delta H_R^0 = \Delta H^0_{f(\,H20)}$$

$$C_{\,(graphite)} + O_{2\,(g)} \xrightarrow{\Delta H_R^0} CO_{2\,(g)} \qquad \Delta H_R^0 = \Delta H^0_{f(\,C2O)}$$

III.4. Determination of standard molar enthalpies of reaction: HESS law (1802-1850)

III.4.1. Use of enthalpies of reaction



If we consider a principal reaction

The secondary reactions R → X et X → P

R: Reactive; P: Products ; X: Intermediate

$$\Delta H_R^0 = \Delta H_1^0 + \Delta H_2^0$$

Example: (a) $C_{\,(graphite)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$ ΔH^0_{298} = -393.13 k.j.mol^{-1}

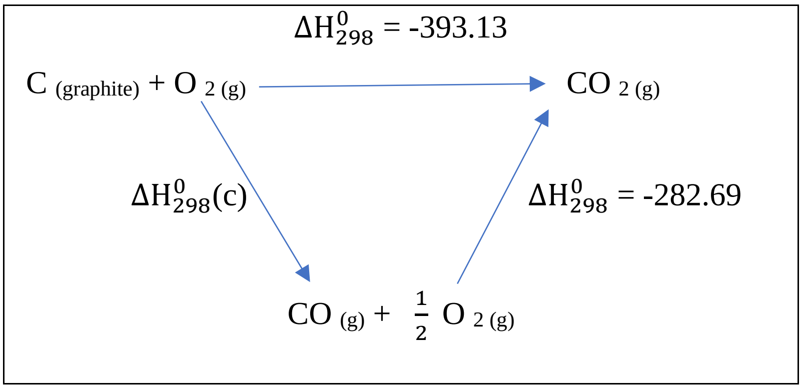
(b) $CO_{\,(g)} + \frac{1}{2}\,O_{2\,(g)} \rightarrow CO_{2\,(g)}$ ΔH^0_{298} = -282.69 k.j.mol^{-1}

What is the standard enthalpy of reaction (c) ?

(c) $C_{\,(graphite)} + \frac{1}{2}\,O_{2\,(g)} \rightarrow CO_{\,(g)}$ ΔH^0_{298} = ?

Note that subtracting equation (a) from equation (b) gives equation (c), So:

$$\Delta H^0_{298}(a) \quad - \quad \Delta H^0_{298}\,(b) \quad = \quad \Delta H^0_{298}(c)$$



HESS's law, or the principle of the initial state and the final state, states that the enthalpy variation of a system is independent of the path followed (law laid down in 1840).

III.4.2 Using enthalpies of formation

HESS's law allows a reaction to be compared to a sequence of reactions along the following path:

Example.1:

We want to calculate the following reaction ΔH^0_R using other chemical reactions:

$$CH_4 \quad + \quad 2\,O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(L)} \qquad \Delta H^0_R(298)=?$$

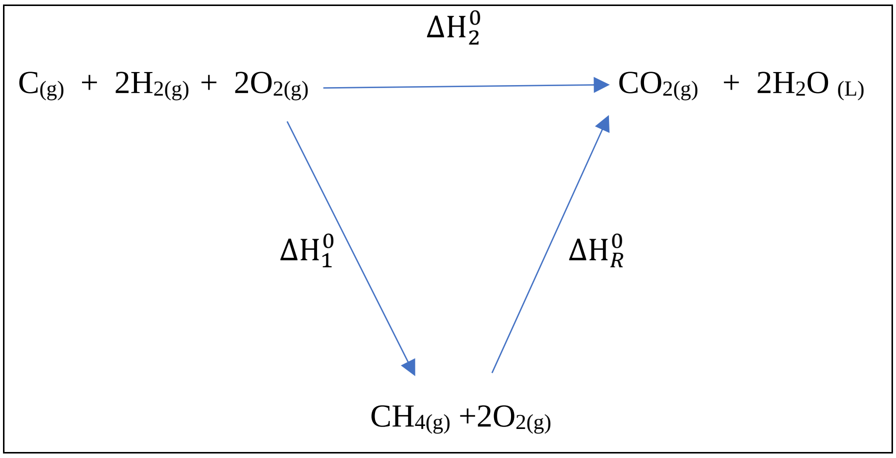
Knowing that:

$$C_{(g)} + 2H_{2(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(L)} \qquad \Delta H^0_1$$

$C_{(g)} + 2H_{2(g)} \rightarrow CH_{4(g)} \qquad \Delta H_2^0$

Using the three reactions, we have:

$$\boxed{\Delta H_{298}^0 = -393.13}$$



So, if we do an energy balance we get:

$$\Delta H_1^0 = \Delta H_2^0 + \Delta H_R^0 \Rightarrow \Delta H_R^0 = \Delta H_1^0 - \Delta H_2^0$$

However, we have: $\Delta H_1^0 = \Delta H_f^0(CO_2)\ g + 2\Delta H_f^0(H_2O)\ L$

$\Delta H_2^0 = \Delta H_f^0(CH_4)\ g$

$$\boxed{\text{And so: } \Delta H_R^0 = \Delta H_f^0(CO_2)\ g + 2\Delta H_f^0(H_2O)\ L - \Delta H_f^0(CH_4)\ g}$$

So, from this equation we can see that the standard enthalpy ΔH_R^0 of a chemical reaction may also be equal to the sum of the enthalpies of formation of the products minus those of the reactants, which can be expressed by the following general relationship known as **HESS's Law**. This demonstration is valid for any chemical reaction:

$$\boxed{\Delta H_R^0 = \sum \Delta H_f^0(Products) - \sum \Delta H_f^0(Reactives)} \qquad \textbf{(III.3)}$$

Exemple.2:

$C_2H_{4(g)} + 3\ O_{2(g)} \rightarrow 2\ CO_{2(g)} + 2H_2O_{\ (L)}$ $\qquad \Delta H_R^0(298)$=?

$\Delta H_R^0 = 2\Delta H_f^0(CO_2)\ g + 2\Delta H_f^0(H_2O)\ L - \Delta H_f^0(C_2H_4)\ g$

Knowing that: $\Delta H_f^0(\ O_2)\ _g = O$ (pure body)

We will have: $\Delta H_R^0 = 2(-94.5) + 2(-68.32) - (12.5)$

$$\boxed{\Delta H_R^0 = 373.24 Kcal\ .mol^{-1} < 0 \text{ (Exothermic reaction)}}$$

- The table below summarises the enthalpies of formation of some compounds in a given physical state and in the standard state.

Reactive	**Compound**	**ΔH_f^0 (Kcal/mol)**
$H_{2(g)} + ½\ O_{2(g)}$	$2H_2O_{(g)}$	**-57.80**
$H_{2(g)} + ½\ O_{2(g)}$	$2H_2O_{\ (L)}$	**-68.30**
$C_{(g)} + O_{2(g}$	$CO_{2(g)}$	**-54.09**
$C_{(g)} + ½\ O_{2(g)}$	$CO_{(g)}$	**-26.42**
$C_{(g)} + 2H_{2(g)}$	$CH_{4(g)}$	**-17.89**
$2C_{(g)} + 2H_{2(g)}$	$C_2H_{4(g)}$	**-12.5**
$2C_{(g)} + 3H_{2(g)}$	$C_3H_{6(g)}$	**-24.82**

Example 3: According to the Born-Haber cycle

$$\begin{tikzcd}
C_3H_{8(L)} + 3\,SO_{2(g)} \arrow[rr, "\Delta H_R^0"] \arrow[dr, "\Delta H_f^0(C_3H_{8\,(L)})"'] & & 3\,CO_{2(g)} + 4H_2O_{\,(L)} \\
& \mathbf{3C_{grafite} + 4H_{2\,(g)}} + SO_{2(g} \arrow[ur, "3\Delta H_f^0(CO_2)\,g + 4\Delta H_f^0(H_2O_{\,(L)})"'] &
\end{tikzcd}$$

$$\Delta H_R^0 = 3\Delta H_f^0(CO_2)\,g + 4\Delta H_f^0(H_2O_{\,(L)}) - \Delta H_f^0(C_3H_{8\,(L)})$$

Example 4: formation of C_2H_2

The heat of formation of can be determined from the following reactions:

$\mathbf{C_{(g)} + O_{2(g}} \xrightarrow{\qquad} \mathbf{CO_{2(g)}}$ ……………ΔH_1^0

$\mathbf{H_{2(g)} + \frac{1}{2}\,O_{2(g)}} \xrightarrow{\qquad} \mathbf{2H_2O_{\,(L)}}$ …………ΔH_2^0

$\mathbf{C_2H_{2(g)} + 5/2O_{2(g)}} \xrightarrow{\qquad} \mathbf{2CO_2 + H_2O}$ ………ΔH_3^0

$\mathbf{H_{2(g)}} \xrightarrow{\qquad} 2H$ …………………Ed (dissociation energy)

Method (1) : Consider the Hess cycle

$$\begin{tikzcd}
\mathbf{C_2H_{2(g)} + 5/2O_{2(g)}} \arrow[rr, "\Delta H_3^0"] \arrow[dr, "-\Delta H_f^0\,\mathbf{C_2H_{2(g)}}"'] & & \mathbf{2CO_2 + H_2O}\ \ldots\ldots\ldots \Delta H_3^0 \\
& \mathbf{2C + H_2 + 5/2O_2} \arrow[ur, "\mathbf{2}\Delta H_1^0 + \Delta H_2^0"'] &
\end{tikzcd}$$

$$\Delta H_3^0 = \mathbf{2}\Delta H_1^0 + \Delta H_2^0 - \Delta H_f^0$$

$$\Delta H_f^0 = \mathbf{2}\Delta H_1^0 + \Delta H_2^0 - \Delta H_3^0$$

ΔH_f^0=379.2 KJ

Method (2):

$2CO_2+H_2O \xrightarrow{\qquad\qquad} C_2H_{2(g)} + 5/2O_{2(g)}$ ………….ΔH_1^0

$H_{2(g)} + ½ O_{2(g} \xrightarrow{\qquad\qquad} 2H_2O_{(L)}$ ……………………….ΔH_2^0

$C_{(g)} + O_{2(g} \xrightarrow{\qquad\qquad} CO_{2(g)}$ ……………………….ΔH_3^0

$2C + H_2 \xrightarrow{\Delta H_f^0} C_2H_{2(g)}$

$\Delta H_f^0\ C_2H_{2(g)} = 2\Delta H_1^0 + \Delta H_2^0 + \Delta H_3^0$

III.5 Standard Enthalpy of Change of State

III.5.1 Change of state

It's a physical transformation.

- **Fusion:** passage from the solid state to the liquid state; the opposite of this transformation being solidification.

Solid $\xrightarrow{\Delta H^0_{fusion}}$ Liquid; Ex: $H_2O_{(S)} \rightarrow H_2O_{(L)}$; With $\Delta H^0_{fusion} - \Delta H^0_{Solidification}$

- **Vaporisation:** change from a liquid to a gas; the opposite of this transformation is liquefaction.

Liquid $\xrightarrow{\Delta H^0_{Vaporisa}}$ Vapour ; Ex : : $H_2O_{(L)} \rightarrow H_2O_{(g)}$;

With $\Delta H^0_{Vaporis} = -\Delta H^0_{Liquéfaction}$

- **Sublimation:** passage from the solid state to the gaseous state; the opposite of this transformation being condensation.

Solid $\xrightarrow{\Delta H^0_{Sublimatio}}$ Vapour; Ex: $I_{2\,(S)} \rightarrow I_{2\,(g)}$;

With $\Delta H^0_{Sublimation} = -\Delta H^0_{Condensati}$

III.5.2. Notation of enthalpies of change of state

These are noted $\Delta_{fus}H$ or L_f ; $\Delta_{Vap}H$ or L_V .also called latent heats of change of state. If the $\Delta_{fus}H$ or L_f is 248kJ/mol, for example, the enthalpy of the reverse transformation is +248kJ/mol.

III.6. Energy (or enthalpy) of bonding

Binding energy is defined as the enthalpy variation accompanying the formation of a bond from isolated atoms in the gaseous state, in 1 atmosphere. It is a released energy, so it is always negative, and is expressed in J/mol. The bond-forming reaction is written as follows:

$A_{(g)} + B_{(g)} \longrightarrow A\text{-}B_{(g)}$; ΔH^0_{A-B} ou E_{A-B} ; Avec A et B are atoms.

Example.1: Consider the following reaction:

$H(g) + Cl(g) \xrightarrow{\Delta H^0_{H-Cl}} H\text{-}Cl$; $\Delta H^0_{H-Cl} = -431 Kj/mol$

The following table summarises the enthalpy of formation values for a few examples of chemical bonds.

Link	**H-H**	**C-H**	**C-C**	**C=C**	**O=C**
ΔH (Kcal/mol)	**-104**	**-99**	**-83**	**-147**	**-118**

The enthalpies of bond formation (ΔH) are always negative, which means that atoms in the free state combine with each other, always releasing large amounts of energy.

Comments:

1 -$\Delta H^0_{H-Cl}$is different from the standard enthalpy of formation of HCl, which is defined in relation to the simple bodies $H_{2(g)}$ et $Cl_{2(g)}$; ΔH^0_f = -$93Kj/mol.$ These energies are expressed in calories or joules.

$\mathbf{2} - \Delta H^0_{A-B}$ Depends on the A-B link, but also on the environment.

Example: The O-H: $\Delta H^0_{O-H} = -498Kj/mol$ in H2O

and $\Delta H^0_{O-H} = -37Kj/mol$ in CH_3COOH

3- The tables generally give an average value for a very large number of compounds containing this bond.

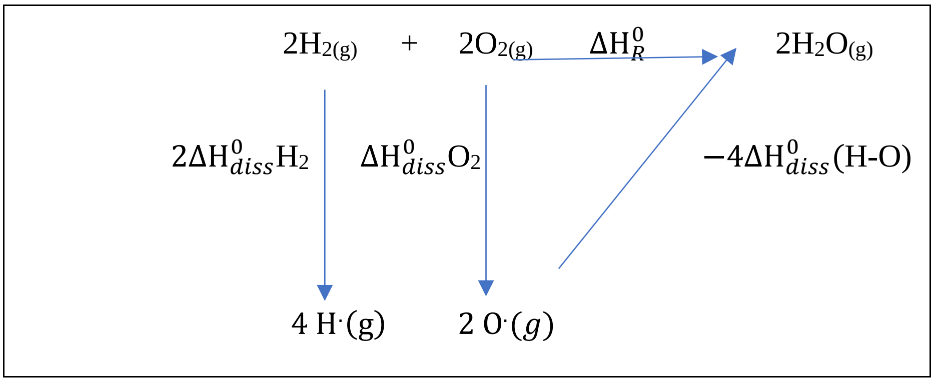
III.6.1 Calculating an enthalpy of reaction from binding energies

Example 1: Calculate the standard molar enthalpy of formation of H_2O at 298k

$$2H_{2\,(g)} + 2O_{2\,(g)} \rightarrow 2H_2O_{(g)}$$

Data for $\Delta H^0_{diss}(O-H) = \frac{428Kj}{mol}$; $\Delta H^0_{diss}(H-H) = \frac{436Kj}{mol}$; $\Delta H^0_{diss}(O=O) = 495Kj/mol$

Two H-H and O=O bonds are broken to give isolated atoms 4H and 2O, then 4 new H-O ($2H_2O$) bonds are formed.



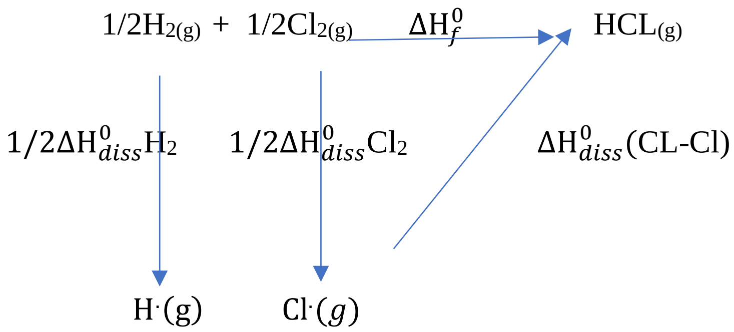
$$\boxed{\Delta H_R^0 = 2\Delta H_{diss}^0(H_2) + 2\Delta H_{diss}^0(O_2) - 4\Delta H_{diss}^0(\text{H-O}) = -345 Kj/mol}$$

Example 2: Calculate the standard molar enthalpy of formation of gaseous hydrochloric acid at 298 k from the following binding enthalpies in KJ/mol: $\Delta H_{H-Cl}^0 =$ - 428 KJ/mol

$\Delta H_{H-H}^0 =$ -423 KJ/mol

$\Delta H_{CL-Cl}^0 =$ -240 KJ/mol

Solution:



$$\boxed{\Delta H_{f(HCl)}^0 = \Delta H_{(CL-Cl)}^0 - 1/2\Delta H_{(H-H)}^0 - 1/2\Delta H_{(H-CL)}^0 = -92 Kj/mol}$$

III.7. Influence of temperature on heats of reaction - KIRCHHOFF's law (1824-1887)

From the value of a heat of reaction, measured at a given temperature, it is interesting to be able to calculate the variation in internal energy or enthalpy that would accompany this reaction if it were carried out at any other temperature.

Consider a chemical reaction carried out at constant pressure, symbolised by

$a\,A_{(*)} + b\,B_{(*)} \rightarrow c\,C_{(*)} + d\,D_{(*)} \quad \Delta H^0_T = ?$

Denoting by C^0_{Pi} the standard molar heat capacity at constant pressure of a component A_i, it follows from the previous definition:

$$\frac{d(\Delta H^0)}{dT} = \Delta C^0_P \quad \text{as well as for } \Delta U^0 ; \frac{d(\Delta U^0)}{dT} = \Delta C^0_V$$

If we know $\Delta H^0(T_0)$ and we want to calculater $\Delta H^0(T)$, just integrate the equation:

KIRCHHOFF's Law

$$\boxed{\begin{array}{l} \Delta H^0(T) = \Delta H^0(T_0) + \int_{T0}^{T} \Delta C^0_P \, dT \\ \\ \Delta U^0(T) = \Delta U^0(T_0) + \int_{T0}^{T} \Delta C^0_V \, dT \end{array}} \qquad \textbf{(III.4)}$$

With: $\Delta C_P = \sum C_P(Products) - \sum C_P(Reactives$

Comments:

1- If Cp is a function of temperature, then Cp = f (T); the KIRCHHOFF expression becomes

$\Delta C_P = a + bT + cT^2$...........

$$\Delta H^0(T) = \Delta H^0(T_0) + a\int_{T0}^{T} dT + b\int_{T0}^{T} T\,dT + c\int_{T0}^{T} T^2\,dT$$

2- If Cp is not a function of temperature, Cp ≠ f (T); the KIRCHHOFF expression becomes: $\Delta H^0(T) = \Delta H^0(T_0) + \Delta C^0_P(T - T_0)$

3- If there is a phase change in the interval [T_0, T], the enthalpies of phase change must be taken into account in the calculation.

Example 1: Consider the reaction to synthesise hydrogen iodide:

$$\tfrac{1}{2}\,H_{2(g)} + \tfrac{1}{2}\,I_{2(g)} \rightarrow HI_{(g)}$$

The thermodynamic quantities, at T_0=298K, for the three gases assumed to be perfect are given in the table below:

Constituents	**H_2**	**I_2**	HI
ΔH_f^0 (Kj.mol^{-1})	**0**	**62.1**	**25.9**
C_P^0(J.mol^{-1}. K^{-1})	**28.8**	**36.8**	**29.1**

KIRCHHOFF's law gives: $\Delta H^0(T) = \Delta H^0(T_0) + \Delta C_P^0(T - T_0)$

$\Delta H^0(T_0) = \Delta H_f^0(HI)g - \tfrac{1}{2}\Delta H_f^0(H_2)\,g - \tfrac{1}{2}\Delta H_f^0(I_2)\,g$

$\Delta H^0(T_0) = 25.9 - \tfrac{1}{2}\,.62.1 =$ **-5.15(Kj.mol^{-1})**

$\Delta C_P^0 = C_P^0(HI) - \tfrac{1}{2}\,C_P^0(H_2) - \tfrac{1}{2}\,C_P^0(I_2)$

$\Delta C_P^0 = 29.1 - \tfrac{1}{2}\cdot 28.8 - \tfrac{1}{2}\cdot 36.8 =$ **$-$ 3.4 (J.mol^{-1}. K^{-1})**

With: $\Delta H^0(T) = -5.15 - 3.4.10^{-3}\,(T - 298)$

$$\boxed{\Delta H^0(T) = -\,4.136 - 0.0034\,T\ \textbf{(Kj.mol}^{-1}\textbf{)}}$$

Chapter IV:

Second principle of thermodynamics

Chapter IV: Second principle of thermodynamics

IV.1 Introduction

The first principle, which asserts the equivalence of different forms of energy, cannot tell us the direction of a given change. Experience shows that when two bodies A and B of respective temperatures T_A and T_B are brought into contact, knowing that T_A is greater than T_B , we will observe the spontaneous passage of heat from the hot body (A) to the cold body (B), until the same temperature T is reached for both bodies. A thermal equilibrium is therefore established, with heat being spontaneously transferred from the hotter body to the colder body until equilibrium is reached.) (Figure III-1). The opposite is never observed spontaneously

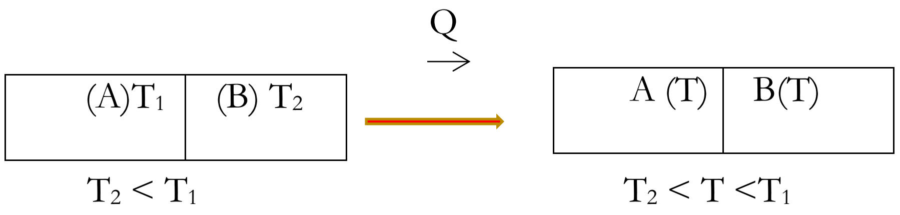


Figure III-1 : Equilibre thermique entre les corps A et B.

If we analyse the reverse transformations. The cold body (body B) gives up heat to the hot body (body A) as it cools (reaches T). The first principle does not allow us to predict the direction of change

Exemple.

- Sugar dissolved in water cannot spontaneously transform into a solid state.

These observations lead us to say that natural (spontaneous) transformation takes place in a well-defined direction; **the opposite transformation is never observed**. From the first principle, we know that the heat balance of two bodies brought into contact with each other is expressed by the irreversible nature of most transformations. This has led us to state a second principle that can tell us about the direction of change in systems.

IV.2 The need for a second principle

The first principle, which stipulates the conservation of energy, does not explain the irreversibility of certain spontaneous or natural transformations. It is therefore necessary to introduce a second principle, also known as the principle of evolution, deduced from experimental facts, which will make it possible to predict the evolution of systems and which therefore makes it possible to specify the nature of a transformation (reversible, irreversible), through a new state function known as **entropy (S**).

In physics, entropy is an abstract quantity that measures the degree of disorder in a system on a microscopic scale and describes its behaviour by maximising it.

IV.3 Statement of the second principle

For any closed system, there is an external, non-conservative state function, called entropy (S), such that its variation between two successive dates t1 and t2 with t1 < t2

Write : $\Delta S_{\text{Sys}}=\Delta S^e + \Delta S^c$ avec $\Delta S^c \geq 0$

ΔS_{sys}: entropy variation of system

ΔS^e : the variation in exchange entropy

ΔS^c : the entropy variation of creation

- Entropy S is an increasing function $\Delta S = S_f - S_i$
- The entropy of an isolated system is an increasing function of $\Delta S = S_f - S_i \geq 0$
- It remains constant if the transformation is reversible $\Delta S = 0$
- It increases if the transformation is irreversible $\Delta S > 0$

IV.3.1. CLAUSIUS' statement

Experimentally, heat never spontaneously passes from a cold body to a hot body.

IV.3.2. KELVIN's statement

It is impossible to extract heat from a substance and convert it entirely into work.

IV.3.3. Mathematical statement

Given the two postulates of Clausius and Kelvin, let us imagine a transformation cycle during which:

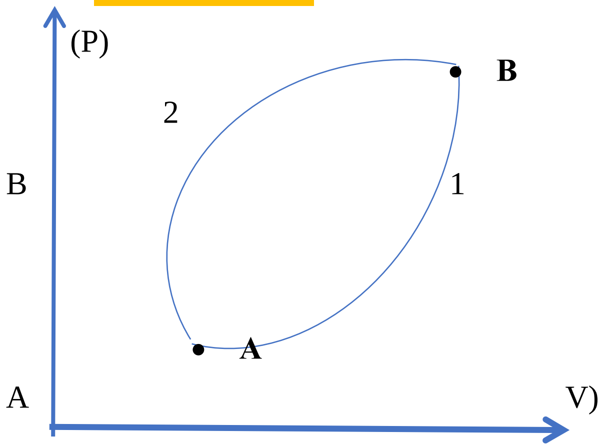
- Une machine prélève de la chaleur Q à une source froide à la température $T_2 < T_1$ et la cède intégralement à une source chaude à la température T_1.
- A machine takes heat Q from a cold source at temperature $T_2 < T_1$ and transfers it in its entirety to a hot source at temperature T_1.
- Since $T_2 < T_1$ this heat transfer is impossible according to Clausius' statement and the cycle is therefore irreversible in practice.

The energy balance for this machine is written as follows:

$$\oint \frac{\mathrm{d}Q}{T} = \frac{\mathrm{d}Q}{T_2} - \frac{\mathrm{d}Q}{T_1}$$

$$\int_A^B \frac{\mathrm{d}Q}{T_2} + \int_B^A \frac{\mathrm{d}Q}{T_1} = \int_A^B \frac{\mathrm{d}Q}{T_2} - \int_A^B \frac{\mathrm{d}Q}{T_1} = \frac{Q}{T_2} - \frac{Q}{T_1}$$

$$\boxed{\Rightarrow \sum \frac{\mathrm{d}Q}{T} > 0} \qquad \textbf{(IV.1)}$$



Cycle of a reversible transformation

Given that the process of transferring a quantity of heat from a cold source and transferring it in its entirety to another hot source is impossible according to Clausius, we can deduce that for a real machine cycle, we need:

CLAUSIUS theorem $$\boxed{\Rightarrow \sum \frac{\mathrm{d}Q}{T} \geq 0} \qquad \textbf{(IV. 2)}$$

We can **therefore** deduce that for a reversible cycle: $\sum \frac{\mathrm{d}Q}{T} = 0$

And for an irreversible cycle: $\sum \frac{\mathrm{d}Q}{T} < 0$

IV.4 The concept of entropy

1- Consider a thermodynamic cycle consisting of **two reversible transformations** from A to B (transformation 1) and from B to A (transformation 2).

Drawing up an energy balance for the cycle: $\sum \frac{dQ}{T} = \int_A^B \frac{dQ_1}{T} + \int_B^A \frac{dQ_2}{T} = 0$

$$\Rightarrow \int_A^B \frac{dQ_1}{T} - \int_A^B \frac{dQ_2}{T} = 0$$

$$\Rightarrow \int_A^B \frac{dQ_1}{T} = \int_A^B \frac{dQ_2}{T} = \int_A^B \frac{dQ_{reve}}{T}$$

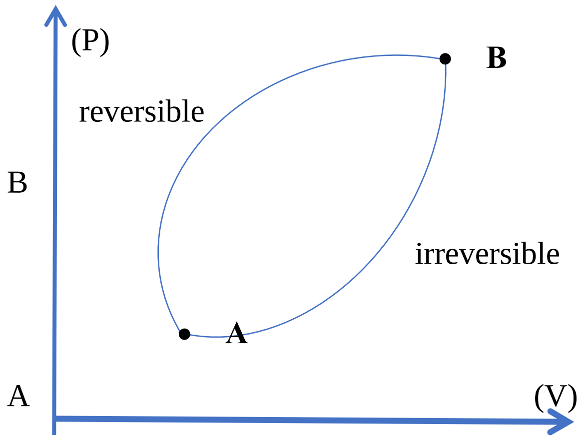
We deduce that the integral $\int_A^B \frac{dQ_{reve}}{T}$ for a reversible transformation:

- Depends only on the initial state (A) and the final state (B).
- Does not depend on the route taken.
- So; $\int_A^B \frac{dQ_{reve}}{T}$ is a state function that we will call entropy (S).

So, if we assume that: $dS = \int_A^B \frac{dQ_{reve}}{T}$

So, the entropy variation: $$\boxed{\Delta S = S_B - S_A = \int_A^B \frac{dQ_{reve}}{T}} \qquad \textbf{(IV. 3)}$$

2- Now consider an irreversible cycle consisting of an irreversible transformation from the initial state (A) to the final state (B) and a reversible transformation from (B) to (A).



Drawing up an energy balance for the cycle: $\sum \frac{dQ}{T} = \int_A^B \frac{dQ_{irr}}{T} + \int_B^A \frac{dQ_{rev}}{T} < 0$

$$\Rightarrow \int_A^B \frac{dQ_{irr}}{T} - \int_A^B \frac{dQ_{rev}}{T} < 0$$

$$\Rightarrow \int_A^B \frac{dQ_{irr}}{T} < \int_A^B \frac{dQ_{rev}}{T}$$

$$\boxed{\frac{dQ_{irr}}{T} < \mathrm{dS} \quad ; \Rightarrow \Delta S > \int_A^B \frac{dQ_{irr}}{T}} \qquad \textbf{(IV. 4)}$$

IV.5. Differential expressions of entropy

The entropy of a thermodynamic system can be calculated according to the type and nature of the transformation it undergoes.

IV.5.1. Isotherme de transformation réversible

$$\Delta S = \int_1^2 \frac{dQ_{rev}}{T} = \frac{1}{T} \int dQ_{rev} = \frac{Q_{rev}}{T}$$

$$T = \mathrm{cste} \quad ; \Rightarrow \ \Delta U = 0 \ \ et \ W = \ -Q$$

$$W_{12} = -\int_1^2 PdV = -\int_1^2 nRT\frac{dV}{V} = -nRT\int_1^2 \frac{dV}{V} = +nRTln\frac{V_1}{V_2}$$

So: $Q_{rev} = nRTln\frac{V_2}{V_1} = nRTln\frac{P_1}{p_2}$

We will have: $\boxed{\Rightarrow \Delta S = \frac{Q_{rev}}{T} = nRln\frac{V_2}{V_1} = nRln\frac{P_1}{P_2}}$ **(IV. 5)**

IV.5.2. Reversible isobaric transformation

$P = \text{cste} \;\; ; \Rightarrow \; dQ_{rev} = dQ_P = nC_P\,dT$

$$\Rightarrow \Delta S = \int_1^2 dS = \int_1^2 \frac{dQ_{rev}}{T} = \int_1^2 \frac{dQ_P}{T} = \int_1^2 \frac{nC_P\,dT}{T}$$

Si $C_P = \text{cste}$,

We will have: $\boxed{\Rightarrow \Delta S = nC_P\,ln\frac{T_2}{T_1}}$ **(IV. 6)**

IV.5.3. Reversible isochore transformation

$V = \text{cste} \;\; ; \Rightarrow dQ_{rev} = dQ_V = nC_V\,dT$

$$\Rightarrow \Delta S = \int_1^2 dS = \int_1^2 \frac{dQ_{rev}}{T} = \int_1^2 \frac{dQ_{PV}}{T} = \int_1^2 \frac{nC_V\,dT}{T}$$

Si $C_P = \text{cste}$,

We will have: $\boxed{\Rightarrow \Delta S = nC_V\,ln\frac{T_2}{T_1}}$ **(IV. 7)**

IV. 5. 4. Transformation reversible adiabatique

$$\boxed{dQ_{rev} = 0 \;\Rightarrow \Delta S = \int_1^2 dS = \int_1^2 \frac{dQ_{rev}}{T} = 0} \qquad \textbf{(IV. 8)}$$

IV.5.5. During a change of state

The quantity of heat that accompanies a change of physical state of matter is latent heat.

So: $dQ_{rev} = \Delta H$

$$\Rightarrow \Delta S = \int_1^2 dS = \int_1^2 \frac{dQ_{rev}}{T} = \int_1^2 \frac{dQ_{PV}}{T} = \frac{Q_{rev}}{T}$$

$$\boxed{\Rightarrow \Delta S = \frac{\Delta H}{T}} \qquad \textbf{(IV. 9)}$$

With: $\boldsymbol{\Delta H}$: Latent heat of vaporisation, fusion or sublimation.

$\boldsymbol{T}$: temperature of the change in the physical state of matter.

IV. 6 New expressions for entropy.

a) Entropy as a function of variables T and V:

According to the 1er principle of thermodynamics

: $dU = dW + dQ$

With: $dW = -PdV$

According to the 2^{éme}principle of thermodynamics

: $\text{dS} = \frac{dQ_{rev}}{T}$

$\Rightarrow dU = TdS - PdV$

$\Rightarrow nC_V \, dT = TdS - PdV$

For one mole of perfect gas: $PV = nRT \quad \Rightarrow P = \frac{RT}{V}$

So: $C_V \, dT = TdS - \frac{RT}{V} dV$

$$\boxed{\Rightarrow dS = C_V \frac{dT}{T} + \mathrm{R}\ \frac{dV}{V}} \quad \dots .\ (1)$$

b) Entropy as a function of the variables T and P:

According to the1^{er} principle of thermodynamics: $dH = dU + (dPV)$

$$\Rightarrow\ dH = dU + PdV + VdP\ ;\ \text{Or}\ \ dU = TdS - PdV$$

$$\Rightarrow\ dH = TdS + VdP$$

For one mole of perfect gas: $PV = nRT \qquad \Rightarrow\ V = \frac{RT}{P}$

So: $C_P\, dT \ \ = TdS - \frac{RT}{P} dP$

$$\boxed{\Rightarrow dS = C_P \frac{dT}{T} + \mathrm{R}\ \frac{dP}{P}} \quad \dots\ (2)$$

c) Entropy as a function of the variables V and P

$$\mathrm{R}\ \frac{dV}{V} = (C_P - C_V)\frac{dT}{T} - R\ \ \frac{dP}{P}$$

Expressions (1) and (2) represent the change in entropy (dS); therefore:

$$dS = C_V \frac{dT}{T} + \mathrm{R}\ \frac{dV}{V} = C_P\ \frac{dT}{T} + \mathrm{R}\ \frac{dP}{P}$$

According to MAYER's relationship: $(C_P - C_V) = R$

$$\text{So:}\quad \boxed{\frac{dT}{T} = \frac{dV}{V} + \frac{dP}{P}} \quad \dots\ (3)$$

Replacing (3) in (1) or (2):

(1) $\Rightarrow dS = C_V\left(\frac{dV}{V}+\frac{dP}{P}\right)+R\frac{dV}{V} = C_V\,\frac{dV}{V}+C_V\,\frac{dP}{P}+C_P\,\frac{dV}{V}-C_V\,\frac{dV}{V}$

Donc : $\boxed{dS = C_P\,\frac{dV}{V}+C_V\,\frac{dP}{P}}$

Ou bien :

(2) $\Rightarrow \boldsymbol{dS} = C_P\left(\frac{dV}{V}+\frac{dP}{P}\right)-R\,\frac{dP}{P} = C_P\,\frac{dV}{V}+C_P\,\frac{dP}{P}$ - $C_P\,\frac{dP}{P}-C_V\,\frac{dP}{P}$

So: $\boxed{dS = C_P\,\frac{dV}{V}+C_V\,\frac{dP}{P}}$ **(IV.10)**

Application:

1. a) Calculate the change in entropy of 2 moles of perfect gas which expands from 30 to 50litres isothermally and irreversibly.

b) Calculate the entropy created.

2. Same question as 1-a, but the expansion is no longer isothermal, the temperature dropping from 300K to 290K. We give Cv = 5

cal.mol^{-1}. K^{-1}

Solution:

1. a) Change in entropy of the system

$$\Delta S_{sys} = \int_1^2 \frac{dQ_{rev}}{T} = \frac{1}{T}\int dQ_{rev} = \frac{Q_{rev}}{T}$$

$$T = \text{cste} \;\; ; \Rightarrow \;\Delta U = 0 \;\; et\; W = -Q$$

$$W_{12} = -\int_1^2 PdV = -\int_1^2 nRT\frac{dV}{V} = -nRT\int_1^2\frac{dV}{V} = +nRTln\frac{V_1}{V_2}$$

$$Q_{rev} = nRTln\frac{V_2}{V_1} = nRTln\frac{P_1}{P_2}$$

$$\boxed{\Delta S_{sys} = \frac{Q_{rev}}{T} = nRln\frac{V_2}{V_1} = 2(8.314)ln\frac{50}{30} = 8.52\,j/k}$$

b) Entropy created :

$$\Delta S_{ech} = \int_1^2 \frac{dQ_{ech}}{\Delta S_{ech}} = \frac{1}{T_{ech}}\int dQ_{irr} = \frac{Q_{err}}{T_{ech}} = \frac{-W_{err}}{T_{ech}}$$

$$\Delta S_{ech} = \frac{1}{T}\int P_{ex}\,dV = \frac{P_{ex}}{T_{ech}}\,(V_2 - V_1)$$

We have: $P_1V_1 = P_2V_2 = nRT \quad \Rightarrow P_2 = \frac{nRT}{V_2}$

$$\boxed{\Delta S_{ech} = \frac{nR}{V_2}\,(V_2 - V_1) = \frac{2(8.314)}{50}\,(50 - 30) = 6.68\,j/k}$$

$$\boxed{\text{So: } \Delta S_{creée} = \Delta S_{sys} - \Delta S_{ech} = 8.52 - 6.68 = 1.84\,j/k}$$

2. System entropy variation

$$\Delta S = \int_1^2 dS = \int_1^2 \frac{dQ_{rev}}{T} = \int_1^2 \frac{dU - dW}{T} = \int_1^2 \frac{nC_v dT}{T} + \int_1^2 \frac{nC_P dT}{T}$$

$$\boxed{\Rightarrow \Delta S = n\left(C_V\,ln\frac{T_2}{T_1} + C_P\,ln\frac{V_2}{V_1}\right) = 7.1\,j/k}$$

IV.7. Entropy and reaction

IV.7.1 Entropy variation during a chemical reaction

The entropy function is used to predict the evolution of a thermodynamic system. It can be positive or zero. In the case of chemical reactions, entropy can be positive if the reaction is spontaneous and zero if it is reversible (balanced).

⇒ The change in entropy of pure bodies during a chemical reaction can be calculated easily: aA + bB → cC +dD

The following relationship gives the change in entropy of a chemical reaction under standard conditions (P = 1 atm and T = 298K) involving

$$\boxed{\Delta S_R^0 = \sum \Delta S_{298}^0(Products) - \sum \Delta S_{298}^0(\text{Reactives})} \qquad \textbf{(III.11)}$$

Example:

$$\mathbf{C_3H_{8\,(g)} + 5O_{2\,(g)} \rightarrow 3CO_2 + 4H_2O_{(g)}}$$

S^0	270	205	213.6	189	j.mol^{-1}. K^{-1}

ΔS_R^0 =(3×213.6 +4×189) - (270 +5×205)

ΔS_R^0 = 101.8 j.mol^{-1}. K^{-1}

IV.7.2. Evolution of reactions

To summarise, we can see that in general a reaction evolves:

- By releasing energy (Exothermic Q> 0)

- By releasing gases (Entropy S> 0)

Reaction enthalpy and entropy are the driving forces behind reactions, so if:

ΔH	ΔS	Consequences
$\Delta H < 0$	$\Delta S > 0$	Total reaction (violent)
$\Delta H > 0$	$\Delta S > 0$	Endothermic balanced reaction (to be activated)
$\Delta H < 0$	$\Delta S < 0$	Exothermic balanced reaction
$\Delta H > 0$	$\Delta S < 0$	Impossible reaction

The change in entropy of a chemical reaction at a **new temperature** is given by **Kirchoff** 's relation:

$$\Delta S_R^0(T) = \Delta S_R^0(T_0) + \int_{T0}^{T} \Delta C_P^0 \frac{dT}{T}$$

Avec : $\Delta C_P = \sum C_P((Products)) - \sum C_P(\text{Reactives})$

Not forgetting the stoichiometric coefficients of the reaction.

Chapter V:

Free energy and enthalpy - Criteria for the evolution of a system

V.1 Gibbs free energy

Gibbs free enthalpy (G) is an essential function for the study of chemical reactions; it allows us to predict whether a chemical reaction carried out at T and P is theoretically possible and in what direction it will evolve. Enthalpy and entropy of reaction. They combine to define Gibbs free energy(G)

The following relationship represents the GIBBS state function known as free enthalpy

$$dG = dH - TdS$$

La variation d'énergie libre de Gibbs $\Delta G = \Delta H - T\Delta S$ permet d'interpréter le comportement des réactions :

The Gibbs free energy variation $\Delta G = \Delta H - T\Delta S$ can be used to interpret the behaviour of reactions:

- If the reaction is spontaneous, $\Delta G < 0$.
- If the reaction is in equilibrium, $\Delta G = 0$.
- If the reaction needs a catalyst, $\Delta G > 0$.

ΔG_R^0 It can also be calculated using the following expression:

$$\boxed{\Delta G_R^0 = \sum \Delta G_{298}^0(Products) - \sum \Delta G_{298}^0(\text{Reactives})} \qquad \textbf{(IV. 12)}$$

ΔG_R^0 Can also be calculated at a temperature T is given by the following relationship:

$$\boxed{\Delta G_T^0 = \Delta H_T^0 - T\Delta S_T^0} \qquad \textbf{(IV. 13)}$$

With ΔG_T^0 et ΔS_T^0 are calculated by applying Kirchoff's law.

The standard free enthalpy of all simple bodies is zero; $\Delta G_R^0 = 0$.

V.2 Free Enthalpy and Chemical Equilibrium

V.2.1. Variation of the molar free enthalpy of a pure substance with temperature and pressure

The free enthalpy "G" or Gibbs energy is defined by the expression:

$$G = H - TS$$

Its differential form is: $dG = d(H - TS)$

$$dG = dH - TdS - SdT \quad ;$$

With: $H = U + PV$ et $dH = dU + PdV + VdP$

$$dG = dU + PdV + VdP - TdS - SdT$$

$dU = dW + dQ$; $dW = -PdV$; if the transformation is reversible;

$$dQ_{irr} = TdS$$

$$\boxed{dG = VdP - SdT} \quad \textbf{(IV. 14)}$$

At constant pressure $(dP = 0)$ we have: $dG = -SdT$

At constant temperature $(dT = 0)$ we have: $dG = VdP$

The free enthalpy G of a gaseous component. $dG = VdP - SdT$ a $T = Cs$; $dT = 0$; d'ou

$dG = VdP$

For one mole of perfect gas: $PV = RT \Rightarrow V = \frac{RT}{P}$

$$dG = \frac{RT}{P} dP$$

$$\int_1^2 dG = RT \int_1^2 \frac{dP}{P}$$

$$\Rightarrow \Delta G = G - G^0 = RT\, ln \frac{P_2}{P_1}$$

Si $P_1 = 1$ atm (standard state) $\Rightarrow$ $\boxed{\Delta G = G - G^0 = RT \ln P_2}$ **(IV. 15)**

With partial pressure of gas i

V.3 Free enthalpy of a chemical mixture or reaction

The reaction is: $aA + bB \rightarrow cC + dD$

- **Let, be the equilibrium constant as a function of partial pressures**

$$K_P = \frac{[P_C]^{\mathrm{c}}.[P_D]^{\mathrm{d}}}{[P_A]^{\mathrm{a}}.[P_B]^{\mathrm{b}}}$$

we have: $\Delta G_R^0 = \sum \Delta G_{298}^0(Products) - \sum \Delta G_{298}^0(Reactifs)$

$= (cG_C + dG_D) - (aG_A + bG_B)$

$= c(G_{C,T}^0 + RTln[P_C]^{\mathrm{c}}) + d(G_{D,T}^0 + RTln[P_D]^{\mathrm{d}}) - a(G_{A,T}^0 + RTln[P_A]^{\mathrm{a}}) - b(G_{B,T}^0 + RTln[P_B]^{\mathrm{b}})$

$= \left(cG_{C,T}^0 + dG_{D,T}^0 - aG_{A,T}^0 - bG_{B,T}^0\right) + RT(c\, Cln[P_C]^{\mathrm{c}} + dln[P_D]^{\mathrm{d}} - a\, ln[P_A]^{\mathrm{a}} - bln[P_B]^{\mathrm{b}})$

$$\Delta G_R^0 = \Delta G^0 + RTln \frac{[P_C]^{\mathrm{c}}.[P_D]^{\mathrm{d}}}{[P_A]^{\mathrm{a}}.[P_B]^{\mathrm{b}}}$$

$$\Delta G_R^0 = \Delta G^0 + RTlnK_P$$

At equilibrium, $\Delta G_R^0 = 0$ (the system is "dead") $\Delta H = 0$ et $\Delta S = 0$

and so we have $$\boxed{\Delta G^0 = -RTlnK_P \text{ ; or } \quad K_P = e^{\frac{-\Delta G^0}{\mathrm{RT}}}} \qquad \textbf{(IV.16)}$$

- **Let, be the equilibrium constant as a function of concentrations**

$$K_C = \frac{[C\ ]^{\mathrm{c}}.[\mathrm{D}]^{\mathrm{d}}}{[\mathrm{A}]^{\mathrm{a}}.[\mathrm{B}]^{\mathrm{b}}}$$

In the gas phase, if the gases are perfect, we have: $P_i V = n_i RT$

$$[\mathrm{A}] = \frac{n_A}{\mathrm{V}} = \frac{P_A}{RT}\ ; \quad [\mathrm{B}] = \frac{n_B}{\mathrm{V}} = \frac{P_B}{RT}; \quad [\mathrm{C}] = \frac{n_C}{\mathrm{V}} = \frac{P_C}{RT}\ ; \quad [\mathrm{D}] = \frac{n_D}{\mathrm{V}} = \frac{P_D}{RT}$$

$[\mathrm{A}]$; $[\mathrm{B}]$; $[\mathrm{C}]$ et $[\mathrm{D}]$ Are the concentrations of the constituents A ; B ; C et D

$$\Rightarrow K_C = \frac{\left[\frac{P_C}{RT}\right]^c . \left[\frac{P_D}{RT}\right]^d}{\left[\frac{P_A}{RT}\right]^a . \left[\frac{P_B}{RT}\right]^b}$$

$$K_C = \frac{[P_C\ ]^c.[P_D]^d}{[P_A]^a.[P_B]^b} \frac{[RT\ ]^{a+b}.}{[RT]^{c+d}.}$$

Where: Δn ; the difference in the number of moles of gaseous compounds between the final state and the initial state

$$\Delta n = (c + d) - (a + b)$$

So : $$\boxed{K_C = K_P[RT\ ]^{-\Delta n}} \qquad \textbf{(IV. 17)}$$

- **Let** K_χ **,be the equilibrium constant as a function of mole fractions** χ_i

$$K_X = \frac{[\chi_\mathrm{C}\ ]^{\mathrm{c}}.[\chi_\mathrm{D}]^{\mathrm{d}}}{[\chi_\mathrm{A}]^{\mathrm{a}}.[\chi_\mathrm{B}]^{\mathrm{b}}}$$

In the gas phase, if the gases are perfect, we have: $P_i V = n_i RT$

$$\chi_i = \frac{n_i}{\sum n_i} = \frac{P_i}{P_t} \text{ ; } avec\ P_t = \ total\ pressure$$

$$\chi_A = \frac{P_A}{P_t} \text{ ; } \chi_B = \frac{P_B}{P_t} \text{ ; } \chi_C = \frac{P_C}{P_t} \text{ ; } \chi_D = \frac{P_D}{P_t}$$

$$\Rightarrow K_X = \frac{\left[\frac{P_C}{P_t}\right]^c \cdot \left[\frac{P_D}{P_t}\right]^d}{\left[\frac{P_A}{P_t}\right]^a \cdot \left[\frac{P_B}{P_t}\right]^b}$$

$$\Rightarrow K_X = \frac{[P_C]^c . [P_D]^d}{[P_A]^a . [P_B]^b} \frac{[P_t]^{a+b}.}{[P_t]^{c+d}}$$

So: $\boxed{K_X = K_P [P_t]^{-\Delta n}}$ **(IV. 18)**

V.4. Variation of the equilibrium constant and evolution of the equilibrium with temperature (Van't Hoff relationship)

In addition, the relationship: $\Delta G^0 = -RTlnK_c$ With: $\Delta G^0 = \Delta H^0 - T\Delta S^0$

On a: $lnK_c = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$

So, we have: $lnK_1 = -\frac{\Delta H^0}{RT_1} + \frac{\Delta S^0}{R}$; et $lnK_2 = -\frac{\Delta H^0}{RT_2} + \frac{\Delta S^0}{R}$

$$lnK_1 - lnK_2 = -\frac{\Delta H^0}{RT_1} + \frac{\Delta S^0}{R} + \frac{\Delta H^0}{RT_2} - \frac{\Delta S^0}{R}$$

Van'Hoff relationship $\boxed{ln\frac{K_2}{K_1} = \frac{\Delta H^0}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]}$ **(IV. 19)**

This is the Van't Hoff relationship. It makes it easy to estimate K at various temperatures from the value of ΔH^0..

Corrected exercises

Exercise 01:

Calculate the standard free enthalpy of formation of ozone (O3) at 298K from the values given below:

$\Delta H°f(O_3) = 34 Kcal. mol^{-1}$

$S°O2(g) = 49$ cal. K^{-1}. mol^{-1}

$S°SO_3(g) = 56.8$ cal. K^{-1}. mol^{-1}

Answers: 1

Calculate the standard free enthalpy ($\Delta G°$)

$O_2 + (1/2)\ O_2 \rightarrow (3/2)\ O_2 \rightarrow O3$

$\Delta G = \Delta(H-TS)$

$\Delta G = \Delta H - T\ \Delta S - S\ \Delta T$

Standard state $T=298K=C_{ste} \rightarrow \Delta T=0$

$\Delta G°r,298 = \Delta H°r, 298 - T\Delta S°r, 298$

$\Delta S° = SO_3(g) - S°O_2(g) = 56,8 - (3/2).49 = -16,7$ $cal.K^{-1}.mol^{-1}$

$\Delta G°r, 298 = 34\ .103 - 298(-16,7) = 39$ Kcal /mol

Exercise 2:

Calculate the change in free enthalpy of 1mol of water during the spontaneous transformation at atmospheric pressure:

$H_2O(Liquid) \rightarrow H_2O(Ice)$

-10°C -10°C

Corrected: $\Delta S \;\; \Delta H_R^0 \;\; \Delta G_T^0$

1.

$$\begin{tikzcd}
H_2O(l) \arrow[r] \arrow[d, "\Delta S_1^0\ \Delta H_1^0 \quad \text{-10°C}"'] & H_2O\ (gla) \arrow[d, "\Delta S_3^0\ \Delta H_3^0 \quad \text{-10°C}"] \\
H_2O(l) \arrow[r, "\Delta S_2^0 \quad \Delta H_2^0"] & H_2O\ (gla)
\end{tikzcd}$$

2.

$$\Delta H_R^0 = \Delta H_1^0 + \Delta H_2^0 + \Delta H_3^0$$

$$\Delta H_1^0 = nc_p(H2O, L).\Delta T = 1.18(273 - 268) = 180cal$$

$$\Delta H_2^0 = nc_p\Delta H_{1fusion\ 273}^0\ (H2O, s) = 1438cal$$

$$\Delta H_3^0 = nc_p(H2O, s).\Delta T = 1.9(263 - 273) = -1348cal$$

3.

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\Delta S_1^0 = mc_p(H2O, L)\ \int_{268}^{273} \frac{dT}{T}$$

$$\Rightarrow \Delta S_1^0 = 1.1.8 \ln\left(\frac{273}{268}\right) = 0.672cal/K$$

$$\Delta S_2^0 = \frac{m\Delta H_{2fusion}^0\ (H2O, s)}{T_{fusion}}$$

$$\Rightarrow \Delta S_2^0 = -1\left(\frac{1438}{273}\right) = -5.27cal/K$$

$$\Delta S_3^0 = nc_p(H2O, l)\int_{268}^{273} \frac{dT}{T}$$

$\Rightarrow \Delta S_3^0$ = 1.9ln (263/278) =-0.336 cal/K

$$\Delta S = 0.672 - 5.27 - 0.336$$

$$\Delta S = -4.39\ cal/K$$

4.

$\Delta G_T^0 = \Delta H_T^0 \ - T\Delta S_T^0$

$\Delta G_T^0 = -1348 - 263(-4.93) = -50.36\, cal$

Exercise3

1.calculate the standard free enthalpy ΔG_T^0 at 25°C of the following reaction:

N_2 (g) + O_2 (g) →2NO (g)

Knowing that: S°298(NO, g) = 50,34 u.e;

S°298 (N_2, g) = 45,77 u.e.

S°298 (O_2, g) = 49,00 u.e ;

Δh°f,298 (NO, g) = 21,6 $kcal.mol^{-1}$,

(Entropy unit: u.e = $cal.mol^{-1}. K^{-1}$).

Answers: 1.

Standard free enthalpy $\Delta G_{298}^0$of the reaction:

$\Delta G_T^0 = \Delta H_T^0 \ - T\Delta S_T^0$

$\Delta H_{298}^0 \ = 2\Delta H_{f\,298}^0\, (NO, g) = 2(21.6) = 43.2Kcal$

$\Delta S_{298}^0 \ = 2S_{298}^0\, (NO, g) - \ S_{298}^0\, (N_2, g) - S_{298}^0\, (O_2, g)$

ΔS_{298}^0 = *2 (50.34) -45.77- 49 = 5.9 ue*

⇨ ΔG_T^0= *43.2- (298 .5.91.10^{-3}) = 41.44 K cal*

$\Delta G_{298\,r}^0$ is positive, so the reaction is impossible in direction 1 (direction of formation of NO (g)

Exercise 4:

At 298K, 100 moles of NH_3, 50 moles of N_2 and 70 moles of H_2 are mixed under a total pressure of 700 bar What is the free enthalpy of the reaction:

(1/2) N_2+ (3/2) $H_2 \leftrightarrow NH_3$

$$\Delta G^0_{NH_3} = -3.97 Kcal/mol$$

1. calculate the standard free enthalpy of the reaction:

$$\Delta G^0_R = RT(n_1 \ln x_1 + n_2 \ln x_2 + n_3 \ln x_3)$$

$$x_1 = \frac{n_1}{(n_1 + n_2 + n_3)} = \frac{100}{100 + 50 + 70} = 0.455$$

$$x_2 = \frac{n_2}{(n_1 + n_2 + n_3)} = \frac{50}{100 + 50 + 70} = 0.455$$

$$x_3 = \frac{n_3}{(n_1 + n_2 + n_3)} = \frac{70}{100 + 50 + 70} = 0.455$$

$$\Delta G^0_{NH_3} = 2(298)(100 ln 0.455) + 50 ln 0.227 + 70 ln 0.318 = 138919\, j$$

2. Calculation of free enthalpy

$$\Delta G = \Delta G^0 + RT ln K_P$$

$$K_P = P_{NH3}/(P_{N_2}^{\frac{3}{2}} + P_{H_2}^{\frac{3}{2}})$$

Calculates partial pressures: $P_i = x_i P$

$$P_{NH3} = x_{NH3}\, P = 0.455 X 700 = 318.5\, bar$$

$$P_{N2} = x_{N2}\, P = 0.227 X 700 = 222.5\, bar$$

$$P_{H2} = x_{H2}\, P = 0.318 X 700 = 222.5\, bar$$

$$K_P = \frac{318.5}{222.5_{N_2}^{\frac{3}{2}} + 222.5_{H_2}^{\frac{3}{2}}} = 0.0076$$

$\Rightarrow \Delta G = \Delta G^0 + RTlnK_P$

$\Delta G = -198919 + 2\,X\,298RTln0.0076 = -141827.25cal$

V.5. Le Chatelier principle

Any change in a state variable leads to a change in the system, which in turn leads to a new equilibrium. Le **Chatelier** 's Principle makes it possible to predict the direction of the change: "A system in equilibrium subjected to a change in one of its state variables reacts in such a way as to reduce or cancel out this change".

- **Influence of pressure**:

  An increase in pressure causes the system to move in the direction that will reduce stress, i.e. reduce pressure (and vice versa).

  Exemples 1 : $N_{2\,(g)} + 3\,H_{2\,(g)} == 2NH_{3\,(g)}$,

  If P increases, the reaction evolves towards NH_3 n of mol (NH_3) = 2< 4

  Examples 2: $H_{2\,(g)} + I_{2\,(g)} == 2NI_{\,(g)}$,

  P does not influence equilibrium (n of mol = 2; 2)

- **Influence of temperature** :

  An increase in temperature causes the system to move in the direction that will absorb the heat, i.e. in the endothermic direction (and conversely: decrease in T => exothermic direction).

  Example 1: $N_{2\,(g)} + 3\,H_{2\,(g)} == 2NH_{3\,(g)}$ $\Delta H_R^0 = -62.2KJ$

  If T increases, the reaction progresses towards N_2 and H_2

  If T decreases, the reaction progresses towards NH_3

- **Influence of composition:**

  The addition of a reagent to a system at equilibrium causes the reaction to proceed in the direction of product formation. (The addition of products regenerates the reactants). Consequently, the elimination of a product (by volatilisation or precipitation) leads to the total consumption of the reagents by shifting the chemical equilibrium.

Example: $H_2SO_4 + NaCl \rightarrow NaHSO_4 + HCl\uparrow$

$AgNO_3 + NaCl \rightarrow Na^+ + NO_3^- + AgCl\downarrow$

V.6. Dissociation coefficient in homogeneous phase

When a substance undergoes dissociation in a homogeneous medium, its characteristic at the equilibrium state is controlled by a number α called the dissociation coefficient.

$\alpha = \frac{n^`}{n_0}$ ; $n^`$: dissociated mole number; n_0: initial mole number

	$AB_{(g)}$	= $A_{(g)}$,	+ $B_{(g)}$,
at T=0	$n_0 = 0$	0	0
at equilibrium	$n_0 - n^`$	$n^`$	$n^`$

That is: $K_P = \frac{P_A.P_B}{P_{AB}}$

Total number of moles at equilibrium:

$$n_t = n_{AB} + n_A + n_B = n_0 - n_0\alpha + n_0\alpha + n_0\alpha$$

$$n_t = n_0(1 + \alpha)$$

$$\alpha = 0\% \rightarrow 100\%$$

t	AB	A	B	α
0	n_0	0	0	0
at equilibrium	$n_0(1-\alpha)$	$n_0\alpha$	$n_0\alpha$	α
n_t	$n_0(1+\alpha)$			1

$$K_P = \frac{P_A.P_B}{P_{AB}} \Rightarrow lnK_P = \frac{-\Delta G^0}{RT}$$

$$P_A = \chi_A\, P_t = \frac{n_A}{n_t}\, P_t = \frac{n_0\alpha}{n_0(1+\alpha)}\, P_t = \frac{\alpha}{(1+\alpha)}\, P_t$$

$$P_B = \chi_B\, P_t = \frac{n_B}{n_t}\, P_t = \frac{n_0\alpha}{n_0(1+\alpha)}\, P_t = \frac{\alpha}{(1+\alpha)}\, P_t$$

$$P_{AB} = \chi_{AB}\, P_t = \frac{n_{AB}}{n_t}\, P_t = \frac{n_0(1-\alpha)}{n_0(1+\alpha)}\, P_t = \frac{(1-\alpha)}{(1+\alpha)}\, P_t$$

$$\text{So: } K_P = \frac{\frac{\alpha}{(1+\alpha)} P_t . \frac{\alpha}{(1+\alpha)} P_t}{\frac{(1-\alpha)}{(1+\alpha)} P_t} = \frac{\alpha^2}{(1-\alpha^2)}\ P_t$$

$$K_P(1-\alpha^2) = \alpha^2\, P_t \Rightarrow \alpha^2(\,P_t + K_P) = K_P$$

$$\boxed{\Rightarrow \alpha^2 = \frac{K_P}{P_t + K_P}\ ;donc\ \alpha = \sqrt{\frac{K_P}{P_t + K_P}}} \qquad \textbf{(IV. 20)}$$

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