THERMODYNAMICS & CHEMICAL EQUILIBRIA

1st year Common Core

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Foreword

Chemical thermodynamics makes it possible to evaluate the energies exchanged between a system and its external environment when it is subjected to a transformation or change of state. It is science that governs these exchanges, which informs us about the spontaneity of chemical reactions, the direction of their movement as well as their n accompanying changes of state and chemical reactions as well as their endothermic or exothermic nature.

This handout of courses entitled "Thermodynamics & Chemical Equilibria" is intended for students in the common core: SNV, agronomy, medical studies and pharmaceutical studies. It focuses on the understanding of energy exchanges between a closed thermodynamic system, the site of a transformation, and the external environment. It consists of five chapters.

The first chapter deals with the basic notions of thermodynamics, such as the signs and conventions of different forms of energy, the different types of systems, state variables, and state functions. Reversible and irreversible transformations are also presented in this chapter.

In chapter 2, we present the 1st law of thermodynamics and its statement.

Chapter 3 illustrates the application of the 1st law to chemistry.

Chapter 4 presents the 2nd and 3rd laws of thermodynamics. Chapter 5 deals with chemical balances. Finally, we support this handout with a series of corrected exercises, carefully chosen for the illustration of the different aspects of Thermodynamics and the presentation of various levels of difficulty. The solutions of the exercises are given to allow the student to self-evaluate.

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Chapter I: Definitions and Conventions in Thermodynamics

I.1. Introduction

Thermodynamics makes it possible to study the exchange of energy between a system and the external environment and, in particular, the transformations of heat energy into any other form of energy. It plays an important role in the chemical industry, as it allows the study of the thermodynamics and kinetics of chemical reactions.

Thermodynamics is divided into two categories: macroscopic thermodynamics, known as classical, and microscopic or statistical thermodynamics.

Classical thermodynamics is based on the study of the influence of macroscopic properties of matter such as pressure, temperature, volume, concentration, and mole fraction, on thermodynamic systems. It is based on three principles established on the basis of experimental data. As for statistical thermodynamics: its aim is to find a microscopic model to explain the complex chemical or physical phenomena observed.

I.2. Definitions and conventions

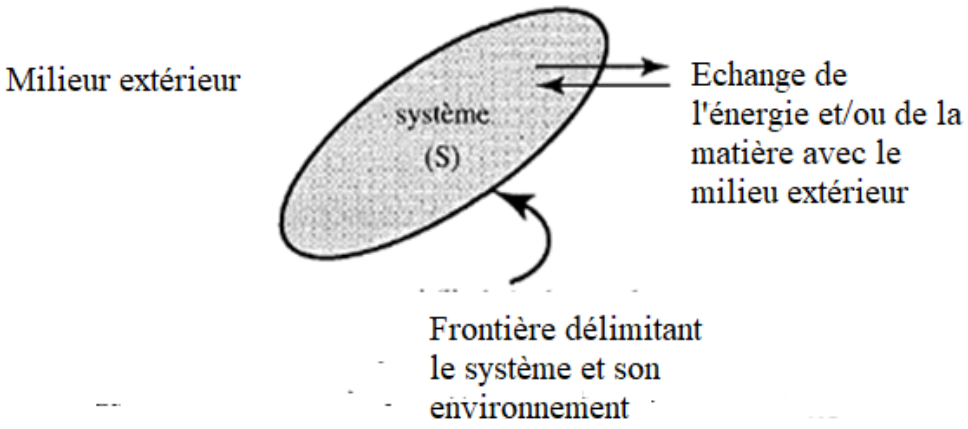
I.2.1.System and external environment

I.2.1.1. Definition of a system

A system is a part of the universe, the seat of a transformation and delimited from the external environment by a boundary (real or fictitious)

In thermodynamics, the universe must be divided into two parts: the ***system*** that constitutes the seat of theoretical and experimental studies, and the ***external environment*** that constitutes the rest of the universe.

Thermodynamics studies the exchange of energy between the system and the external environment (Figure 1).



System, external environment and universe

I.2.1.2.Types of systems

Classical or macroscopic thermodynamics studies the transformations that a system can undergo when it exchanges work and heat as well as matter with the external environment.

When the system exchanges matter with its environment, it is said to be ***open***; if, on the other hand, any exchange of matter is impossible or forbidden, the system is ***closed***. If, finally, any exchange of matter and energy is impossible, the system is ***isolated***.

It is essential to describe the system studied perfectly:

I.2.1.3. Constituents of a system

A system can be described by a set of chemical species that make it up by knowing their physical properties and chemical composition.

I.2.2. Different Forms of Energy and Units and Sign Conventions Used

The energy exchanged between a system and the external environment can be of different forms, distinguishing: **mechanical, wind, solar, water, calorific, radiant**

energy. These different forms have the characteristic of transforming themselves directly or indirectly into each other.

The transformations which are the subject of the various transformations considered in the following will involve two forms of energy, these are ***calorific energy*** or ***heat***, symbolized by Q, and ***mechanical energy*** or ***labor***, symbolized by W; these transformations are called **thermomechanical transformations.**

The unit of labor in the MKSA system is the joule.

The most suitable unit for heat energy is the calorie, which is defined as the amount of heat needed to raise the temperature of 1g of water from 14.5°C to 15.5°C; it is equal to 4.18 joules.

I.2.3. Sign conventions used during energy exchanges between a system and its external environment

When a system receives energy from the external environment, it is assigned sign (+), When a system gives energy to the external environment, it is assigned sign (-).

If Q and W are greater than zero, the system gains heat and mechanical energy from the external environment.

If Q and W are less than zero, the system loses heat and mechanical energy.

Figure 2 shows the different cases of energy exchanges between a system and the external environment

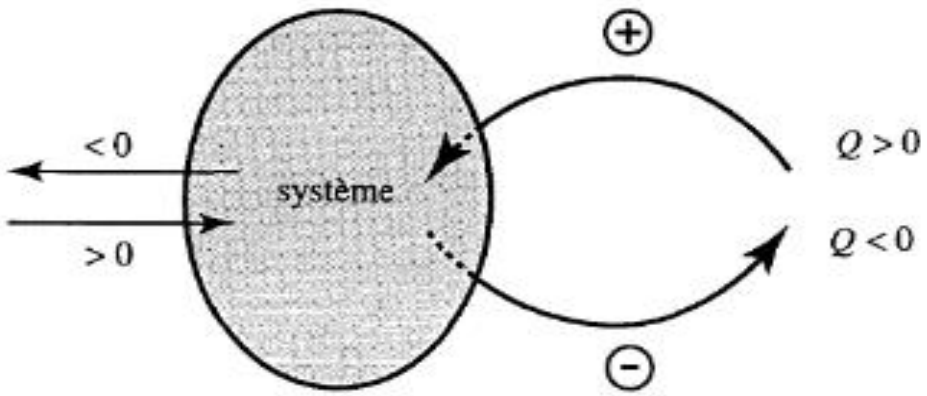


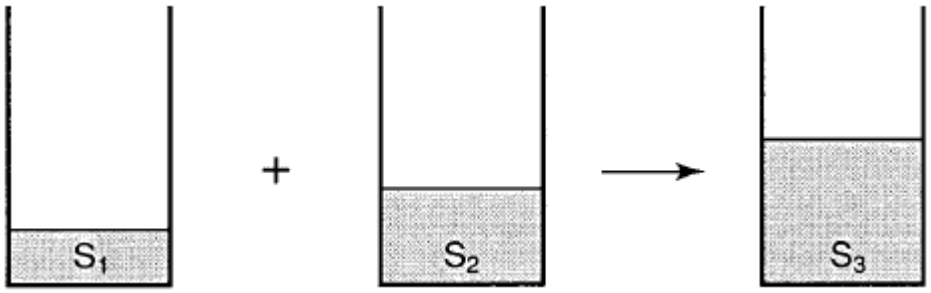
Figure 2: Sign conventions during energy exchanges between a system and the external environment

I.2.4. State of a system

A thermodynamic system is described by knowing a certain number of quantities such as temperature, pressure, volume, chemical composition, known as ***state variables***. A distinction is made between extensive and intensive state variables.

- Extensive variables: these are additive, proportional to the amount of matter in the system such as volume, mass, number of moles, etc.

Example: Let us consider a solution of one liter of HCl (1N) at 25°C, we add 2 liters of HCl (1N) at 25°C. The final volume is 3 liters, which is the sum of the two volumes of the two HCl solutions.



- Intensive variables: they are independent of the quantity of matter such as temperature, pressure, composition, concentration, etc.).

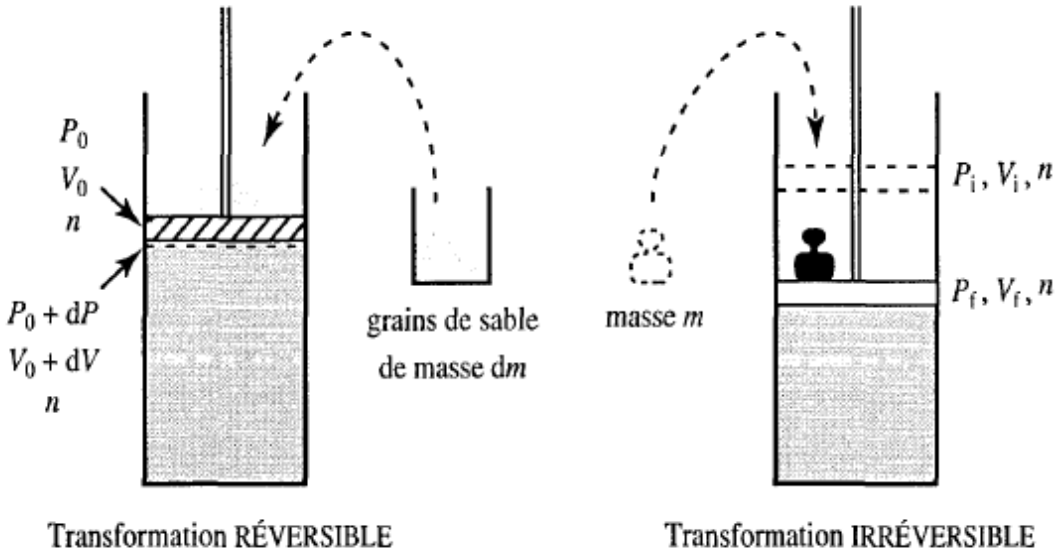
I.2.5. Steady state

Thermodynamic equilibrium is achieved when the system state variables remain constant. If at any point in the system, the temperature, pressure and composition remain constant as a function of time, the system is in mechanical, thermal and chemical equilibrium

I.3. Transformation of a system

I.3.1.Reversible transformation. Irreversible transformation

When a system undergoes a transformation, the value of at least one of the state variables changes, and a new equilibrium state is reached, and consequently it is characterized by new values of state variables.



I.3.1.1.Reversible transformation

If the system passes infinitesimally from one state of equilibrium to another by passing through a succession of states of equilibrium, the transformation is reversible, it is characterized by infinitesimal variations of the state variables between two successive states of equilibrium. On the other hand, at each instant, the state variables of the system differ from those of the external medium only by equally infinitesimal quantities.

I.3.1.2. Irreversible transformation

If, on the other hand, the state variables change abruptly from one equilibrium state to another equilibrium state, then the transformation is irreversible.

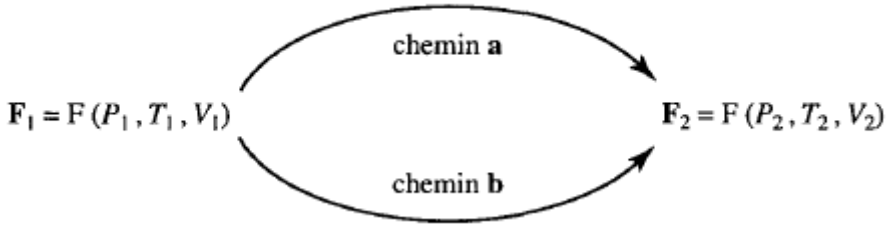
Important special cases:

- **Thermodynamic cycle:**

When a system undergoes a succession of transformations that bring it back to its initial state, it is then said to have gone through a thermodynamic cycle.

I.4. State Function

An F function of (P, V, T) does not depend on the transformation (path followed) that a system can undergo, it is only a function of state variables. Such a function is called a state function.



Example:

We consider a thermodynamic system formed by one mole of ideal gas contained in a closed container, the site of a transformation and described with the help of two independent state variables, the choice of the pairs of which is summarized in the table below:

Variables	⟶	Duties
P, T	⟶	V= V(P,T)
V, T	⟶	P=P(P,V)
P,V	⟶	T=T(P,V)

It is necessary during a thermodynamic study to highlight the choice of variables.

I.4.1. Mathematical treatment of F(x,y)

When a system undergoes an infinitely small transformation, dF is an exact total differential, given by the expression:

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy$$

The characteristic properties of an exact total differential are as follows:

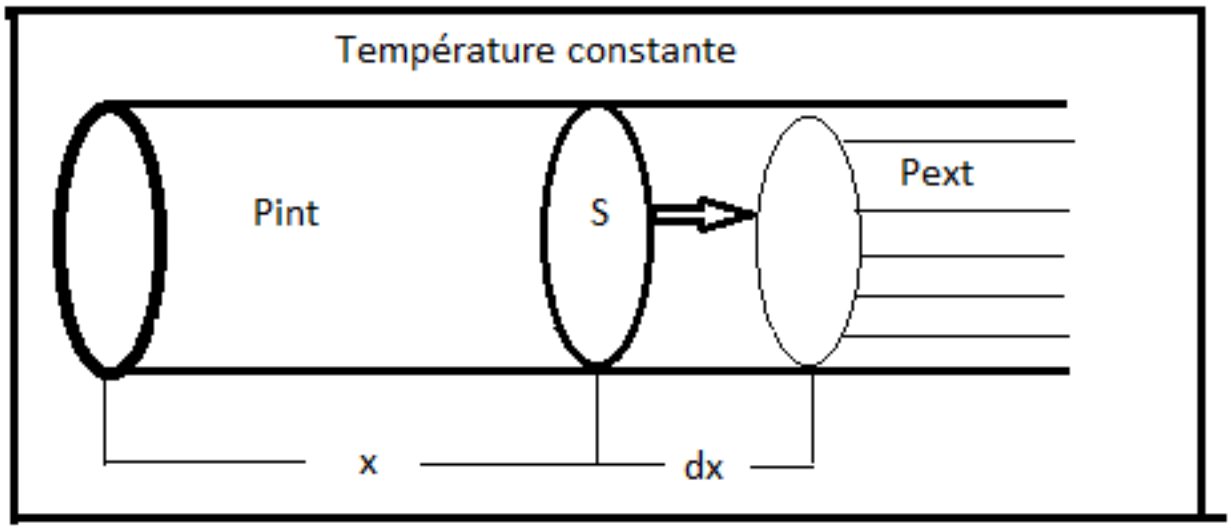
$$\int_{Etat1(x_1,y_1}^{Etat2(x_2,y_2} dF\,(x,y) = F[Etat2(x_2,y_2)] - [F(x_1,y_1)]$$

For a closed thermodynamic cycle:

$$\int dF(x,y) = F(Etat1) - F(Etat\ 1) = 0$$

And finally: $\frac{d}{dy}\left(\frac{\partial F}{\partial x}\right) = \frac{d}{dx}\left(\frac{\partial F}{\partial y}\right)$

Let us consider a system consisting of an ideal gas contained in a cylinder closed by a piston, the whole being placed in a thermostat so that all the transformations carried out take place at a constant temperature. The bottom of the cylinder and the walls form a fixed boundary with the external environment, the piston of section s constitutes a moving boundary. The position of the piston in state 1 is indicated by its abscissa x in relation to the bottom of the cylinder (Figure 1).



Working with an ideal gas during an isothermal thermomechanical transformation

In state 2, the piston has undergone an infinitely small displacement dx and its abscissa is x + dx. The work δW, exchanged when passing from state 1 to state 2, is then

$$\boldsymbol{\delta W = P_{ext} S dx}$$

Gold: system volume variation$Sdx = dV$

Therefore: $$\boldsymbol{\delta W = P_{ext} dV}$$

If we respect the sign conventions adopted previously, is positive if the system has received work and negative if it has given up work. In the case of our example, we have:δW

$$x < x + dx$$

Hence dV is positive: the system has undergone an increase in volume. During this increase, he gave up work; is therefore must be negative and we write:δW

$$\boldsymbol{\delta W = -P_{ext} dV}$$

In the case where dV is negative, there is a decrease in volume, the system receives work and the relationship:

$$\boldsymbol{\delta W = -P_{ext} dV}$$

translates a positive value of .δW

For a finite transformation, symbolized by A, the WA work is given by the expression:

$$\boldsymbol{W_A = -\int_A P_{ext}\, dV}$$

In the case where the transformation can be carried out irreversibly, we then have:

$$\boldsymbol{W_{irr} = -P_{atm} \int_1^2 dV = -P_{atm}\,(V_2 - V_1)}$$

In the case where the **transformation is reversible** :

$$\boldsymbol{P_{ext} = P_{gaz}}$$

Since the gas is perfect

$\boldsymbol{P_{gaz} V = nRT}$ Where from $\boldsymbol{P_{gaz} = \frac{nRT}{V}}$

The work will then be equal to:$W_{rév}$

$$\boldsymbol{W_{rév} = -\int_1^2 P_{ext}\, dV}$$

$$\boldsymbol{W_{rév} = -\int_1^2 nRT \frac{dV}{V}}$$

$$\boldsymbol{W_{rév} = -nRTLn \frac{V_2}{V_1}}$$

W depends on the transformation envisaged, so it is not a state function.

I.5. Degree of freedom

This is the minimum number of state quantities necessary to describe this transformation. It is also the maximum number of independent state quantities.

I.6. Phases

The set of homogeneous portions with the same properties is called a phase, regardless of their respective situations.

Remark:

A phase is by definition homogeneous, in particular it has a well-defined chemical composition.

The characteristic properties of a phase must be independent of the extent of that phase. For extensive quantities, the corresponding specific quantities must be defined, i.e. the values of these quantities in relation to a reference phase fraction defined by its volume, mass or corresponding to a mole.

Example:

Density: $g.l^{-1}$, $g.cm^{-3}$, $kg.m^{-3}$

Mass volume: cm^3g^{-1}, $l.\ g^{-1}$, m^3kg^{-1}

Molar mass: $g.mol^{-1}$, $kg.mol^{-1}$

Molar volume: $l.mol^{-1}$, $m^3.mol^{-1}$

I.7. Reminder on units

Volume: $1m^3=10^3$ l (litre)= 10^3 cc ($1cc=1cm^3=1ml$)

Pressure: the international unit is Pascal (Pa); 1 atm = $1.013 * 10^5$ Pa; 1bar = 10^5 Pa

Energy: the international unit of energy is the joule (J); Calorie (1cal=4.18 joules)

Temperature: in $^{\circ}C$ (degree Celcius) or Kelvin: $1K=1^{\circ}C+273.15$

Chapter II: First Principle of Thermodynamics

II.1. Introduction

Suppose a closed system undergoing a transformation from an initial state 1 to a final state 2. During this transformation, it exchanges heat energy Q and mechanical energy W with the external environment.

In the first principle, the algebraic sum W + Q remains constant, regardless of the type of transformation. This energy can neither be created nor destroyed; it corresponds to the variation of the total energy of the system, called the internal energy U. This principle is expressed by the following relationship:

$$\Delta \boldsymbol{U} = \boldsymbol{W} + \boldsymbol{Q} = \boldsymbol{Cte}$$

Where: the change in the internal energy of the system during the transformation. ΔU

ΔU of a system passing from a state 1 to a state 2 is equal to the algebraic sum of all the energies exchanged with the external medium during this transformation.

The internal energy U of a system in a given state depends only on the state of the system. is equal to:ΔU

$$\Delta \boldsymbol{U} = \boldsymbol{U_2} - \boldsymbol{U_1}$$

If two processes A and B are used to transform the system from state 1 to state 2 and if WA, QA and WB, QB, are the energies exchanged respectively during processes A and B, we have:

$$\Delta \boldsymbol{U} = \boldsymbol{U_2} - \boldsymbol{U_1} = \boldsymbol{W_A} + \boldsymbol{Q_A} = \boldsymbol{W_B} + \boldsymbol{Q_B}$$

Note that this equality: does not necessarily imply that: and $W_A + Q_A = W_B + Q_B W_A = W_B Q_A = Q_B$

Indeed, W and Q are not state functions because the values of W and

For an infinitesimal transformation: $\boldsymbol{dU = \delta W + \delta Q}$

ΔU of a finite transformation is given by the expression:

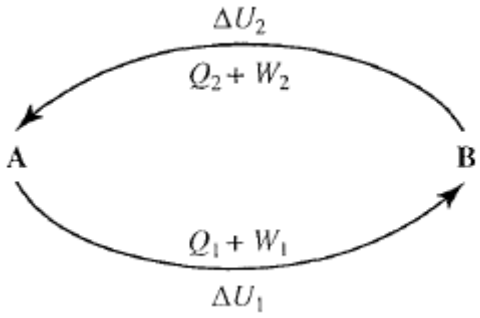
$$\boldsymbol{\Delta U = \int_1^2 dU = \int_1^2 \delta W + \int_1^2 \delta Q}$$

II.2. Special cases

1) For a thermodynamic cycle:

$$\boldsymbol{\Delta U = U_1 - U_1 = 0}$$

W+Q=0



2) For a thermodynamically isolated system that is the site of transformations leading it to a final state, we have in this case: W=0; Q=0 so =0.ΔU

II.3. Thermomechanical transformations

Let us consider a system in a given state of equilibrium, which is perfectly known. If the latter undergoes a transformation, the final state can be determined by knowing the transformation performed.

Thermomechanical Transformations	
Transformation	**Meaning**
Isotherm	Transformation at (**T=cte)**
Isobar	Transformation at **(P=cte)**
Isochorus	Transformation at **(V=cte)**
Adiabatic	Transformation without heat exchange with the outside **(Q=0)**

II.3.1. Thermomechanical transformation carried out at a constant volume

According to the first principle:

$$\boldsymbol{dU = \delta W + \delta Q}$$

At constant volume:

$$\boldsymbol{\delta W = -P_{ext} dV}\text{=0}$$

Where from:

$$\boldsymbol{dU = \delta Q}$$

We then have: $\boldsymbol{\Delta U = \int dU = \int \delta Q = Q_V}$

$\boldsymbol{Q_V}$ is the heat energy exchanged at a constant volume.

II.3.2. Thermomechanical transformation carried out at constant pressure. Enthalpy function

Let us say a thermomechanical transformation made under atmospheric pressure. In the initial state, the system has, a mass m, a pressure P, a temperature T and a volume V1. In the final state, it is characterized by a mass m (closed system), a pressure P, a temperature T2 and a volume V2. of the system is therefore equal to: $\boldsymbol{\Delta U}$

$$\boldsymbol{\Delta U = U_2 - U_1 = W + Q_P}$$

Q_P represents the value of the heat exchanged at constant pressure.

For such a transformation:

$$\boldsymbol{W = -P(V_2 - V_1)}$$

Where from: $\boldsymbol{U_2 - U_1 = Q_P - P(V_2 - V_1)}$

We then have: $\boldsymbol{Q_P = (U_2 + PV_2) - (U_1 + PV_1)}$

The U+PV function, symbolized by H, is the enthalpy function. It is a state function that has the dimension of an energy.

$$\boldsymbol{Q_P = H_2 - H_1 = \Delta H}$$

$\boldsymbol{Q_P}$ is the heat energy exchanged at P= Cte.

In the case where the pressure is variable, the enthalpy variation would be written:

$$\boldsymbol{\Delta H = H_2 - H_1 = (U_2 + P_2V_2) - (U_1 + P_1V_1)}$$

P1 and P2 being the pressure for states 1 and 2 respectively.

Sign convention

Any quantity received by the system will be positive. Any quantity given by the system will be negative.

A balance sheet will be an algebraic number: the sign will indicate the direction of the exchange and the absolute value will indicate the quantity involved.

Chapter III: Thermochemistry

III.1. Mixing heat

III.1.1. Constant Volume Reaction Heat Q_V

Let the chemical reaction:

$$aA + bB \rightarrow cC + dD$$

At constant volume, the reaction below exchanges heat energy Q_V.

Q_V corresponds to between the initial state and the final state: it therefore becomes a function of state at constant V.ΔU

$$\Delta U = U_2 - U_1 = Q_V$$

$Q_V > 0$, the reaction is endothermic, the system receives heat energy, the internal energy of the reactants (A and B) is lower than the internal energy of the products (C and D).

$Q_V < 0$, the reaction is exothermic, the system gives up heat energy, the internal energy of the reactants (A and B) is greater than the internal energy of the products (C and D).

III.1.2. Reaction heat at constant pressure Q_P

Q_P is equal to the enthalpy variation that accompanies the reaction:ΔH

$$Q_P = \Delta H$$

This results in a state function. Q_P

$Q_P > 0$, the reaction is endothermic, the system receives enthalpy from the external environment, the enthalpy of the reactants (A and B) is less than the enthalpy of the products (C and D).

$Q_P < 0$, the reaction is exothermic, the system gives up enthalpy to its external environment: H1 of the reactants (A and B) is greater than H2 of the products (C and D).

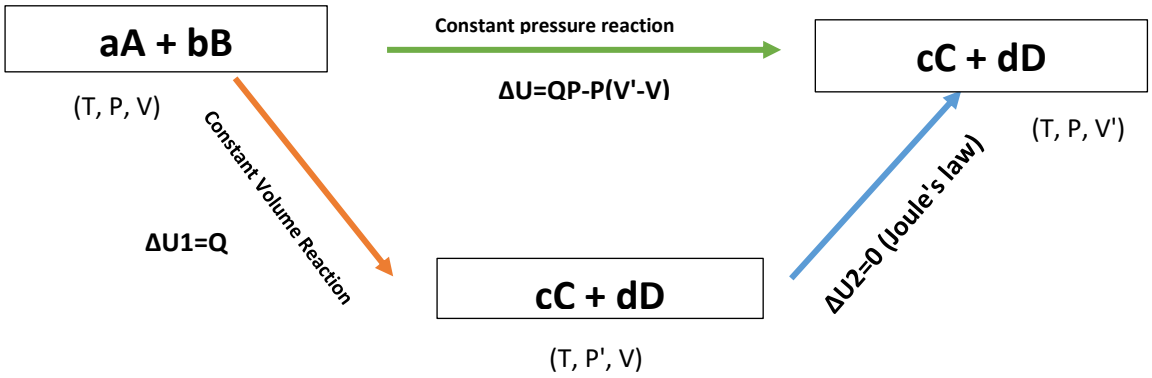
III.2. Standard State

This is the most stable physical state that a pure body can have under standard conditions (P = 1 atm, and T most often equals 298 K). When the body is solid, the standard state, at 298 K for example, will be represented by the most stable crystalline form existing at this temperature under a pressure of 1 atmosphere. In the case of carbon, the standard state at 298 K, is represented by graphite.

III.3. Relationship between Q_V and Q_P

Let us consider the reaction below, which takes place between ideal gases at constant T according to the following diagram:.

$$aA + bB \rightarrow cC + dD$$



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<u>The internal energy of an ideal gas depends only on its temperature (joule effect).</u>

According to the 1st law of thermodynamics, we have:

$$\Delta U = \Delta U_1 + \Delta U_2$$

Therefore: $$Q_P - P(V' - V) = Q_V + 0 = Q_V$$

The reaction takes place between ideal gases. We know that:

$$PV' = (c + d)RT$$

$$PV = (a + b)RT$$

Where from

$$Q_P = Q_V + [(c + d) - (a + b)]RT$$

What can be written:

$$Q_P = Q_V + \Delta nRT$$

Where is the difference between the number of moles of gaseous products formed and the number of moles of gaseous reactants; R is the ideal gas constant and T is the temperature at which reactants and products are considered.Δn

III.4. Variation of the heat of reaction as a function of T

III.4.1. Molar Heat Capacity at Constant Pressure and Volume

CV, is the heat energy that a mole of a pure body requires, for its temperature to increase by 1K. The heat energy QV is equal to:

$$Q_V = \Delta U = \int_{T_1}^{T_2} C_V dT$$

Where from: $C_V = \frac{\partial Q_V}{\partial T}$

The molar calorific capacity can be expressed by a function of the temperature of the form:

$$C_V = a + bT + cT^2$$

a, b, c, being constants characteristic of the pure body and of the temperature range considered. Under these conditions, the value of the heat energy is:Q_V

$$Q_V = \int_{T_1}^{T_2} C_V dT = \int_{T_1}^{T_2} adT + \int_{T_1}^{T_2} bTdt + \int_{T_1}^{T_2} cT^2\, dT$$

$$Q_V = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3)$$

If is constant in the temperature range (T1, T2), we will have:C_V

$$Q_V = C_V(T_2 - T_1)$$

The table below brings together some values of the molar heat capacities at constant volume, of some pure bodies (gases):C_V

Gas	**Ar**	**He**	**N_2**	**H_2**	**O_2**	**NH_3**	**CO_2**	**CH_4**	**C_2H_2**
C_V cal/mol. K	**2,98**	**2,98**	**4,95**	**4,88**	**5,04**	**6,65**	**6,80**	**6,50**	**8,20**

C_P, is the heat energy that a mole of a pure body requires, for its temperature to increase by 1K at constant pressure. The heat energy QP is equal to:

$$Q_P = \Delta H = \int_{T_1}^{T_2} C_P dT$$

Where from: $C_P = \frac{\partial Q_P}{\partial T}$

The molar calorific capacity can be expressed by a function of the temperature of the form:

$$C_P = a + bT + cT^2$$

a, b, c, being constants characteristic of the pure body and of the temperature range considered. Under these conditions, the value of the heat energy is:Q_P

$$Q_P = \int_{T_1}^{T_2} C_P dT = \int_{T_1}^{T_2} a dT + \int_{T_1}^{T_2} bT dt + \int_{T_1}^{T_2} cT^2\, dT$$

$$Q_P = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3)$$

If the molar heat capacity can be considered as constant in the temperature range (TC_{P1}, T2), we will have:

$$Q_P = C_P(T_2 - T_1)$$

III.4.2. Relationship between C_P and C_V

Let be one mole of ideal gas:

By definition **H=U+PV,** or **PV=RT** hence **H=U+PV**

Since U is only a function of temperature, the same is true for H

Drifting with respect to temperature, we will have:

$$\frac{dH}{dT} = \frac{dU}{dT} + \frac{d(PV)}{dT}$$

And$\left(\frac{dH}{dT}\right)_P = \frac{dH}{dT} = C_P$; $\left(\frac{dU}{dY}\right)_V = \frac{dU}{dT} = C_V$ $\frac{d(PV)}{dT} = \frac{dRT}{dT} = R$

Hence $C_P = C_V + R$ **(Mayer's relation)**

The ratio of the heat capacities: $\gamma = \frac{C_P}{C_V}$

Monoatomic gas (e.g. Ar, Ne, etc....): $C_V = \frac{3}{2}R$; $C_P = \frac{5}{2}R$

Diatomic gas (e.g. H_2, O_2, Cl_2, etc.) $\boldsymbol{C_V = \frac{5}{2}R;\ C_P = \frac{7}{2}R}$

R is the ideal gas constant:

R=0.082 atm.l.K^{-1}.mol^{-1} = 8.314 J.K^{-1}.mol^{-1} = 2 cal. K^{-1}.mol^{-1}

III.5. Adiabatic transformation

During an adiabatic transformation, the system does not exchange heat energy Q (heat) with the external medium, hence δQ=0.

According to the 1st principle:

$$dU = \partial W + \partial Q$$

Where from: $\boldsymbol{dU = \partial W = -PdV}$

$\boldsymbol{dU = C_V dT = -PdV}$ **; P=RT/V** (ideal gas)

$\boldsymbol{C_V dT = -\frac{RT}{V}dV}$ therefore: $\boldsymbol{C_V \frac{dT}{T} = -R\frac{dV}{V}}$ **from where** $\boldsymbol{\frac{dT}{T} = -\frac{R}{C_V}\frac{dT}{T}}$

Like: - we then have:$C_P C_V = R$

$$\boldsymbol{\frac{dT}{T} = -\left(\frac{C_P - C_V}{C_V}\right)\frac{dV}{V} = -\left(\frac{C_P}{C_V} - 1\right)\frac{dV}{V}}$$

As so: $\boldsymbol{\frac{C_P}{C_V} = \gamma\frac{dT}{T} = -(\gamma - 1)\frac{dV}{V}}$

By integration**:** $\boldsymbol{lnT = (1-\gamma)lnV + Cte}$ therefore: $\boldsymbol{lnT - ln(V)^{1-\gamma}}$**= Cte** whence: $\boldsymbol{\frac{T}{V^{1-\gamma}} = Cte \rightarrow}$

<u>Relationship between T and V</u>: $\boldsymbol{TV^{\gamma-1} = Cte}$

<u>Relationship between P and V</u>: PV=nRT ; for 1 mole of ideal gas: PV=RT so: T=PV/R

$$\boldsymbol{\frac{PV}{R}V^{\gamma-1} = Cte \rightarrow PV^{\gamma} = Cte}$$

<u>Relationship between T and P</u>: V=RT/P so:

$$\boldsymbol{P\left(\frac{RT}{P}\right)^{\gamma} = Cte \rightarrow P^{(1-\gamma)}R^{\gamma}T^{\gamma} = Cte \rightarrow P^{(1-\gamma)}T^{\gamma} = Cte \rightarrow TP^{\frac{1-\gamma}{\gamma}} = Cte}$$

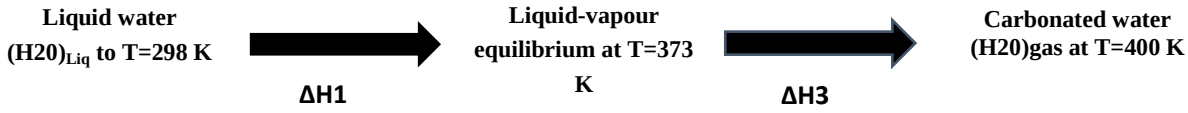
The expressions of the different forms of energy exchanged when the transformation is reversible, are gathered in the table below:

Energy / Transformation	Work W	Heat Q	Internal Energy Variation ΔU	Enthalpy variation ΔH
Isothermal transformation (T=Cte)	$W_{isotherme} = -nRTln\frac{V_{final}}{V_{initial}}$	$Q_{isotherme} = -W_{isotherme}$	$\Delta U_{isotherme} = 0$	$\Delta H_{isotherme} = 0$
Isochoric transformation (V=Cte)	$W_{isochore} = 0$	$Q_{isochore} = \Delta U = nC_V(T_{finan} - T_{initial})$	$\Delta U_{isochore} = nC_V(T_{final} - T_{initial})$	$\Delta H_{isochore} = nC_P(T_{final} - T_{initial})$
Isobaric transformation (P=Cte)	$W_{isobare} = -P_{ext}(V_{final} - V_{initial})$	$Q_{isochore} = \Delta H = nC_P(T_{final} - T_{initial})$	$\Delta U_{isobare} = nC_V(T_{final} - T_{initial})$	$\Delta H_{isobare} = nC_P(T_{final} - T_{initial})$
Adiabatic transformation (Q=0)	$W_{adiabatique} = C_V(T_{final} - T_{initial})$ $W_{adiabatique} = \frac{1}{\gamma - 1}[P_{final}V_{final} - P_{initial}V_{initial}]$	$Q_{adiabatique} = 0$	$\Delta U_{adiabatique} = nC_V(T_f - T_i)$	$\Delta H_{adiabatique} = nC_P(T_{final} - T_{initial})$

III.6. Latent heat of change of state

When, at constant pressure, a pure body undergoes a change of state, ***melting***, ***solidification, vaporization, liquefaction, or sublimation***, the temperature remains constant during this change of state, but the system exchanges heat energy and work with the external environment.

We consider the changes of state that a mole of liquid water undergoes, which will go from T= 298 K to T=400K under a pressure P (P=1atm) and at the temperature T, according to the diagram below:



According to the transformation, the energies exchanged are as follows:

a) Heat required to raise the temperature from 298 to 373 K, i.e.:

$$\Delta H_1 = \int_{298K}^{373K} C_{P(H2O\ liq)}\, dT$$

b) The enthalpy of vaporization of a mole of water at 373 K, under a pressure of 1 atmosphere, i.e.:

$$\Delta H_2 = L_p$$

c) The amount of energy absorbed from 373 K to 400 K, i.e.:

$$\Delta H_3 = \int_{373K}^{400K} C_{P(H2O\ gaz)}\, dT$$

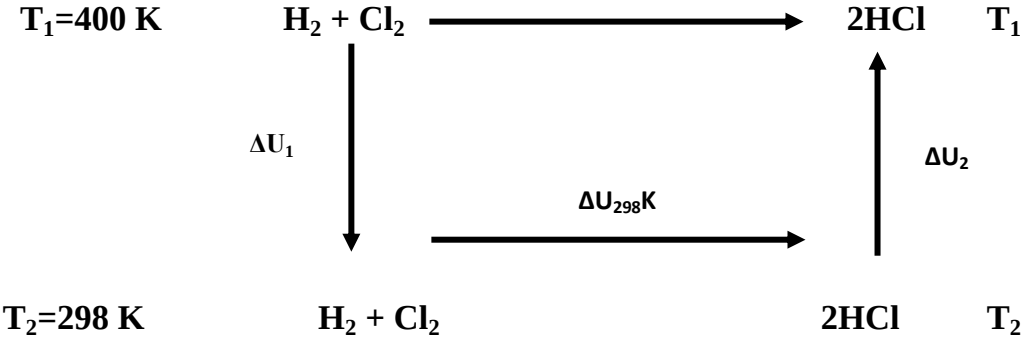
The heat energy required to carry out the envisaged transformation will therefore be:

$$Q_P = \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

i.e.: $\Delta H = \int_{298K}^{373K} C_{P(H2O\ liq)}\, dT + L_p + \int_{373K}^{400K} C_{P(H2O\ gaz)}\, dT$

III.7. Calculation of Reaction Heats at Different Temperatures

Example 1: Calculation of a reaction heat at constant volume, at 298 K, based on an experimental measurement at another temperature (see the transformation cycle below):



According to the 1st principle, we have:

$$\Delta U_{400K} = \Delta U_1 + \Delta U_{298K} + \Delta U_2$$

hence the value of ΔU_{298K}

$$\Delta U_{298K} = \Delta U_{400K} - \Delta U_1 - \Delta U_2$$

The values of and can be calculated by knowing CV of the reactants and products (assumed to be constant in the temperature range (298K, 400K). We then have:$\Delta U_1 \Delta U_2$

$$\Delta U_1 = C_{V(H_2)}(T_2 - T_1) + C_{V(Cl_2)}(T_2 - T_1) \qquad \Delta U_1 < 0$$

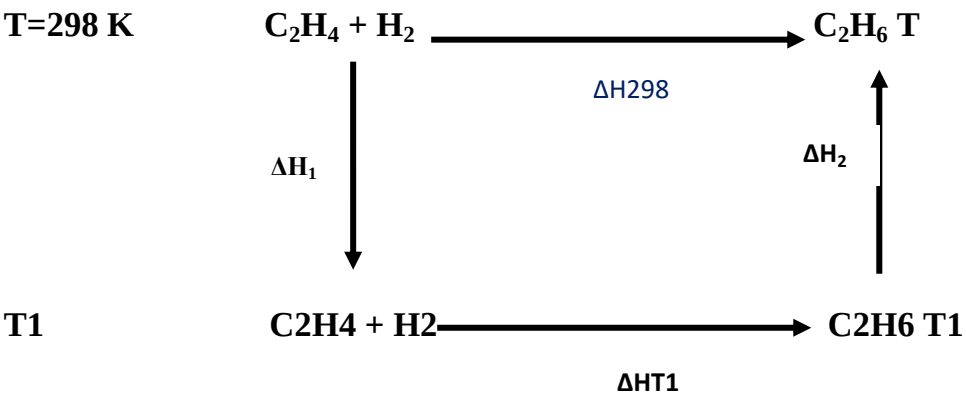
$$\Delta U_2 = 2C_{V(HCl)}(T_1 - T_2) \qquad \Delta U_2 > 0$$

In this case, the value of is:ΔU_{298K}

$$\Delta U_{298K} = \Delta U_{400K} + (T_2 - T_1)\left(2C_{V(HCl)} - C_{V(H_2)} - C_{V(Cl_2)}\right)$$

Example 2: Calculation of a reaction heat at constant pressure (P=1atm), knowing its value at 298 K

Thus, the following diagram allows us to perform this calculation:



$$\Delta H_{298K} = \Delta H_1 + \Delta H_{T1} + \Delta H_2$$

ΔHT1 represents the heat of reaction at T1 K, under a pressure of 1 atm.

Knowing the molar heat capacities at constant pressure of the reactants and products, assumed to be constant in the temperature range, we can calculate and :$\Delta H_1 \Delta H_2$

$$\Delta H_1 = \int_{298K}^{T_1} C_{P(C_2H_4)} + C_{P(H)_2} dT$$

$$\Delta H_2 = \int_{T_1}^{298K} C_{P(C_2H_6)}\, dT$$

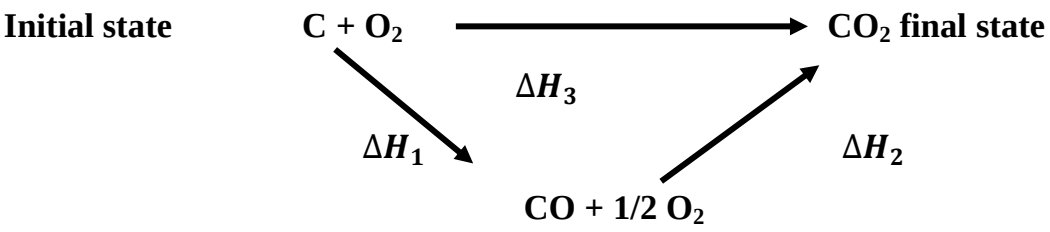
And we deduce the value of ΔH_{T1} :

$$\Delta H_{T1} = \Delta H_{298K} - \Delta H_1 - \Delta H_2 = \Delta H_{298K} - \int_{298K}^{T1} (C_{P(C_2H_4)} + C_{P(H)_2} - C_{P(C_2H_6)}) dT$$

III.8. Application of the concepts of heat of reaction

III.8.1. Indirect determination of the heat of reaction

Let us consider the reaction process below:



The direct process is the combustion of carbon into carbon dioxide CO2 for which the enthalpy variation is . The indirect process corresponds to two steps: a first step which is the oxidation of C to CO and a second step which consists of the combustion of CO to CO2.

Since the enthalpy is a function of state, we will have:

$$\Delta H_3 = \Delta H_1 + \Delta H_2$$

hence: $\Delta H_1 = \Delta H_3 - \Delta H_2$**=-94+67.6=-26.4 kcal/mole**

III.8.2. Enthalpy of formation

It is equal to the ***enthalpy variation that accompanies the reaction of forming a mole of a compound from its elements.***

The enthalpy of formation varies with temperature. is the standard enthalpy of formation under standard temperature and pressure conditions.ΔH_f°

Example: CH_4 is formed from its elements, namely: carbon, oxygen and hydrogen according to the balance:

$$\mathbf{C + 2\ H_2 \rightarrow CH_4}$$

The table below brings together some standard enthalpies of formation;

Standard enthalpies of formation in kJ/mol	
CH_3COOH	-485.1
Fe_2O_3	-842.2
C_2H_6	-84.7
CH_4	-74.8
NO_2	+33.2
C_6H_6	+49
C_2H_4	+52.3
C_2H_2	+228
H_2O	-285.6
CO_2	-393.1
SO_2	-296.8
HNO_3	-174.1
$CHCl_3$	-134.5
CH_3COOH	-485.5

III.8.3. Enthalpy of decomposition

This is the enthalpy that accompanies the reverse reaction of formation. It is equal in absolute value to the enthalpy of formation.

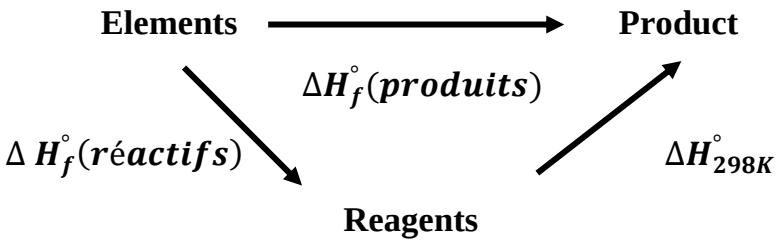
Examples

$$C + O_2 \rightarrow CO_2 \qquad \Delta H^{\circ}_{formation}$$

$$CO_2 \rightarrow C + O_2 \qquad \Delta H^{\circ}_{décomposition}$$

III.8.4. Determination of reaction heats by means of enthalpies of formation

The enthalpy variations accompanying the reactions can be determined without experimentation, by knowing the enthalpies of formation of reactants and products (Hess's law), by applying the following thermodynamic cycle:



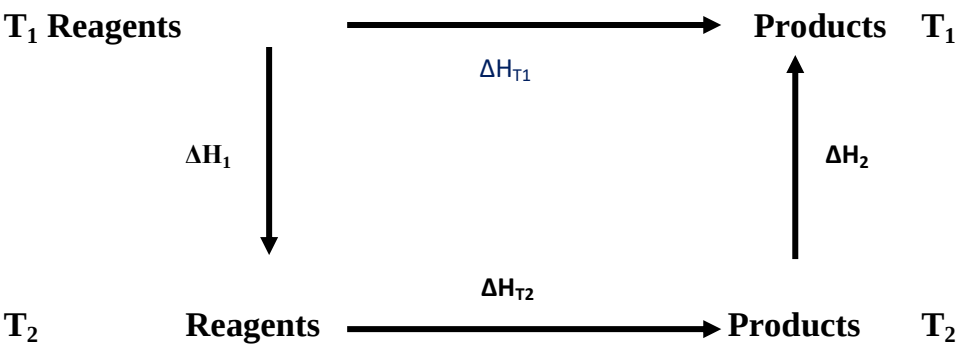
The thermodynamic balance of these reactions is:

$$\Delta H^{\circ}_{298K} = \sum \Delta H^{\circ}_f(products) - \Delta H^{\circ}_f(reagents) \qquad \textbf{(Hess's Law)}$$

Kirchoff's Law

If, for a chemical reaction, the change in enthalpy $\Delta H°_{T1}$ at temperature T_1 is known, but unknown at temperature T_2, Kirchoff's law allows us to calculate ΔH°_{T2}

The transformation is carried out according to the process:



$$\Delta H°_{298K} = \Delta H_1 + \Delta H_{T1} + \Delta H_2$$

$$\Delta H_1 = \int_{T_1}^{T_2} C_{P(reagents)}\, dT$$

$$\Delta H_2 = \int_{T_2}^{T_1} C_{P(products}\, dT = -\int_{T_1}^{T_2} C_{P(reagents)}\, dT$$

And we deduce the value of ΔH_{T1} :

$$\Delta H°_{T2} = \Delta H°_{T1} - \Delta H°_1 - \Delta H°_2 = \Delta H°_{T1} + \int_{T1}^{T2} \left(C_{P(products)} - C_{P(reagents}\right) dT$$

$$\Delta H°_{T2} = \Delta H°_{T1} + \int_{T1}^{T2} \Delta C_P dT \qquad \textbf{(Kirchoff's Law)}$$

III.8.5. Binding energy

Covalent Bond Energy

It is ***the energy released when two atoms in the gaseous state form a covalent bond.***

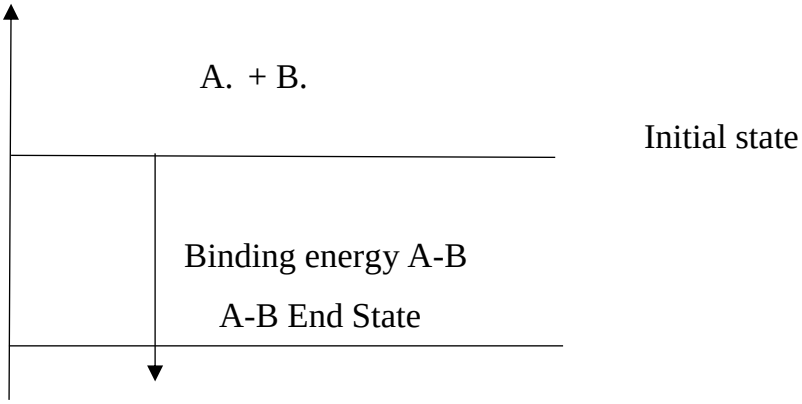
Given two atoms A and B in the gaseous state, the energy of the A-B bond is equal to during the following reaction under standard conditions: ΔH_{A-B}

$$\mathbf{Ag + B_g \rightarrow A\text{-}B}$$

ΔH_{A-B} is expressed in kcal/mole.

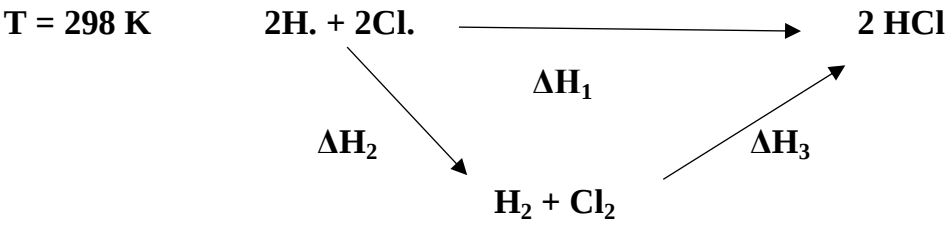
This binding energy is always negative; The figure below shows the energy levels of the initial and final state.ΔH_{A-B}

Energy



Determination of binding energies

1st example: Calculation of the energy of the H-Cl bond, by the following thermodynamic process:

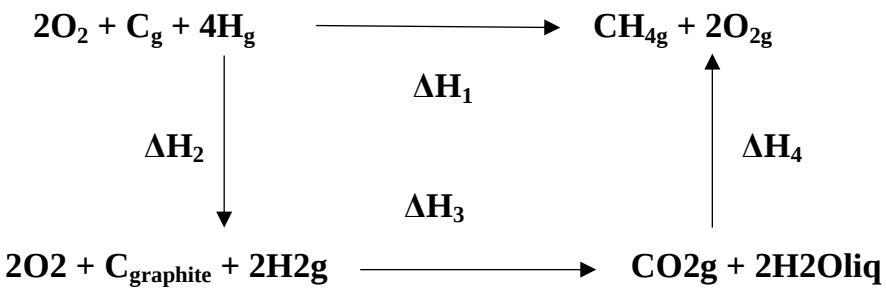


According to the first law of thermodynamics:

$$\Delta H_1 = 2\ \Delta H_{298\ K}(H\text{-}Cl)$$

Example 2

Calculation of the energy of the C-H bond in CH_4 based on the transformation diagram below:



Reaction 1: Formation of 4 C-H bonds. The enthalpy variation is ΔH_1

Reaction 2: Transformation of gaseous carbon into graphite carbon, and formation of two H-H bonds. The enthalpy variation is ΔH_2

Reaction 3: Combustion of graphite carbon and hydrogen and formation of CO2 and H2O from their elements:

$$\Delta H_3 = \Delta H_{f(CO_2} + 2\Delta H_{f(H_2O)}$$

Reaction 4: Finally, reaction 4 is the opposite reaction of methane combustion.

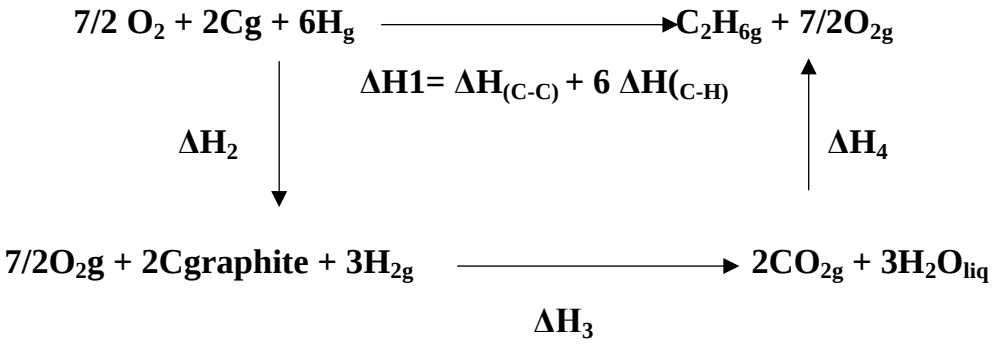
$$\Delta H_4 = -\Delta H_{combustion\ de\ CH_4)}$$

According to the first law of thermodynamics:

$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$$

$$\Delta H_{298K(C-H)} = \frac{\Delta H_1}{4}$$

Knowing the C-H bond energy, we can, for example, calculate the C-C bond energy by applying the following diagram to ethane:



- **Calculation of a Reaction Heat from Bond Energies**

The hydrogenation reaction of acetylene to ethane is considered:

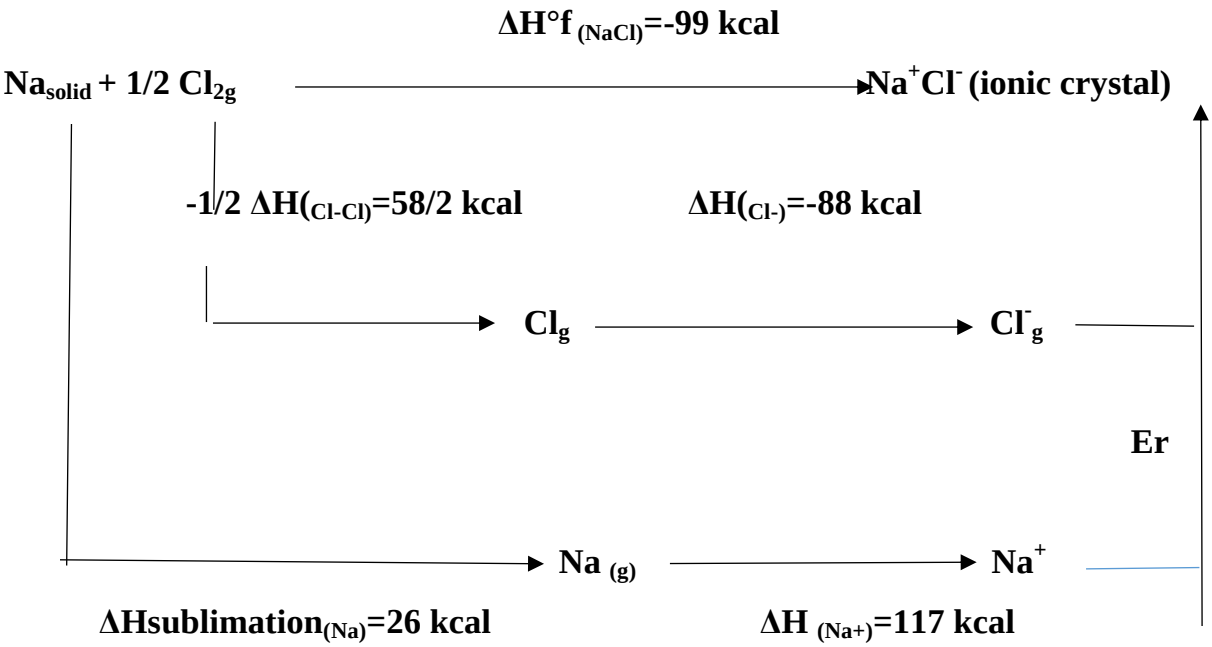
$$\text{H-C}\equiv\text{C-H} + 2\text{H2} \longrightarrow \text{CH3-CH3}$$

The enthalpy variation accompanying this reaction is equal to:

$$\Delta H = \Delta H_{(C-C)} + 4\Delta H_{(C-H)} - \Delta H_{(C\equiv C)} - 2\Delta H_{(H-H)}$$

III.8.6. Energy of an Ionic Crystal

This is the energy of formation of a mole of the crystal from the gaseous ions, called "reticular energy" and symbolized by Er. It can be calculated by a cyclic process, called the Born-Haber cycle and schematized as follows:



The thermodynamic balance is as follows:

$$\Delta H_f^{\circ} = \Delta H_1 + \Delta H_2 + E_r$$

$$E_r = \Delta H_f^{\circ} - \Delta H_1 - \Delta H_2 = -183\ kcal/mole$$

Chapter IV: Second and Third Principles of Thermodynamics

IV.1. Entropy function

Physical or chemical transformations take place in a well-defined sense, they are spontaneous transformations also called natural transformations. Inverse transformations are not spontaneous, for example: a cold body does not give up heat energy spontaneously to a hot body. It is therefore important to know the criteria of spontaneity, which require knowledge of a new state function called entropy, represented by S. Its total differential is dS. Indeed, the values of ΔU and ΔH cannot predict the direction of chemical reactions. Spontaneous chemical reactions can be exothermic or endothermic.

Experience shows that some transformations are spontaneous and that the opposite reactions never occur without external intervention. This led to the following principle: Natural transformations are irreversible.

- **Notion of entropy**

We consider a thermodynamic system, undergoing a reversible transformation by exchanging heat with the external environment at a temperature T.

The entropy variation during this transformation is defined by:

$$dS = \frac{\delta Q_{rev}}{T}$$

- For a reversible transformation from an initial state to a final state, the corresponding entropy variation will therefore be:

$$\Delta S = S_{final} - S_{initial} = \int_{initial}^{final} \frac{\delta Q_{rev}}{T}$$

$$\Delta S = \frac{Q_{rev}}{T}$$

Where is the heat energy exchanged during the reversible transformation.Q_{rev}

- For a spontaneous process carried out at a constant temperature, we have:

$$dS > \frac{\delta Q_{irrév}}{T} \; et \; \Delta S > \frac{Q_{irrév}}{T}$$

Entropy is a function of state, which depends only on the initial state and the final state. It is independent of the process

The heat energy exchanged is not the same when a process is carried out at a constant temperature, according to a reversible or irreversible process, so we have, for any transformation from an initial state 1 to a final state 2:

$$(S_2 - S_1)_{rev} = (S_2 - S_1)_{irrev} = \frac{Q_{rev}}{T}$$

$$(S_2 - S_1)_{rev} = (S_2 - S_1)_{irrev} > \frac{Q_{irrév}}{T}$$

The second principle therefore implies:

$$\frac{Q_{rev}}{T} > \frac{Q_{irrév}}{T}$$

$$Q_{irrév} < Q_{rev}$$

The entropy variation of a spontaneous process is determined by imagining a reversible process, given that S is a state function:

$$\Delta S = S_{final} - S_{initial} = \int_{initial}^{final} \frac{\delta Q_{rev}}{T}$$

IV.2. Application of the second principle to the case of isolated systems

Isolated systems do not exchange heat energy with the external environment.

$$\boldsymbol{Q_{rev} = 0} \text{ Where from } \boldsymbol{\Delta S = 0}$$

For a spontaneous transformation:

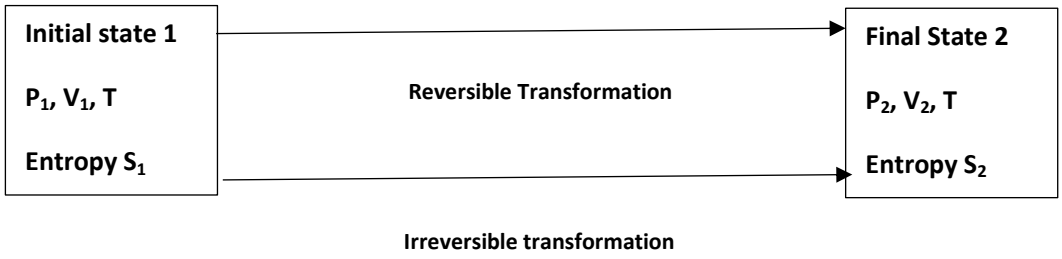
$$\boldsymbol{Q_{irrév} = O} \text{ entraîne } \boldsymbol{\Delta S > 0}$$

For isolated systems, the forbidden processes are those for which the entropy variation is negative.

Examples of Calculation

- **Isothermal expansion of an ideal gas**

Let be one mole of ideal gas characterized by the following thermodynamic transformations:



The transformation can take place according to two thermodynamic processes: reversible or irreversible. The variation of the entropy is therefore:

$$\boldsymbol{\Delta S = S_2 - S_1}$$

For a reversible isothermal transformation:

$$\boldsymbol{\Delta S = \frac{Q_{rev}}{T}}$$

According to the 1st principle,

$$\boldsymbol{\Delta U = Q_{rev} + W_{rev} = 0} \quad \textbf{(joule effect)}$$

Where from: $$Q_{rev} = -W_{rev}$$

$$W_{rev} = -RTLn\frac{V_2}{V_1}$$

So the heat energy is equal to:

$$Q_{rev} = RTLn\frac{V_2}{V_1}$$

and

$$\Delta S = S_2 - S_1 = \frac{RT}{T} Ln\frac{V_2}{V_1}$$

$$\Delta S = RLn\frac{V_2}{V_1}$$

If the isothermal transformation is carried out on n moles of ideal gas, the entropy variation will then be:

$$\Delta S = nRLn\frac{V_2}{V_1}$$

Entropy is an extensive quantity.

IV.3. Variation of entropy during the change of state of a pure body

Let be one mole of ideal gas, which undergoes a reversible transformation at constant pressure, from an initial state to a final state. The expression for the change in entropy is written:

$$\Delta S = \frac{\Delta H}{T}$$

IV.4. Variation of entropy of a pure body with temperature

A pure body undergoes a reversible transformation at constant pressure. is then:ΔS

$$\Delta S = \int_{état\ 1}^{état2} \frac{\delta Q_{rev}}{T}$$

According to the 1st law of thermodynamics:

$$\delta Q = dH = C_p dT$$

Where is the molar heat capacity at constant pressure.C_p

If we assume that constant in the temperature range considered, we will then have:C_p

$$\Delta S = C_p \int_{T_1}^{T_2} \frac{dT}{T}$$

Either $$\Delta S = C_p Ln \frac{T_2}{T_1}$$

In the case of a temperature variation at a constant volume, the variation in entropy will be expressed by an analogous expression, involving, we will therefore have:C_v

$$\Delta S = C_v \int_{T_1}^{T_2} \frac{dT}{T}$$

Either: $$\Delta S = C_v Ln \frac{T_2}{T_1}$$

I.5. Statement of the Third Principle

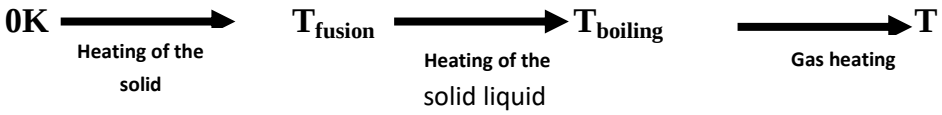
At the temperature of absolute zero, pure bodies are in a perfect order which translates into zero entropy.

Perfect Crystal at 0K Real Crystal at Room Temperature

I.6. Absolute entropies

The third law of thermodynamics allows us to assign absolute entropy to all pure bodies, considered at any temperature.

Consider the following thermodynamic transformation:



The entropy variation is then:

$$\Delta S = S_T - S_0$$

$$= \int_{0\,K}^{T_f} \frac{C_{p\ solide}}{T} dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_{eb}} \frac{C_{p\ liquide}}{T} dT + \frac{\Delta H_{eb}}{T_{eb}} + \int_{T_{eb}}^{T} \frac{C_{p\ gaz}}{T} dT$$

Since the entropy of the crystallized pure body is zero at absolute zero, we will have:

$$S_T = \int_{0\,K}^{T_f} \frac{C_{p\ solide}}{T} dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_{eb}} \frac{C_{p\ liquide}}{T} dT + \frac{\Delta H_{eb}}{T_{eb}} + \int_{T_{eb}}^{T} \frac{C_{p\ gaz}}{T} dT$$

Where S: the absolute entropy of the pure body, at temperature T, under the pressure of an atmosphere. It can be calculated at any temperature, by knowing the molar heat capacities in the solid, liquid, gaseous state as well as the enthalpy variations during changes of state (melting, vaporization, sublimation).

Tables 1 & 2 bring together the absolute entropies of some pure bodies under the standard conditions of temperature and pressure.

Table 1: Absolute entropies at 298K under the pressure of an atmosphere expressed in cal.mole-1. K-1 [1] of some inorganic compounds

S° in cal.mole-1. K-1									
Monoatomic Solid Solid polyatomics		**Liquid**		**Monoatomic gases**		**Diatomic gases**		**Polyatomic gases**	
Ag	10,20	Br_2	36,4	He	30,13	H_2	31,21	H_2O	45,1
Ly	6,77	H_2O	16,73	Ne	34,95	D_2	34,6	CO_2	51,1
B	1,7	Hg	18,17	Ar	36,98	F_2	48,6	SO_2	59,4
Ba	15,1			Kr	39,19	Cl_2	53,3	H_2S	49,1
C (graphite)	1,37			Xe	40,53	Br_2	58,6	NO_2	57,5
C (diamond)	0,6			H	27,39	CO	47,3	N_2O	52,6
CA	9,95			F	37,92	NO	50,3	NH_3	46,0
Cu	7,97			Cl	39,46	N_2	45,7	O_3	56,8
Fe	6,49			Br	41,80	O_2	49,0		
I2	27,76			I	43,18	HF	41,5		
Na	12,2			N	36,61	HCl	44,6		
S	7,62			C	37,76	HBr	47,4		
If	4,51								
Zn	9,95								
AgCl	23,00								
AgBr	25,6								
Acted	27,6								
Bao	16,8								
$BaCO_3$	26,8								
$BaSO_4$	31,6								
Cd	9,5								
$Ca(OH)_2$	17,4								
$CaCO_3$	22,2								
CuO	10,4								
Cu_2O	24,1								
Fe_2O_3	21,5								
SiO2	10,0								
ZnO	10,5								

Table 2: Absolute entropies at 298K under the pressure of an atmosphere expressed in cal.mole-1. $^{K-1}$ of some organic compounds.

Organic compounds			
Gas	**S°**	**Liquids**	**S°**
Methane	44,5	Benzene	41,3
Ethane	54,8	$CHCl_3$	48,5
Propane	64,5	CCl_4	51,2
n-Butane	74,1		
Isobutane	70,4		
n-Pentane	83,4		
Isopentane	82,1		
Neopentane	73,2		
Ethylene	52,45		
Acetylene	49,99		
But-1-ene	73,48		
cis-But-2-ene	71,9		
trans-But-2-ene	70,9		
Isobutene	70,2		
1,3-butandiene	66,62		
Methyl chloride	55,97		

I.7. Calculation of the variation of entropy during a chemical reaction

Let the chemical reaction carried out at temperature T:

$$aA + bB \rightarrow cC + dD$$

The change in entropy is calculated by the expression:ΔS_T

$$\Delta S_T = cS_T(C) + dS_T(D) - aS_T(A) - bS_T(B)$$

$$\Delta S_T = \sum S_T(Products) - \sum S_T\,(reagents)$$

The standard entropy variation is:ΔS°_{298K}

$$\Delta S^\circ_{298K} = \sum S^\circ_{298K}(Products) - \sum S^\circ_{298K}(reagents)$$

For a training reaction:

$$A + B \rightarrow AB$$

$$\Delta S^\circ_f(AB) = S^\circ(AB) - [S^\circ(A) + S^\circ(B)]$$

And therefore, is different from since, under standard conditions, at 298 K, the absolute entropies of elements A and B are not zero.$\Delta S^\circ_f(AB) S^\circ(AB) S^\circ(A) et S^\circ(B)$

Examples

1. Determine the standard entropy variation of the following reaction: $\Delta S^\circ_{f,298K}$

$$\mathbf{1/2\,H_2 + 1/2\,Cl_2 \rightarrow HCl}$$

$$\Delta S^\circ_f(HCl) = S^\circ(HCl) - [\mathbf{1/2}\,S^\circ(\boldsymbol{H_2}) + \mathbf{1/2}\,S^\circ(\boldsymbol{Cl_2})]$$

$$\Delta S^\circ_f(HCl) = 2{,}4\ u.e$$

The entropy variation accompanying this reaction is low because the reaction takes place in the gas phase without any change in the number of moles of gas.

2. Consider the CaCO3 decomposition reaction carried out at 298 K, under an atmosphere:

$$\boldsymbol{CaCO_3(solid) \rightarrow CaO(solid) + CO_2(gas)}$$

$$\boldsymbol{\Delta S^\circ_{298K} = S^\circ_{298K}(CaO) + S^\circ_{298K}(CO_2) - S^\circ_{298K}(CaCO_3)}$$

$$\boldsymbol{\Delta S^\circ_{298K} = 38{,}4\ u.e}$$

The variation in entropy is positive and it is large because, starting from the solid reactant, one of the products formed is in a gaseous state. The end state is less orderly than the initial state.

3. Let us consider the reactions of acetylene and ethane formation under a pressure of one atmosphere and at T=298K:

$$2C_{graphite} + H_{2(g)} \rightarrow C_2H_{2(g)}$$

$$\Delta S^{\circ}_{298K}(C_2H_{2(g)}) = S^{\circ}_{298K}(C_2H_{2(g)}) - 2S^{\circ}_{298K}(C_{graphite}) - S^{\circ}_{298K}(H_{2(g)})$$

$$\Delta S^{\circ}_{298K}(C_2H_{2(g)}) = 16,04\ u.e$$

$$2C_{graphite} + 3H_{2(g)} \rightarrow C_2H_{6(g)}$$

$$\Delta S^{\circ}_{298K}(C_2H_{6(g)}) = S^{\circ}_{298K}(C_2H_{6(g)}) - 2S^{\circ}_{298K}(C_{graphite}) - 3S^{\circ}_{298K}(H_{2(g)})$$

$$\Delta S^{\circ}_{298K}(C_2H_{6(g)}) = -41,57\ u.e$$

During the formation of ethane, the reaction is accompanied by a decrease in entropy since, in particular, the reactants comprise 3 molecules of gas while only one molecule of gas is formed. This decrease in the number of molecules corresponds to a decrease in the number of microscopic states of the system. The end state is more orderly than the initial state. During the formation of acetylene, the opposite case occurs.$(H_{2(g)})$
But the comparison of the absolute entropies of ethane and acetylene shows that ethane has a greater degree of freedom than that of acetylene.

Chapter V: Chemical Equilibria

V.1. Free enthalpy G and usable energy A

The free enthalpy is defined by:

$$G = H - TS = U + PV - TS$$

Free enthalpy is a state function, because it is a difference of two state functions. dG is an exact total differential:

$$dG = dH - TdS - SdT$$

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

The usable energy A is defined by:

$$A = U - TS$$

A is a state function, its exact total differential dA is given by:

$$dA = dU - TdS - Sdt$$

Let us consider a closed system that is the site of a thermodynamic transformation carried out at a constant temperature. According to the 1st law of thermodynamics:

$$dU = \delta Q + \delta W$$

$$dT = 0$$

The exact total differentials dG and dA become, in this case:

$$dG = dH - TdS = dU + pdV + Vdp - TdS = \delta Q + VdP - Tds$$

$$dA = dU - TdS = \delta Q - PdV - Tds$$

For a finished transformation:

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

$$\Delta A = \Delta U - T\Delta S$$

According to the 2nd principle:

- Reversible transformations: $\boldsymbol{dS = \frac{\delta Q_{rev}}{T}}$ d'où $\boldsymbol{TdS = \delta Q_{rev}}$

- Irreversible transformations: hence $\boldsymbol{dS > \frac{\delta Q_{irrév}}{T}}$ $\boldsymbol{TdS > \delta Q_{irrév}}$

A T and P constants:

- For reversible processes:

  $\boldsymbol{\delta Q_P - TdS = 0}$ $soit\ dH - TdS = 0$ $ce\ qui\ se\ traduit\ par\ dG = 0$

- For irreversible processes: $\boldsymbol{\delta Q_P - TdS}$ **<0** or $\boldsymbol{dH - TdS}$ **<0** so **dG0<**

And for a finite transformation:

Reversible process:

$$\boldsymbol{Q_P - T\Delta S = 0}$$

$$\boldsymbol{\Delta H - T\Delta S = 0}$$

$$\boldsymbol{\Delta G = 0}$$

Irreversible process:

$$\boldsymbol{Q_P - T\Delta S < 0}$$

$$\boldsymbol{\Delta H - T\Delta S < 0}$$

$$\boldsymbol{\Delta G < 0}$$

At constant V and T:

- ***Reversible process:***

$$\boldsymbol{\delta Q_V - TdS = 0}$$
$$\boldsymbol{dU - TdS = 0}$$
$$\boldsymbol{dA = 0}$$

And for a finite transformation:

$$\boldsymbol{Q_V - T\Delta S = 0}$$

$$\boldsymbol{\Delta U - T\Delta S = 0}$$

Either: $$\boldsymbol{\Delta A = 0}$$

- ***Irreversible process:***

$$\boldsymbol{Q_V - T\Delta S < 0}$$

$$\boldsymbol{\Delta U - T\Delta S < 0}$$

Either: $$\boldsymbol{\Delta A < 0}$$

The balance criteria can be summarized as follows:

- ✓ $\boldsymbol{\Delta G = 0}$ **(Constant T and P)**
- ✓ $\boldsymbol{\Delta A = 0}$ **(Constant T and V)**

Criteria for spontaneity:

- ✓ $\Delta G < 0$ **(Constant T and P)**
- ✓ $\Delta A < 0$ **(Constant T and V)**

V.2. Free enthalpy and evolution of chemical reactions

A spontaneous reaction results in a negative free enthalpy, which can be explained by the decrease in the free enthalpy of the products. If the variation of the free enthalpy is zero, the process is reversible, that is, the existence in equilibrium of the two states of the system: the initial and the final state. The free enthalpy has an extremum **dG=0**.

The table below summarizes the sign of the different thermodynamic functions:

	Sign			Conclusion
	ΔH	ΔS	ΔG	
1	-	+	-	**Spontaneous transformation**
2	+	-	+	**Non-spontaneous transformation**
3	-	-	?	**Spontaneous transformation at low temperatures**
4	+	+	?	**Spontaneous transformation at high temperature**

1. These are exothermic reactions that take place with an increase in entropy. These reactions occur spontaneously.
2. These are endothermic reactions with entropy decrease. These reactions do not occur spontaneously.
3. These are exothermic reactions that take place with a decrease in entropy. These reactions occur spontaneously at low temperatures.
4. These are endothermic reactions that take place with an increase in entropy. These reactions occur spontaneously at high temperatures.

V.3. Calculation of the free enthalpy variation during a chemical reaction

The change in free enthalpy of a chemical reaction is equal to:

$$\Delta G_T^0 = \sum \Delta G^\circ_{f,T(products)} - \sum \Delta G^\circ_{f,T(reagents)}$$

<u>ΔG training standard</u>

The standard free enthalpy of formation of a pure body at temperature T is equal to the variation of the free enthalpy of the formation reaction of this pure body from its elements considered in their most stable physical state at temperature T.

For any element:

$$\Delta G^{\circ}_{f,T} = 0$$

Example: the standard free enthalpy of CO_2(g) formation at 298 K is equal to:

$$\Delta G^{\circ}_{f,298K} = \Delta G^{\circ}_{f,298K}(CO_2) - \Delta G^{\circ}_{f,298K}(C_{graphite}) - = \Delta G^{\circ}_{f,298K}(O_2)$$

$$= \Delta G^{\circ}_{f,298K}(CO_2)$$

The table below shows the free enthalpies of formation of some compounds expressed in kcal.mole-1.

Table 1: Standard free enthalpies of formation expressed in kcal.mole-1.

$\Delta G^{\circ}_{f,298K}$ (kcal.mole-1)							
Gas		**Solid**		**Liquids**		**Organic compounds**	
H2O	-54,64	AgCl	-26,22	CH_3OH	-39,73	CH_4	-12,14
H_2O_2	-24,7	AgBr	-22,39	C_2H_5OH	-41,77	C_2H_6	-7,86
O_3	39,06	AgI	-15,81	CH_3COOH	-93,8	C_3H_8	-5,61
HCl	-22,77	Bao	-126,3	C_6H_6	29,76	n-C_4H_{10}	-3,75
HBr	-12,72	$BaSO_4$	-350,2	$CHCl_3$	-17,1	C_4H_{10}	-4,3
HI	0,31	$BaCO_3$	-272,2	CCl_4	-16,4	n-C_5H_{12}	-2,0
SO_2	-71,79	CaO	-144,4			C_5H_{12}	-3,5
SO_3	-88,52	$CaCO_3$	-269,8			C_6H_{14}	-3,6
H_2S	-7,89	$Ca(OH)_2$	-214,3			C_2H_4	16,28
N_2O	24,9	SiO_2	-192,4			C_2H_2	50,00
NO	20,72	Fe_2O_3	-177,1			C_4H_8	17,09
NO_2	12,39	Al_2O_3	-376,8			*cis*- C_4H_{10}	15,74
NH_3	-3,97	CuO	-30,4			*trans*- C_4H_{10}	15,05
CO	-32,81	Cu_2O	-34,98			Isobutene	13,88
CO_2	-94,26	ZnO	-76,05			1,3-butandiene	36,01
						CH_3Cl	-14,0

V.4. Variation of the molar free enthalpy of a pure body with temperature and pressure

In a thermomechanical transformation, the differential of the free enthalpy is written:

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

According to the 1st principle:

$$\delta W = -PdV$$

If the transformation is reversible:

$$\delta Q = TdS$$

Where from

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

$$dG = VdP - SdT$$

If the transformation is carried out at constant pressure dP=0, the variation of the free enthalpy with temperature is equal to:

$$\left(\frac{\delta G}{\delta T}\right)_P = -S$$

If the transformation is isothermal dT=0, the variation of the free enthalpy with pressure is:

$$\left(\frac{\delta G}{\delta P}\right)_T = V$$

The change in the free enthalpy of an ideal gas that undergoes a reversible thermomechanical transformation at constant temperature is equal to:

$$\Delta G = G_{finale} - G_{initiale} = \int_{P_{initiale}}^{P_{finale}} VdP$$

The gas is assumed to be perfect:

$$V = \frac{RT}{P}$$

Where from

$$\Delta G = RT \ln \frac{P_{final}}{P_{initial}}$$

The above expression is valid for an isothermal irreversible transformation since the free enthalpy is a function of state.

If the initial pressure is equal to 1 atmosphere. The free enthalpy of one mole of an ideal gas at temperature T under pressure P, is therefore equal to:

$$\Delta G = RT \ln \frac{P_{final}}{1}$$

$$\Delta G = G_T^P - G_T^\circ = RT \ln P$$

G_T° is the free enthalpy of one mole of gas under standard conditions at temperature T.

The free enthalpy of one mole of an ideal gas at temperature T and under pressure P is given by the following expression:

$$G_T^P = G_T^\circ + RT \ln P$$

V.5. Study of equilibria

V.5.1. Variation of free enthalpy as a function of partial pressures during a chemical reaction carried out between ideal gases

Let us consider the following reaction carried out at a constant temperature between ideal gases:

$$aA + bB \rightarrow cC + dD$$

In the initial state, we have a moles of A and b moles of B. The partial pressures of A and B are P,$_{A,}$ and PB, respectively.

The final state corresponds to c moles of C and d moles of D. The partial pressures are PC and PD respectively.

The free enthalpy variation during this reaction is:

$$\Delta G_T = \Delta G_T^\circ + RT \ln \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

V.5.2. Law of Mass Action

Let us consider the reaction:

$$aA + bB \leftrightarrow cC + dD$$

At breakeven:

$$\Delta G_T = 0$$

$$\ln \frac{P_C^c P_D^d}{P_A^a P_B^b} = \frac{-\Delta G_T^\circ}{RT}$$

Where PA, PB, PC, PD are the partial pressures of A, B, C, and D, respectively. being the free enthalpy variation under standard conditions, it is constant.ΔG_T°

$$\frac{P_C^c P_D^d}{P_A^a P_B^b} = e^{\frac{-\Delta G_T^\circ}{RT}} = K_P(T)$$

K_P is the constant of equilibrium. For a given reaction, the following is a function of the temperature:K_P

$$-\Delta G_T^\circ = -RT \ln K_P$$

$\frac{P_C^c P_D^d}{P_A^a P_B^b}$ can be given according to the concentrations of these same reagents and products.

$$[A] = \frac{n_A}{V_{total}}$$

Since gas is perfect:

$$P_A V = n_A RT$$

Therefore $$P_A = \frac{n_A}{V} RT$$

$$P_A = [A]RT$$

Similar relationships allow the partial pressures of PB, PC and PD to be expressed as a function of concentrations $[B], [C]\ et\ [D]$

The expression of can be written:K_P

$$K_P = \frac{[C]^c [RT]^c [D]^d [RT]^d}{[A]^a [RT]^a [B]^b [RT]^b}$$

$$K_P = \frac{[C]^c [D]^d}{[A]^a [B]^b} [RT]^{[(c+d)]-(a+b)}$$

$$K_P = \frac{[C]^c [D]^d}{[A]^a [B]^b} [RT]^{\Delta n}$$

The relationship is constant, it is called $\frac{[C]^c [D]^d}{[A]^a [B]^b} K_C$

Either:

$$K_P = K_C [RT]^{\Delta n}$$

Where from

$$K_C = K_P [RT]^{-\Delta n}$$

The equations express the law of mass action (Guldberg-Waage's law).

K_P can be expressed in terms of the molar fractions x_i with:

$$x_i = \frac{n_i}{n_{tot}}$$

Where is the number of moles of constituent i;n_i

n_{tot} is the total number of moles.

The partial molar pressure of a constituent i is:

$$\boldsymbol{P_i = \frac{n_i}{n_{tot}} P = x_i P}$$

Where from:

$$\boldsymbol{K_P = \frac{x_C^c x_D^d}{x_A^a x_B^b} P^{\Delta n}}$$

The ratio corresponds to , the equilibrium constant at P and T determined. $\frac{x_C^c x_D^d}{x_A^a x_B^b} \boldsymbol{K_x}$

$$\boldsymbol{K_x(P,T) = \frac{x_C^c x_D^d}{x_A^a x_B^b} K_P P^{-\Delta n}}$$

V.5.3. Law of equilibrium displacement

Let us consider the reaction:

$$\boldsymbol{aA + bB \leftrightarrow cC + dD}$$

At breakeven:

$$\boldsymbol{\ln \frac{P_C^c P_D^d}{P_A^a P_B^b} = -\frac{\Delta G_T^\circ}{RT} = \ln K_P}$$

If an external disturbance causes the value of one of the terms of the previous equality to vary, the system evolves to reach a new state of equilibrium. This transition from one state of equilibrium to another under the influence of an external disturbance is called equilibrium shifting.

V.5.4. Variation of the equilibrium constant with temperature

At breakeven:

$$\ln K_P = -\frac{\Delta G_T^\circ}{RT}$$

$$\frac{d \ln K_P}{dT} = -\frac{d}{dT}\left(\frac{\Delta G_T^\circ}{RT}\right) = -\frac{1}{R}\frac{d}{dT}\left(\frac{\Delta G_T^\circ}{T}\right)$$

ΔG_T° is a function of temperature; So we have:

$$\frac{d}{dT}\left(\frac{\Delta G_T^\circ}{T}\right) = -\frac{\Delta G_T^\circ}{T^2} + \frac{1}{T}\frac{d\Delta G_T^\circ}{dT}$$

We have:

$$\left(\frac{dG}{dT}\right)_P = -S$$

Where from:

$$\frac{d}{dT}\left(\frac{\Delta G_T^\circ}{T}\right) = -\frac{\Delta G_T^\circ}{T^2} - \frac{\Delta S_T^\circ}{T}$$

With:

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

The expression becomes:

$$\frac{d}{dT}\left(\frac{\Delta G_T^\circ}{T}\right) = -\frac{\Delta H_T^\circ}{T^2}$$

Where from

$$\frac{d \ln K_P}{dT} = \frac{\Delta H_T^\circ}{T^2}$$ **(Van'tHoff equation)**

When is positive (endothermic reaction, is positive. believes with T. $\Delta \boldsymbol{H_T^\circ} \frac{\boldsymbol{d \ln K_P}}{\boldsymbol{dT}} \boldsymbol{K_P}$

If the reaction is exothermic is negative), is negative. decreases with T ($\Delta \boldsymbol{H_T^\circ} \frac{\boldsymbol{d \ln K_P}}{\boldsymbol{dT}} \boldsymbol{K_P}$

The qualitative meaning of this variation is given by Le Châtelier's law:

- An endothermic reaction is favoured by an increase in temperature
- A decrease in temperature favours an equilibrium reaction in the sense that it is exothermic.

The Van't Hoff equation can be integrated to give a relationship between the equilibrium constants at two temperatures:

$$\ln \frac{\boldsymbol{K_{T2}}}{\boldsymbol{K_{T1}}} = \int_{\boldsymbol{T1}}^{\boldsymbol{T2}} \frac{\boldsymbol{\Delta H_T^\circ}}{\boldsymbol{RT^2}} \boldsymbol{dT}$$

If we assume constant in the temperature range, we will therefore have:ΔH_T°

$$\ln \frac{K_{T2}}{K_{T1}} = \frac{\Delta H_T^\circ}{R} \int_{T1}^{T2} \frac{1}{T^2} dT$$

$$\ln \frac{K_{T2}}{K_{T1}} = \frac{\Delta H_T^\circ}{R} \left[-\frac{1}{T} \right]_{T1}^{T2}$$

$$\ln \frac{K_{T2}}{K_{T1}} = \frac{\Delta H_T^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

V.5.5. Influence of pressure on equilibrium displacements

The following chemical reaction is considered:

$$\boldsymbol{aA + bB \leftrightarrow cC + dD}$$

Kx is expressed by the expression:

$$K_x = \frac{x_C^c x_D^d}{x_A^a x_B^b} = K_P P^{-\Delta n}$$

At constant temperature:

$$\frac{\delta \ln K_x}{\delta P} = -\frac{\Delta n}{P}$$

If is zero, a change in pressure does not cause the equilibrium to shift.Δn

If is non-zero, it can be positive or negativeΔn

1. Δn is positive, which results in being negative; and decrease with the increase in pressure. The system moves to reach a new equilibrium state in which is smaller than in the initial state. The system moves in direction 2.$\frac{\delta \ln K_x}{\delta P} \ln K_x K_x \frac{x_C^c x_D^d}{x_A^a x_B^b}$
2. Δn is negative, which results in is positive; and are functions increasing with increasing pressure. The system moves to reach a new state of equilibrium in which is greater than in the initial state. The system moves in direction 1.$\frac{\delta \ln K_x}{\delta P} \ln K_x K_x \frac{x_C^c x_D^d}{x_A^a x_B^b}$

V.5.6. Influence of a change in composition on the shift in equilibrium

<u>Composition change at constant temperature and pressure</u>

K_x is given by the expression:

$$K_x = \frac{x_C^c x_D^d}{x_A^a x_B^b} = \frac{n_C^c n_D^d}{n_A^a n_B^b} N^{-\Delta n} = \textbf{Cte}$$ for constant T and P

If is zero, and one of the constituents A or B is added, the system moves in the direction of the disappearance of this constituent since it must remain constant.$\Delta n \frac{n_C^c n_D^d}{n_A^a n_B^b}$

When is positive and one of the constituents A or B is added, decreases. The system moves in the direction of the compensation of C and D, i.e. in direction 1.$\Delta n \frac{n_C^c n_D^d}{n_A^a n_B^b}$

If, under the same conditions, one of the constituents C or D is added, it increases and decreases. The system follows the law of moderation and moves in direction 2, corresponding to the decrease of the added constituent.$\frac{n_C^c n_D^d}{n_A^a n_B^b} N^{-\Delta n}$

If

is negative, the system also generally reacts in the direction of moderating the number of moles of the added component.Δn

Influence of the addition of an inert substance on the displacement of equilibria

If is zero, the equilibrium undergoes no displacement;Δn

If is nonzero, the equilibrium shifts in the direction of increasing the number of moles, regardless of the sign of .$\Delta n \Delta n$

Chapter VI: Application Exercises & Corrections

Exercise 1:

An ideal gas initially defined by (T_A=293k, P_A=1 atm, V_A=12liters) undergoes the following transformations:

From A to B: reversible adiabatic transformation with T_B=400 K

From B to C: Reversible compression at constant T up to V_C=1 liter

From C to D: Reversible adiabatic expansion

From D to A: Reversible isothermal expansion Calculate the number of moles of gas.

1. Completing thermodynamic states
2. Calculate the work, heat, internal energy variation, and enthalpy variance of the different transformations undergone by the ideal gas.

Data: C_V=3R/2 and R=8.314 $J.K^{-1}.mol^{-1}$.

Exercise 1 solution

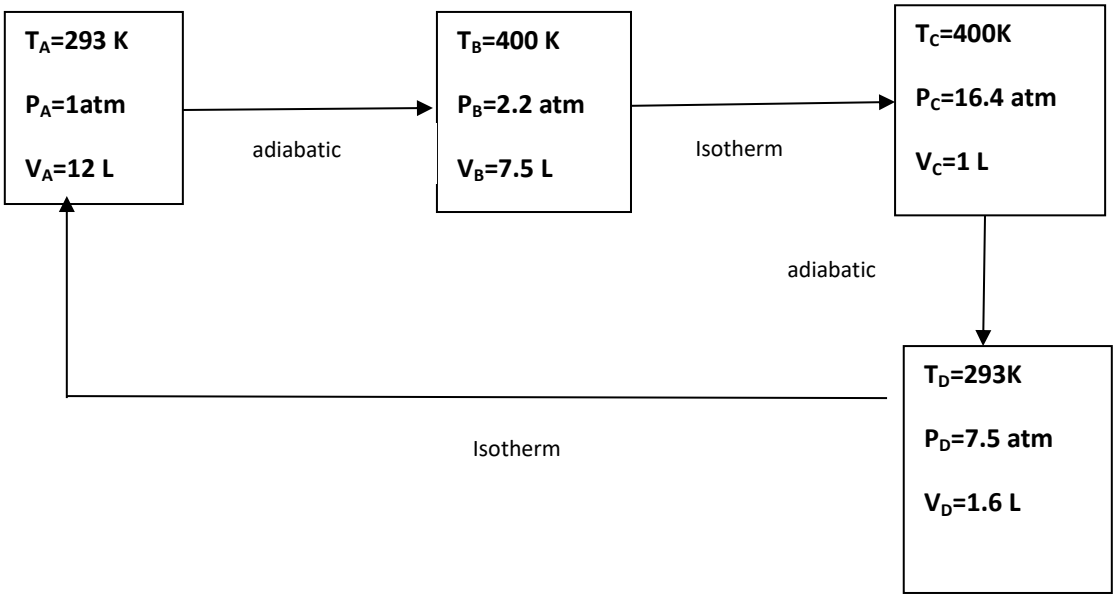
The gas is perfect, it is governed by the equation:

$P_AV_A=nRT_A$

The number of moles is equal to:

n=12/0.082.293= 0.5 mol

Let us fill in the thermodynamic states corresponding to the different transformations that the gas has undergone:



2. Calculation of W, Q, ΔU and ΔH of the different transformations:

The expressions and results are summarized in the table below:

Transformation	W	Q	ΔU	ΔH
Adiabatic	$nC_V(T_B-T_A)$ =667.2 J	Q=0	$nC_V(T_B-T_A)$ =667.2 J	$nC_P(T_B-T_A)$ 1112 J
Isotherm	$-nRTLnV_C/V_B$ =3350 J	$nRTLnV_C/V_B$ = -3350 J	0	0
Adiabatic	$nC_V(T_D-T_C)$ =-667.2 J	Q=O	$nC_V(T_D-T_C)$ = -667.2 J	$nC_P(T_D-TC)$ = -1112 J
Isotherm	$-nRTLnV_A/V_D$ =-2454 J	$nRTLnV_A/V_D$ =2454 J	0	0

Exercise 2

Let be one mole of a gas (NO) considered to be perfect and which has undergone the following cycle of transformations:

From 1 to 2: reversible compression at constant T;

From 2 to 3: Reversible expansion without heat energy exchange;

From 3 to 1: An isobaric heater.

1. Complete the following table:

	Statement 1	Statement 2	Statement 3
V(l)			
P(atm)	2	10	2
T(°K)	300		

2. Calculate the different forms of energy exchanged between NO and the external environment.

We give: Cv=3/2R

Exercise 2 Solution

Calculating the different state variables:

	Statement 1	Statement 2	Statement 3
V(l)	12,3	2,46	7,76
P(atm)	2	10	2
T(°K)	300	300	189,3

Calculation for the different transformations, W, Q, ΔU and ΔH

From 1 to 2:

$$W_{isotherme} = -nRTLn\frac{V_2}{V_1}$$

$$W_{isotherme} = -8,314.300Ln\frac{2,46}{12,3}$$

$$W_{isotherme} = 3930\,J$$

Transformation	W	Q	ΔU	ΔH
Isotherm	$\boldsymbol{W_{isotherme}} = -\boldsymbol{nRTLn}\frac{\boldsymbol{V_2}}{\boldsymbol{V_1}}$ =3930 J	$\boldsymbol{Q_{isotherme}} = \boldsymbol{W_{isotherme}} = +\boldsymbol{nRTLn}\frac{\boldsymbol{V_2}}{\boldsymbol{V_1}}$ =-3930 J	$nC_V(T_B-T_A)$ =0	$nC_P(T_B-T_A)$ 0
Adiabatic	$nC_V(T_C-T_B)$ =-1776 J	Q=O	$nC_V(T_C-T_B)$ = -1776 J	$nC_P(T_C-T_B)$ = -2960 J
Isobar	$\boldsymbol{W_{isobare}} = -\boldsymbol{P_{ext}}(\boldsymbol{V_A} - \boldsymbol{V_C})$ =-1184 J	$\boldsymbol{Q_{isobare}} = \Delta\boldsymbol{H_{isobare}} = \boldsymbol{nC_P}(\boldsymbol{T_A} - \boldsymbol{T_C})$=2960 J	$\Delta\boldsymbol{U_{isobare}} = \boldsymbol{nC_V}(\boldsymbol{T_A} - \boldsymbol{T_C})$=1385 J	$\Delta\boldsymbol{H_{isobare}} = \boldsymbol{nC_P}(\boldsymbol{T_A} - \boldsymbol{T_C})$=2960 J

Exercise 3

An ideal gas (CO_2) is defined in its initial state A by: V_A= 50 L, T_A = 298 K and and P_A = 1 bar. It underwent the following successive transformations:

a) From state 1 to state 2: Isothermal compression up to $_{VB}$ = 10 L.

b) From state 2 to state 3: Isobaric expansion up to V_C = 20 L.

c) From state 3 to state 4: Isothermal expansion up to V_D= 50 L.

d) Return to the initial state by an isochorous transformation.

We give: the ideal gas constant: R = 8.314 J.mol-1. K-1; C_p = 33.5 J·mol^{-1} · K^{-1}; C_v = 25.1 J·mol^{-1} · K^{-1}; 1 bar = 10^5 Pa.

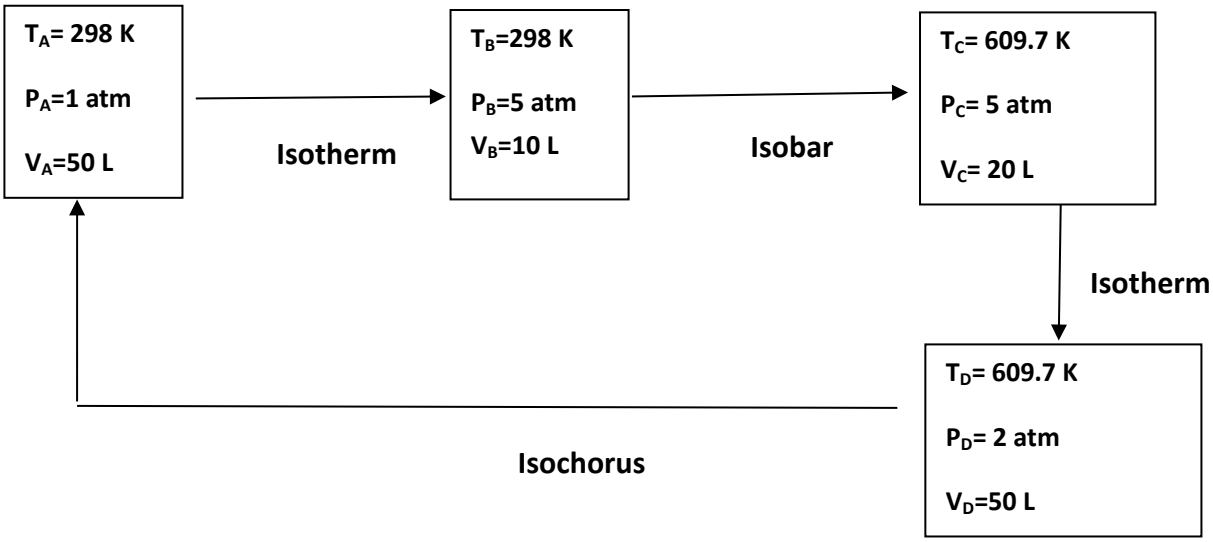
1. Calculate the number of moles of CO_2.
2. Fill in the different thermodynamic states corresponding to the different transformations.
3. Calculate the energies exchanged during these transformations.

Exercise 3 Solution

Calculate the number of moles n of carbon dioxide (CO2)

$n=P_AV_A/RT_A=1.50/0.082.298 = 2$ moles

Complete the different thermodynamic states.



Complete the table below:

Transformation	W	Q	ΔU	ΔH
Isotherm	-nRTLn V_B/V_A W_{AB}=797.5 J	nRTLn V_B/V_A -797.5J	0	0
Isobar	-P(VC-VB) -5000 J	$nC_P(T_C-T_B)$ =20883 J	$nC_V(T_C-T_B)$ =15647 J	$nC_P(T_C-T_B)$ =20883 J
Isotherm	-nRTLn V_D/V_C =-9289.4 J	nRTLn V_D/V_C 9289.4 J	0	0
Isochorus	0	$nC_V(T_A-T_D)$ =-15647 J	$nC_V(T_A-T_D)$ =-15647 J	$nC_p(T_A-T_D)$ =-20883 J

Exercise 4

Let us have the following reaction:

$$CH_4\ (g) + 4\ Cl_2\ (g) \dashrightarrow CCl_4(g) + 4\ HCl\ (g)$$

The enthalpy variation of this reaction at 298 K is: $\Delta_r H° = -401.08$ kJ/mol

Calculate the standard enthalpy of this reaction at 650 K.

Calculate the standard enthalpy of formation of CCl4 (g).

Data:

Compound	CH_4 (g)	Cl_2(g)	HCl(g)	CCl_4 (g)
ΔH°(kJ/mol)	-74,6	0	-92,3	?
Cp°(J K^{-1} mol^{-1})	35,71	33,93	29,12	83,51

Exercise 4 solution

The calculation of the change in enthalpy at T=650°C is done by applying Kirchoff's law:

$$\mathbf{\Delta_r H(650\ K) = \Delta_{rH}°(298\ K) + \int_{298}^{650} \Delta C_P dT}$$

$$\Delta \boldsymbol{C_P} = \sum \boldsymbol{C_P}(\boldsymbol{products}) - \sum \boldsymbol{C_P}(reagents)$$

$$\Delta \boldsymbol{C_P} = [Cp(CCl_4)+4C_P(HCl)]-[C_P(CH_4)+4C_P(Cl_2)]$$

$$\mathbf{\Delta rH_{650K} = -391.03\ kJ/mol}$$

Knowing the standard enthalpies of formation of compounds at 298 K, calculate the standard enthalpy of formation of CCl_4 (g).

By application of Hess's law:

$$\mathbf{\Delta rH°(298K)} = \sum \mathbf{\Delta rH°}(\boldsymbol{products}) - \sum \mathbf{\Delta rH°}(reagents)$$

$$\mathbf{\Delta rH°(CCl4) = -106.48\ kJ/mol}$$

Exercise 5

Two moles of diatomic gas N_2, initially in state A (V_A=8.2 liters, P_A=1 atm), undergo the series of reversible transformations:

Isothermal Compression

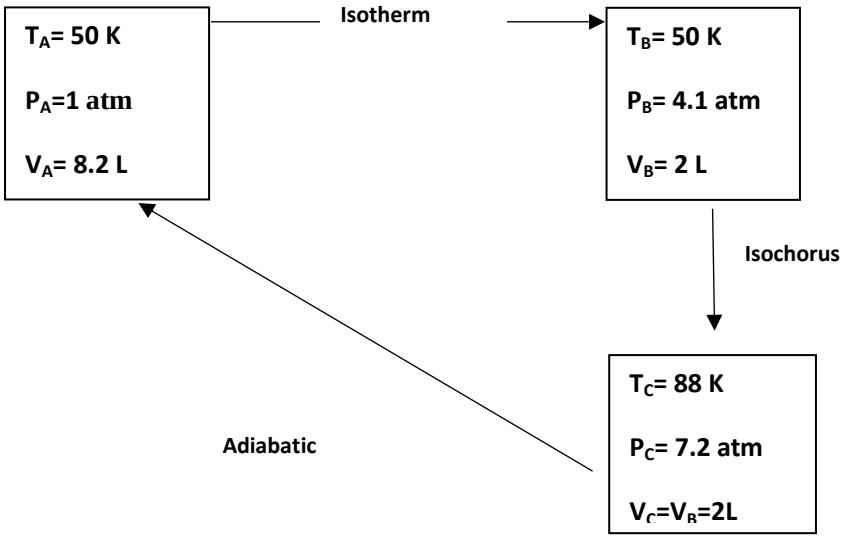
Isochoric transformation up to temperature T_C

Adiabatic transformation to the initial state.

We give R=0.082atm.L. $K^{-1}mol^{-1}$; R=8.314 $J.K_{-1}.mol^{-1}$; 1 atm=10^5 Pa; $1m^3=10^3$ liters.

Solution for Exercise 5

Complete the following thermodynamic states:



Complete the table below:

Transformation	W	Q	ΔU	ΔH
Isotherm	$-nRTLnV_B/V_A$ =1173J	$nRTLnV_B/V_A$ =-1173 J	0	0
Isochorus	0	$Q=nC_V(T_C-T_B)$=1579 J	$\Delta U=nC_V(T_C-T_B)$= 1579 J	$\Delta H=nC_P(T_C-T_B)$ =2228 J
Adiabatic	$W=\Delta U=nC_V(T_A-T_C)$= -1579 J	0	$\Delta U=nC_V(T_A-T_C)$= -1579 J	$\Delta H=nC_P(T_A-T_C)$ =-2228 J

Exercise 6

A monoatomic gas (Ar) undergoes a reversible adiabatic expansion from V_1=0.5 l to V_2= 100 l. The temperature and pressure of argon (Ar) in the initial state are 298K and 100kPa.

Calculate:

1. The final temperature of the gas,
2. The final pressure of the gas,
3. The variations of internal energy and the enthalpy of the gas,
4. The work done during relaxation.

Data: Cv= 12.48 J.k-1mol-1

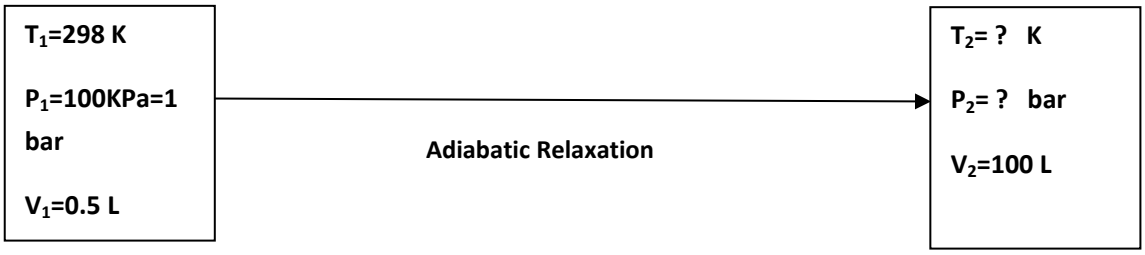
Solution for Exercise 6

- Determination of final T and p

The gas is perfect: calculation of the number of moles:

$$\boldsymbol{PV = nRT \leftrightarrow n = \frac{PV}{RT}}$$

$$\boldsymbol{n = \frac{0,5}{0,082 * 298} = 0,02\ mole}$$



- The final temperature is calculated from the equation:

$\boldsymbol{T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}}$

The gas is perfect:

$$\boldsymbol{P_2 V_2 = nRT_2}$$

- Determination of the different forms of energy involved during this transformation:

Internal energy:

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

YEAR:

Enthalpy:

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

The work:

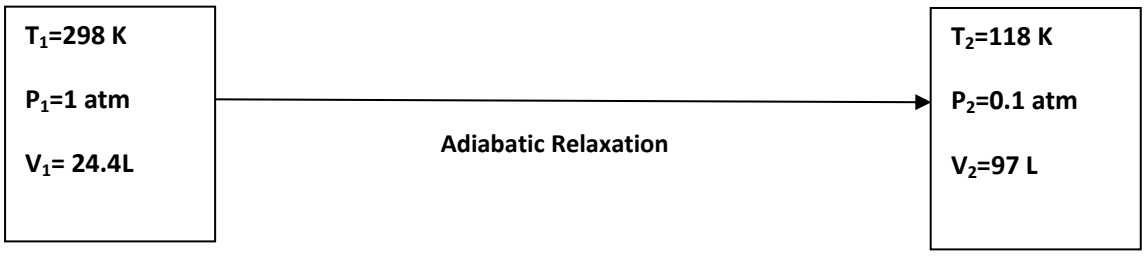
$$W = \Delta U = nC_V(T_2 - T_1)$$

Exercise 7

1. Calculate the work, heat, ΔU, ΔS and ΔH, of a mole of helium, which undergoes adiabatic expansion of an initial state 1, characterized by: T_1=25°C; P1=1atm to a final state 2, defined by: P_2=0.1 atm.
2. Determine the work W, the heat Q, the variation in internal energy, entropy and enthalpy during this transformation.

Solution for Exercise 7

- Let us fill thermodynamic states 1 and 2:



- Determine W, Q, , and during this transformation.ΔU, ΔH and ΔS

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

The gas is monoatomic:

$$\boldsymbol{W_{adiabatic}} = -3492 \text{ J}$$

$$\boldsymbol{Q_{adiabatic} = 0}$$

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

$$\boldsymbol{\Delta U} = -3492 \text{ J}$$

$$\boldsymbol{\Delta H = nC_P(T_2 - T_1)}$$

$$\boldsymbol{\Delta H = -3742\, J}$$

$$\boldsymbol{\Delta S_{adiabatic} = \frac{Q_{adiabatique}}{T} = 0}$$

Exercise 8

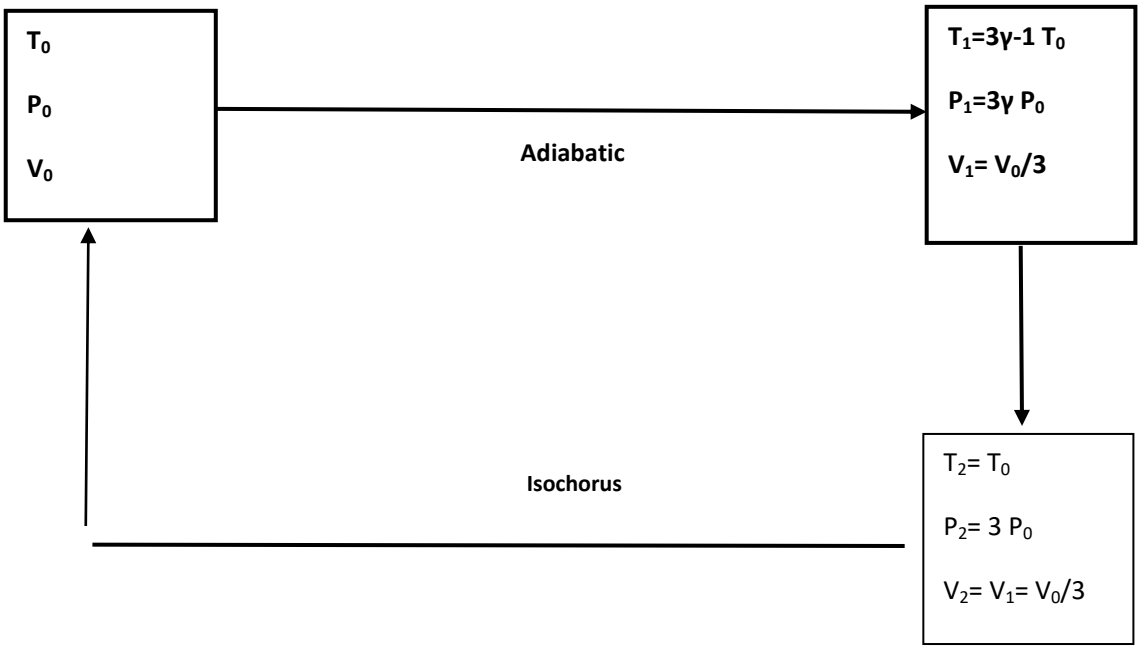
Let be an ideal gas initially defined by (P_0, V_0, T_0). It is subjected to the following reversible transformations:

- Adiabatic transformation bringing the gas to the state ($V_1 = \frac{V_0}{3}, P_1, T_1$).
- Constant volume transformation bringing the gas from the state (P_1, V_1, T_1) to the state ($V_2 = V_1, P_2, T_2 = T_0$).
- Isothermal transformation that brings it back from the state (P_2, V_2, T_2) to the initial state.
  1. Calculate state variables.
  2. Write down the expressions of work and heat during the three transformations.

N.B: $\gamma \succ 1$

Solution of Exercise 8

- ✓ Let's calculate the state variables by filling out the diagram below:



✓ Determine T_1, P_1, P_2 as a function of T0, P0 and $\gamma = \frac{C_p}{C_v}$

Let's recapitulate the coordinates of the different thermodynamic states A, B and C:

$$\boldsymbol{A(T_0, P_0, V_0)} \quad \boldsymbol{B\left(T_1, P_1, V_1 = {V_0}/{3}\right)} \quad \boldsymbol{C\left(T_2 = T_0, P_2 = 3P_0, V_2 = {V_0}/{3}\right)}$$

Knowing that:

The transformation is adiabatic characterized by the following expressions:

$$\boldsymbol{PV^{\gamma} = Cte} \qquad (1)$$

$$\boldsymbol{TV^{\gamma-1} = Cte} \qquad (2)$$

$$\boldsymbol{TP^{1-\gamma/\gamma} = Cte} \qquad (3)$$

By applying equation 2, we can deduce T1

$$\boldsymbol{T_0 V_0^{\gamma-1} = T_1 V_1^{\gamma-1}}$$

Therefore:

$$\boldsymbol{T_1 = T_0 \left(\frac{V_0}{V_1}\right)^{\gamma-1} = T_0 \left(\frac{V_0}{V_0/3}\right)^{\gamma-1} = T_0 \left(\frac{V_0}{V_0/3}\right)^{\frac{C_P}{C_V}-1}}$$

✓ Expressions of mechanical and calorific energy:

- *Adiabatic:*

$$W_{Adiabatic} = nC_V(T_1 - T_0) \text{ with n=1mole}$$

$$W_{Adiabatic} = \Delta U = C_V T_0(3\gamma\text{-}1\text{-}1)$$

$$Q_{Adiabatic} = 0$$

- *Isochore:*

Calculation of the work and heat exchanged during the transition from state B to state C

$$W_{Isochor} = 0$$

$$Q_{Isochor} = \Delta U = nC_V(T_2 - T_1)$$

$$Q_{Isochor} = \Delta U = C_V(T_0 - 3^{\gamma-1}T_0) = C_V T_0(1 - 3^{\gamma-1}) = -W_{Adiabatique}$$

- *Isotherm:*

$$W_{Isotherm} = -nRTLn\frac{V_0}{V_2}$$

$$W_{Isotherm} = -RT_0Ln\frac{V_0}{3V_0} = RT_0Ln3$$

$$Q_{Isotherm} = -W = nRTLn\frac{V_0}{V_2} = -RT_0Ln3$$

$$\Delta U_{isotherm} = 0$$

Exercise 9

We consider a mass of 1.2 kg of CO_2 under a pressure of 1 atm and contained in a volume of 0.8 m^3.

Determine in joules and calories the quantity of heat that must be supplied to this gas to raise its pressure to 5 atm.

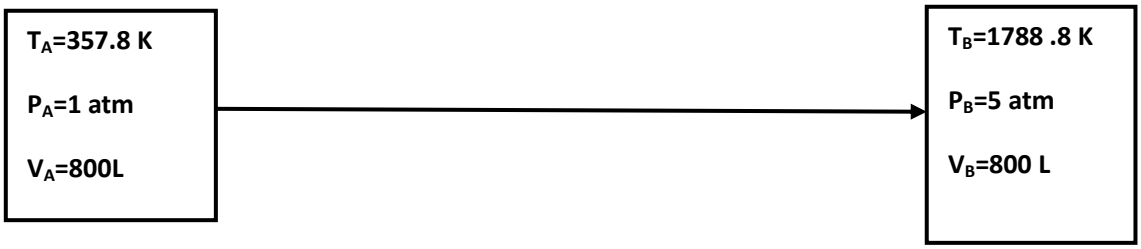
We give:

A_O=16 g/mol; A_C=12 g/mol; γ=1,29; R=8.314 $J.mol^{-1}.K^{-1}$

Solution of Exercise 9

Calculation of the number of moles of gas assumed to be perfect:

$$n = \frac{m}{M} = 27,27 \quad moles$$



By application of the 1st law of thermodynamics:

$$\Delta U = Q + W$$

$$W = 0$$

Where from

$$Q = nC_V(T_B - T_A)$$

AN:

$$Q = 1118.8 \text{ kJ} = 267.7 \text{ kcal}$$

Exercise 10

- We consider an ideal gas of n=1mol, defined in the initial state by P_A=1 atm and V_A=10 L. This gas undergoes reversible adiabatic compression up to the B state defined by: $T_B=1.6T_A$
    1. Calculate gas during this transformation.ΔS
    2. Calculate the final volume.

❖ We start from the same initial state (A) to subject a mole of this gas to an irreversible adiabatic compression up to the state C defined by: P_C=2.5 atm

1. Calculate V_C and T_C.
2. Calculate gas during this transformation.ΔS

We give: C_P=21 $J.K^{-1}.mol^{-1}$; R=8.314 $J.K^{-1}.mol^{-1}$

Exercise 10 Solution

The transformation is adiabatic Q_{rev}=0

$$\Delta S = \frac{Q_{rev}}{T}=0$$

Calculation of BV

For adiabatic transformation:

$$T_A V_A^{\gamma-1} = T_B V_B^{\gamma-1}$$

$V_B = V_A(T_A/T_B)^{1-\gamma}$ with $\gamma = C_P/C_P - R$

$$V_B = 4,9\ L$$

a) According to the 1st principle:

$$\Delta U = W_{irrev} = \frac{1}{\gamma-1}(P_C V_C/P_A V_A) = -P_C(V_C - V_A)$$

$$V_C = 6,4\ L$$

The gas is perfect:

$$P_C V_C = nRT_C$$

$$T_C = P_C V_C/nR$$

$$T_C = 195\ K$$

Calculation of the variation in entropy of the gas during this transformation:

$$dS = C_P \frac{dT}{T}$$

$$\Delta S = C_P Ln\, T_C/T_A$$

$$\Delta S = 2,25\ JK^{-1}$$

Exercise 11

Calculate the entropy of lead vapour at 25°C and 1 atm from the following data:

C_P(Solid Pb)	6.7 cal. K^{-1}.mol^{-1}
C_P(Liquid Pb)	6.3 cal. K^{-1}.mol^{-1}
C_P(Steam Pb)	4.97 cal. K^{-1}.mol^{-1}
T_f (Pb)	600 °K
T_{eb}(Pb)	2023 °K
Pb fusion entropy	1.9 cal. K^{-1}.mol^{-1}
Pb boiling entropy	22.4 cal. K^{-1}.mol^{-1}
Entropy of solid Pb at 25°C	15.53 cal. K^{-1}.mol^{-1}

Solution for Exercise 11

Pb(solid) ⟶ Pb(liquid) ⟶ Pb (vapor) T=298K, P=1atm

$$\Delta S = \Delta S_{25°C} + \Delta S_1 + \Delta S_{fusion} + \Delta S_2 + \Delta S_{vap} + \Delta S_3$$

$$\Delta S_1 = C_{P(Pb\ solide)} Ln \frac{T_f}{298}$$

$$\Delta S_{12} = 6,7 Ln \frac{600}{298} = 4,68\ cal\ K^{-1}$$

$$\Delta S_2 = C_{P(Pb\ liquid)} Ln \frac{T_{vap}}{T_f}$$

$$\Delta S_1 = 6,3 Ln \frac{2023}{600} = 4,68\ cal\ K^{-1} mol^{-1} = 7,65\ cal\ K^{-1}$$

$$\Delta S_2 = C_{P(Pb\ vapor)} Ln \frac{298}{T_{vap}}$$

$$\Delta S_3 = 4,97 Ln \frac{298}{2023} = 4,68\ cal\ K^{-1} mol^{-1} = -9,5\ cal\ K^{-1}$$

$$\Delta S = \Delta S_{25°C} + \Delta S_1 + \Delta S_{fusion} + \Delta S_2 + \Delta S_{vap} + \Delta S_3$$

YEAR:

$$\Delta S = 15,53 + 4,68 + 7,65 + 1,9 + 22,4 - 9,5 = 42,64\ cal\ K^{-1}$$

Exercise 12

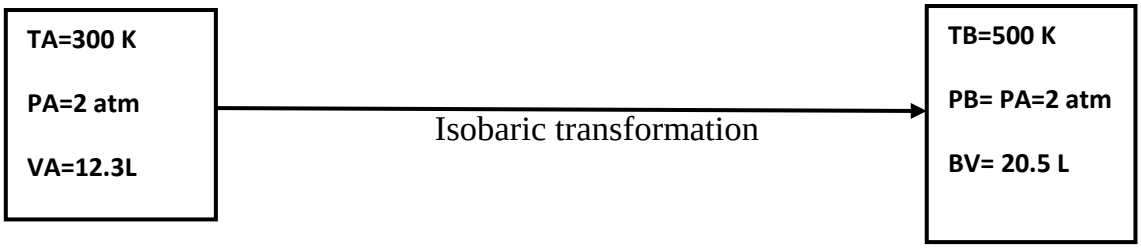
1. We consider a mole of ideal gas, subjected to transformations according to reversible processes:

This gas goes from state A defined by values (P_1, V_1, T_1) to state (B) defined by values (P_1, V_2, T_2). Give the expression of the work and the quantity of heat exchanged, the variation of internal energy and the variation of the enthalpy of the gas during this transformation.

2. This mole of ideal gas now goes from the state (B) defined by the values (P_1, V_2, T_2) to the state C defined by the values (P_2, V_2, T_1). Express the work and the amount of heat exchanged, the variation in internal energy and the variation in enthalpy of the gas during this new transformation.
3. The gas now moves from the (A) state defined by the values (P_1, V_1, T_1) to the C state defined by the values (P_2, V_2, T_1). What happens to the variations in the internal energy and enthalpy of the gas? Give the expressions of the work and the amount of heat exchanged.

Data:P_A=2atm;TA=300K; T_B=500K; R=8.31J. $K^{-1.}mol^{-1}$; C_v=20.77J. $K^{-1.}mol^{-1}$; C_p=29.08J. K-1.mol-1

Exercise 12 Solution



Let's fill in the thermodynamic states above:

The gas is perfect, it is governed by the equation:

$$PV = nRT \text{ with n=1mole}$$

Let's calculate VA

$$P_A V_A = RT_A$$

$$V_A = \frac{RT_A}{P_A}$$

$$V_A = 12.3 \text{ L}$$

$$P_B V_B = RT_B$$

$$V_B = \frac{RT_B}{P_B}$$

$$V_B = 20.5 \text{ L}$$

Let us calculate the work, the heat, the variation of the internal energy and the enthalpy of the different transformations:

1st transformation: Isobaric transformation:

$$W_{AB} = W_{isobare} = -P_{ext}(V_B - V_A)$$

$$W_{AB} = W_{isobare} = -1640\ J$$

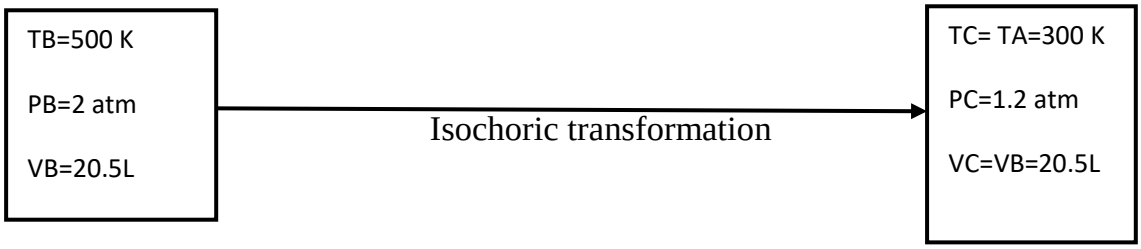
$$Q_{AB} = Q_{isobare} = \Delta H_{AB} = C_P(T_B - T_A)$$

$$Q_{isobare} = 5816J$$

$$\Delta U_{AB} = C_V(T_B - T_A)$$

$$\Delta U_{AB} = +4154\,J$$

B→C transformation: isochoric transformation that corresponds to the filling of the thermodynamic states B and C below:



Let's calculate the work, the heat, the variation of the internal energy and the enthalpy of the 2nd transformation: Isochoric transformation:

$$W_{BC} = W_{isochore} = 0\,J$$

$$Q_{BC} = Q_{isochore} = \Delta U_{BC} = C_V(T_C - T_B)$$

$$Q_{isochore} = -4154\,J$$

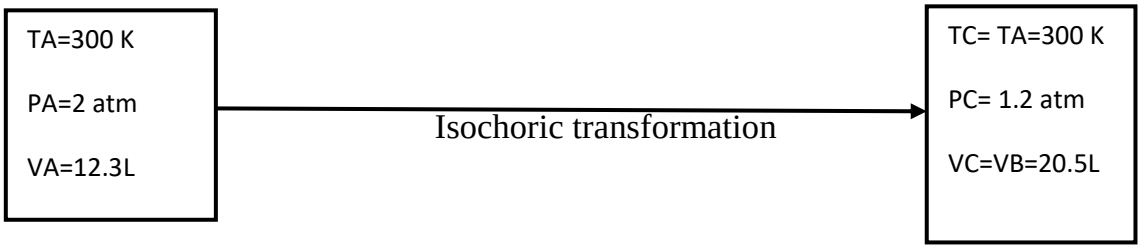
$$\Delta U_{BC} = C_V(T_C - T_B)$$

$$\Delta U_{AB} = -4154\,J$$

$$\Delta H_{BC} = C_P(T_C - T_B)$$

$$\Delta H_{BC} = 5816J$$

A→C transformation: isothermal transformation that corresponds to the filling of the thermodynamic states A and C below:



Let's calculate the work, the heat, the variation of the internal energy and the enthalpy of the 3rd transformation: Isothermal transformation:

$$\boldsymbol{W_{AC} = W_{isotherm} = -nRTLn\frac{V_C}{V_A}}$$

$$\boldsymbol{W_{AC} = W_{isotherm} = -1274\,J}$$

$$\boldsymbol{Q_{AC} = Q_{isotherm} = -W_{isotherm} = 1274\,J}$$

$$\boldsymbol{Q_{isotherm} = 1274\,J}$$

$$\boldsymbol{\Delta U_{AC} = C_V(T_C - T_B)}$$

$$\boldsymbol{\Delta U_{AB} = 0\,J}$$

$$\boldsymbol{\Delta H_{AC} = C_P(T_C - T_B)}$$

$$\boldsymbol{\Delta H_{BC} = 0\,J}$$

Exercise 13

A mole of a monoatomic ideal gas, with an initial temperature of 300 °K, undergoes a transformation from 10 atm to 1 atm. Calculate T_f, V_f, and W when this transformation is:

- Reversible
- Irreversible, at constant external pressure equal to 1 atm.

Solution for Exercise 13

Let's calculate the state variables by filling in the thermodynamic states below:

For an adiabatic transformation, we have the following expressions:

$$PV^{\gamma} = Cte$$

$$TV^{\gamma-1} = Cte$$

$$TP^{1-\gamma/\gamma} = Cte$$

$$P_A V_A^{\gamma} = P_B V_B^{\gamma}$$

Let's shoot V_B

$$V_B = \left(\frac{P_A}{P_B}\right)^{1/\gamma} V_A$$

$V_B = 36\ L$

Exercise 14

The combustion reaction of benzene is:

$$C_6H_6(liq) + 15/2\ O_2(g) \rightarrow 6CO_2(g) + 3H_2O(liq)$$

The standard molar enthalpies of formation at 25°C are shown in the table below:

	$CO_2(g)$	$H_2O(liq)$	$C_6H_6(liq)$
$\Delta H°_f$(kJ.mol-1)	-393.5	-285.8	+49.0

Calculate the standard enthalpy of benzene combustion at 25°C.

At 25°C, the standard enthalpy of the reaction:

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$$

is $\Delta H° = -2.84kJ$.

Using the above data, calculate the standard molar enthalpy of carbon monoxide formation. The standard molar enthalpy of water vaporization at 25°C is given: +44.27 kJ.mol^{-1}.

Solution for Exercise 14

We apply Hess's law:

$$\mathbf{\Delta rH°(298K)} = \sum \mathbf{\Delta rH°}(\boldsymbol{products}) - \sum \mathbf{\Delta rH°}(reagents)$$

$$\mathbf{\Delta rH°(298K)} = \left(\mathbf{6}\Delta \boldsymbol{H^0_{f(CO2,g)}} + \mathbf{3}\Delta \boldsymbol{H^0_{f(H2O,l)}}\right) - \left(\Delta \boldsymbol{H^0_{f(C6H6,g)}} + \mathbf{15/2}\Delta \boldsymbol{H^0_{f(O2,g)}}\right)$$

$$\mathbf{\Delta rH°(298K)} = \mathbf{-3169}\,\boldsymbol{kJmol^{-1}}$$

At 25°C, the standard enthalpy of the reaction:

$$\mathbf{CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)}$$

is Δ H° = -2.84kJ

Calculation of the standard molar enthalpy of carbon monoxide formation. The standard molar enthalpy of water vaporization at 25°C is given: +44.27 kJ.mol-1.

$$\mathbf{\Delta rH°(298K)} = \sum \mathbf{\Delta rH°}(\boldsymbol{products}) - \sum \mathbf{\Delta rH°}(\boldsymbol{reagents})$$

$$\Delta H^0_{Reaction} = \left[\Delta H^0_{f(CO)} + \Delta H^0_{f(H2O)}\right] - \left[\Delta H^0_{f(CO2)} - \Delta H^0_{f(H2)}\right]$$

With:

$$\Delta H^{\circ}_{Vap,H2O} = \Delta H^{\circ}_{f,H2O(g)} - \Delta H^{\circ}_{f,H2O(l)}$$

Exercise 15

Knowing the enthalpy of formation of hydrocyanic acid in aqueous solution at 20°C: Δ H°f (HCN,aq)= 105.4 kj.mol-1 and the enthalpy at 20°C of the synthesis reaction of adenine C5H5N5 in aqueous solution from hydrocyanic acid:

$$\mathbf{5\ HCN(aq) \longrightarrow C_{5H5N5}(aq) \qquad \Delta H°= -422.4\ kJ}$$

Give the molar enthalpy of formation of adenine in aqueous solution under the same experimental conditions.

Solution for Exercise 15

$$\mathbf{\Delta rH°(298K)} = \sum \mathbf{\Delta rH°}(\boldsymbol{products}) - \sum \mathbf{\Delta rH°}(\boldsymbol{reagents})$$

$$\mathbf{\Delta rH°(293K)} = \left(\Delta \boldsymbol{Hf}^{\circ}_{\mathbf{C5H5N5}}\right) - \mathbf{5}\left(\Delta \boldsymbol{Hf}^{\circ}_{\mathbf{HCN}}\right)$$

$$\Delta \boldsymbol{Hf}^{\circ}_{\mathbf{C5H5N5}} = \mathbf{\Delta rH°(293K)} + \mathbf{5}\left(\Delta \boldsymbol{H}^{\circ}_{\mathbf{HCN}}\right)$$

$$\Delta \boldsymbol{Hf}^{\circ}_{\mathbf{C5H5N5}} = \mathbf{105\ kJ}$$

Exercise 16

1. Calculate the enthalpy of the reaction at 25°C:

$$\mathbf{CO(NH_2)_2(c) + H_2O(l) \longrightarrow CO_2(g) + 2NH_3(g)}$$

Knowing at the same temperature, the following enthalpies of reactions:

$1/2H_2(g) + 1/2Cl_2(g) \rightarrow HCl(g)$	**$\Delta H°_2 = -92.30\ kJ.mol^{-1}$**
$CO(g) + H_2O\ (g) \rightarrow CO_2(g) + H_2(g)$	**$\Delta H°_3 = -41.13\ kJ$**
$CO(g) + Cl_2(g) \rightarrow COCl_2(g)$	**$\Delta H°_4 = -112.5\ kJ$**
$H_2O(l) \rightarrow H_2O(g)$	**$\Delta H°_5 = 44.27 kJ.mol^{-1}$**
$COCl_2(g) + 2NH_3(g) \rightarrow CO(NH_2)_2(c) + 2HCl(g)$	**$\Delta H°_6 = -201.0\ kJ.$**

2. The decomposition of urea by CO_2 and NH_3 water is catalyzed by the enzyme urease in aqueous solution. Using the result obtained in the first question, calculate the enthalpy of the reaction at 25°C:

$$CONH_2(aq) + H_2O(l) \rightarrow CO_2(aq) + 2NH_3(aq)$$

At 25°C, the molar enthalpies of dissolution of compounds with infinite dilution are given:

	Urea	CO_2	NH_3
$\Delta H°_d$(kJ.mol-1)	13.93	-19.41	-34.64

Exercise 16 Solution

Reaction 1 is a combination of reactions 2 to 6:

$$\Delta H_1^\circ = 2\Delta H_2^\circ + \Delta H_3^\circ - \Delta H_4^\circ + \Delta H_5^\circ - \Delta H_6^\circ$$

YEAR:

$\Delta H_1^\circ = \mathbf{132,04}$ kJ.mol-1

Exercise 17

Let us consider the reaction:

$$\mathbf{C_6H_5CH_3(g) + 3H_2(g) \longrightarrow C6H11CH_3(g)}$$

What is the enthalpy of the above reaction at 25°C? At 125°C?

	$C_6H_5CH_3(g)$	$H_2(g)$	$C_6H_{11}CH_3(g)$
$\Delta H°_f$ (kj.mol^{-1})	50.0	0	-154.8
$C_p^0\left(j.k^{-1}mol^{-1}\right)$	81.59	28.53	135.14

Data:

Solution for Exercise 17

$$\mathbf{\Delta rH°(298K)} = \sum \mathbf{\Delta rH°}(\boldsymbol{products}) - \sum \mathbf{\Delta rH°}(\boldsymbol{reagents})$$

$$\mathbf{\Delta rH°(298\ K)} = [(\mathrm{C}\ \mathbf{\Delta rH°}_{6H11CH3}) - (\mathrm{C}\ \mathbf{\Delta rH°}_{6H5CH3})]$$

$$\mathbf{\Delta rH°(298\ K) = -205\ kJ/mol}$$

At 125°C: we apply Kirchoff's law:

$$\mathbf{\Delta_{rH}(398.15\ K) = \Delta_{rH}°(298.15\ K)} + \int_{298,15}^{398,15} \Delta C_P dT$$

$$\Delta C_P = \sum C_P(products) - \sum C_P(reagents)$$

$$\Delta C_P = 25\ kJ/mol$$

ΔrH650K=-202.3 kJ/mol

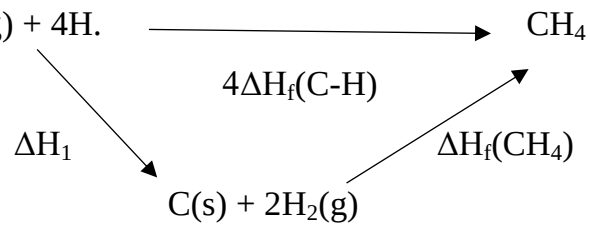
Exercise 18

Determine the energy of the C-H bond in methane from the data summarized in the table:

ΔfH° (CH_4)	ΔsubH° (Cs)	ΔLH° (H-H)
74.8 kJ.mol-1	717 kJ	-436 kJ

Solution for Exercise 18

T = 298 K



$$\Delta H_{cycle} = 0$$

$$\Delta H_{cycle} = 4\Delta H_{f(C-H)} - \Delta H_{f(CH4)} + \Delta H_{sub(C,S)} - \Delta H_{f(H-H} = 0$$

$$\Delta H_{f(C-H)} = -269,55\ kJ/mol$$

Exercise 19

Determine the heat of methane formation (CH4) at 20°C and 500°C from the following data:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H^{\circ}_{298K} = -94,2\ kCal.mol^{-1}$$

$$H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(g)} \qquad \Delta H^{\circ}_{298K} = -68,35\ kCal.mol^{-1}$$

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)} \qquad \Delta H^{\circ} = -212,98\ kCal.mol^{-1}$$

We give:

$$C_{P(Cs)}(cal.mol^{-1}.K^{-1}) = 1,1 + 48.10^{-4}T + 12.10^{-7}T^2$$

$$C_{P(H_{2(g)})}(cal.mol^{-1}.K^{-1}) = 6,5 + 9.10^{-1}T$$

$$C_{P(CH_{4(g)})}(cal.mol^{-1}.K^{-1}) = 5,34 + 1140.10^{-4}T$$

Exercise 19 Solution

Heat of methane formation at 298.15K:

$$\Delta H_R = \Delta H_{f(CH4)} - \Delta H_{f(CO2)} - 2\Delta H_{f(H2O)}$$

$$\Delta H_{f(CH4)} = \Delta H_R + \Delta H_{f(CO2)} + 2\Delta H_{f(H2O)}$$

$$\Delta H_{f(CH4)} = 444\ kCal.mol^{-1}$$

Exercise 20

Let us consider the following reactions at 298K:

1) $C_{(s)} + 2H_2O_{(g)} \rightarrow CO_{2(g)} + 2H_{2(g)}$ ΔH_1°= ?

2) $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ $\Delta H_2^{\circ} = 74,9\ kJ.mol^{-1}$

3) $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$ $\Delta H_3^{\circ} = -804,2\ kJ.mol^{-1}$

4) $H_2O_{(g)} \rightarrow H_{2(g)} + 1/2O_{2(g)}$ $\Delta H_4^{\circ} = 231,8\ kJ.mol^{-1}$

Calculate the heats of reaction (1) at constant pressure and constant volume at 500K.

Data:

$C_P(C_s) = 16,84 + 4,77.10^{-3}T$ JK-1mol-1

$C_P(H_2O_{(g)}) = 3,54 + 1,29.10^{-3}T$ JK-1mol-1

$C_P(H_{2(g)}) = 27,28 + 3,26.10^{-3}T$ JK-1mol-1

$C_P(CO_{2(g)}) = 44,22 + 8,79.10^{-3}T$ JK-1mol-1

Exercise 20 Solution

$$\Delta H_1^\circ = \Delta H_2^\circ - \Delta H_3^\circ + 4\Delta H_4^\circ$$

AN: $$\Delta H_1^\circ = 1806.3\ kJ.mol^{-1}$$

To calculate the enthalpy change of the reaction at 500 K, we must apply Kirchoff's law:

$$\Delta_{rH}(500\ K) = \Delta_{rH}°(298.15\ K) + \int_{298,15}^{500} \Delta C_P dT$$

Heat at constant volume represents the variation of internal energy.

According to the 1st principle:

$$\Delta rH(500\ K)\ \Delta = {}_{rU}(500\ K) + \Delta nRT$$

Exercise 21

Let us consider the following chemical reaction:

$$C_2H_{4(g)} + H_2O_{(g)} \leftrightarrow C_2H_5OH_{(g)}$$

1. Calculate the standard free enthalpy of the reaction at 25°C.
2. Is this reaction favourable to the formation of $C_2H_5OH_{(g)}$?
3. Calculate the equilibrium constant at 25°C.
4. Calculate the equilibrium constant at 573 K assuming that ΔH° of the reaction is constant in the temperature range considered.
5. How can we promote the formation of $C_2H_5OH_{(g)}$?
6. It is assumed that at the initial instant, one mole of and one mole of water is mixed at 573 K. Calculate in moles the composition of the mixture at equilibrium, knowing that the final pressure is 20 atm.C_2H_4

Data:

Compounds	ΔH_f° (kJ.mol-1)	ΔG_f° (kJ.mol-1)
$C_2H_{4(g)}$	52,28	68,12
$H_2O_{(g)}$	-241,83	-228,59
$C_2H_5OH_{(g)}$	-235,08	-168,45

Exercise 21 solution

$$C_2H_{4(g)} + H_2O_{(g)} \leftrightarrow C_2H_5OH_{(g)}$$

Calculation of the standard free enthalpy at 25°C of the reaction.

$$\Delta G^0_{réaction} = \sum \Delta G^0_{f(produits)} - \sum \Delta G^0_{f(réactifs)}$$

$$\Delta G^0_{réaction} = -7,98\ kJ$$

$\Delta G^0_{réaction}$ is less than 0, the reaction is spontaneous. It is favourable to the formation of ethanol.$C_2H_5OH_{(g)}$

Calculation of the equilibrium constant at 25°C:

$$\Delta G^\circ_{298K} = -RTLnK$$

$$K = 25$$

Let us now calculate the equilibrium constant K at the temperature of 573.15 K

In this case, we apply the vant'Hoff equation:

$$\frac{d \ln K_P}{dT} = \frac{\Delta H^\circ_T}{T^2}$$

$$\ln \frac{K_{T2}}{K_{T1}} = \int_{T1}^{T2} \frac{\Delta H^\circ_T}{RT^2} dT$$

ΔH°_T is assumed to be constant in the temperature range:

$$\ln \frac{K_{T2}}{K_{T1}} = \frac{\Delta H^\circ_T}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Let's calculate at temperature T1=298K: To do this, we apply Hess's law:ΔH°_T

$$\Delta H^0_{réaction} = \sum \Delta H^0_{f(products)} - \sum \Delta H^0_{f(reagents)}$$

YEAR:

$$\Delta H^{0}_{réaction} = -45,53\ kJ$$

$$K_{573,15} = 3,75.10^{-3}$$

Exercise 22

The gas phase equilibrium is considered as follows:

$$N_{2(g)} + O_{2(g)} \leftrightarrow 2NO_{(g)}$$

1. Calculate the enthalpy of the above reaction at temperature T_1=328 K. It will be assumed that the molar heat capacities are constant in the temperature range considered.
2. Calculate the value of the equilibrium constant at temperature T_1.
3. In which direction does the equilibrium move when the temperature rises?
4. What is the influence of the introduction of an inert gas?
5. Air is heated to 2000 K; at this temperature nitrogen and oxygen react according to the above equilibrium. The equilibrium constant is 4.10^{-4}.

What is the value of the partial pressure of NO, the total pressure being 1 atm. We will assume that air is made up of 20% oxygen and 80% nitrogen.

Data:

T0298K	$N_{2(g)}$	$O_{2(g)}$	$NO_{(g)}$
CP /J.K-1.mol-1	29,12	29,36	29,86
S°/ J.K-1.mol-1	191,49	205,03	210,62
ΔH°/ kJ.mol-1			90,37
ΔG°/ kJ.mol-1			

Exercise 22 solution

To calculate the enthalpy variation at temperature T_1=328 K, we apply Kirchoff's law, given by the expression below:

$$\Delta \boldsymbol{H}^{\circ}_{\boldsymbol{328K}} = \Delta \boldsymbol{H}^{\circ}_{\boldsymbol{298K}} + \int_{\boldsymbol{298K}}^{\boldsymbol{T_1=328K}} \Delta \boldsymbol{C_P dT}$$

The molar heat capacities at constant pressure are assumed to be constant in the temperature range. The variation is given by the expression below:ΔC_P

$$\Delta \boldsymbol{C_P} = \sum \boldsymbol{nC_{P(products)}} - \boldsymbol{nC_{P(reagents)}}$$

$$\Delta \boldsymbol{C_P} = \boldsymbol{2C_{P(NO)}} - \left[\boldsymbol{C_{P(N_2)}} + \boldsymbol{C_{P(O_2)}}\right]$$

$\Delta \boldsymbol{C_P}$ =1.24 J $^{\text{K-1 mol-1}}$

Where from

$$\Delta \boldsymbol{H}^{\circ}_{\boldsymbol{328K}} = \boldsymbol{180,77J}$$

The reaction is endothermic

Let us calculate the change in entropy at temperature T1=328 K:

$$\Delta S^{\circ}_{328K} = \Delta S^{\circ}_{298K} + \int_{298K}^{T_1=328K} \Delta C_P \left(\frac{dT}{T}\right)$$

$$\Delta \boldsymbol{S}^{\circ}_{\boldsymbol{328K}} = \Delta \boldsymbol{S}^{\circ}_{\boldsymbol{298K}} + \Delta \boldsymbol{C_P Ln}\left(\frac{\boldsymbol{T1}}{\boldsymbol{298}}\right)$$

$$\Delta \boldsymbol{S}^{\circ}_{\boldsymbol{298K}} = \sum \boldsymbol{S}^{\circ}_{\boldsymbol{Products}} - \sum \boldsymbol{S}^{\circ}_{reagents}$$

$\Delta \boldsymbol{S}^{\circ}_{\boldsymbol{298K}} = \boldsymbol{24,72}$ J $^{\text{K-1}}$

$\Delta \boldsymbol{S}^{\circ}_{\boldsymbol{328K}} = \boldsymbol{24,83}$ J $^{\text{K-1}}$

The free enthalpy variation of this reaction at 328K:

$$\Delta \boldsymbol{G}^{\circ}_{\boldsymbol{328K}} = \Delta \boldsymbol{H}^{\circ}_{\boldsymbol{328K}} - \boldsymbol{T}\Delta \boldsymbol{S}^{\circ}_{\boldsymbol{328K}}$$

$$\Delta \boldsymbol{G}^{\circ}_{\boldsymbol{328K}} = \boldsymbol{-172,6\ kJ}$$

$\Delta \boldsymbol{G}^{\circ}_{\boldsymbol{328K}}$ is less than zero, so the reaction is spontaneous and the equilibrium moves in direction 1

The equilibrium constant is calculated from the expression below:

$$\Delta \boldsymbol{G}^{\circ}_{\boldsymbol{328K}} = -RTLnK$$

$K = e^{-\frac{\Delta G^{\circ}_{328K}}{RT}}$ = 3.1027

The equilibrium constant is very large, so this reaction is practically total in sense 1.

The qualitative meaning of this variation as a function of temperature is given by Le Châtelier's law:

An increase in temperature favours an equilibrium reaction in the sense that it is endothermic.

The introduction of an inert gas has no influence on the direction of displacement of this equilibrium since Δn=0 (no variation in the number of moles)

	N_2(g)	O_2(g)	NO(g)	total
The initial number of moles	4n	n	0	5n
The number of moles in equilibrium	n(4-α)	n(1-α)	2n α	5n
Partial pressure	$\frac{4-\alpha}{5}P_T$	$\frac{1-\alpha}{5}P_T$	$\frac{2\alpha}{5}P_T$	P_T

Exercise 23

Calculate the entropy variation at 25°C of the reaction:

$$\boldsymbol{CaCO_3 \rightarrow CaO + CO_2}$$

Knowing the following entropies:

Constituents	$CaCO_3$	CaO	CO_2
Entropy/ cal.mol^{-1}. K^{-1}	22,2	9,5	51,1

Calculate the change in free enthalpy during the reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

Knowing that:

$CO + \frac{1}{2}O_2 \rightarrow CO_2$ ΔG=-61.4 cal

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ ΔG=-54.63 cal

Exercise 23 solution

Calculation of the variation of the reaction (1)$\Delta S^{\circ}_{R(298K)}$

$$\Delta \boldsymbol{S^{\circ}_{R(298K)}} = \sum \boldsymbol{S^{\circ}_{Products}} - \sum \boldsymbol{S^{\circ}_{Reagents}}$$

YEAR:

$$\Delta \boldsymbol{S^{\circ}_{R(298K)}} = \boldsymbol{38,4\ cal.mol^{-1}.K^{-1}}$$

Calculation of the variation of reaction (2) based on the free enthalpies of reactions (3) and (4):ΔG°_R

Reaction (2) is the subtraction of reactions (3) and (4), therefore:

$$\boldsymbol{\Delta G_2 = \Delta G_3 - \Delta G_4}$$

$\boldsymbol{\Delta G_2}$ =-6.77 kcal

Exercise 24

1. Calculate the variation in internal energy involved when going from a molecule-gram of liquid water at 100°C to a molecule-gram of water vapour at the same temperature. The latent heat of vaporization is given to be equal to 499 cal/g.
2. Methyl alcohol has a boiling point of around 65°C. You need to provide 263 cal to vaporize 1g of liquid alcohol at 65°C under a pressure of 1 atm.

Calculate the variation in internal energy involved when passing from a molecule-gram of liquid methyl alcohol at 65°C to a molecule-gram of methyl alcohol vapor at the same temperature.

3. It will be assumed that the vapor of methyl alcohol behaves like an ideal gas. The volume of the liquid should be neglected.

Solution for exercise 24

The change in internal energy in a chemical reaction or a change of state is equal to the heat of that constant-volume transformation.

Recall that the latent heat of a change of state is equal to the heat brought into play by this change at a fixed temperature. To transform 1g of liquid water into 1g of steam water at 100°C, 499 cal. For a gram molecule:

$$\Delta U = 499 * 18 = 8982\ cal$$

Let us calculate the total energy required to vaporize a molecule-gram of methyl alcohol at 65°C: molecular weight of alcohol CH3OH = 32 g/mol.

For 1g you need 263 cal, for 32 g you need 32*263= 8416 cal/mol; i.e. Q=8.416 kcal/mol .

This energy represents:

The variation of internal energy during the change of state;ΔU

The work done externally by the variation in the volume of methyl alcohol during its vaporization, i.e. -P.ΔV

ΔV corresponds to the change in volume when going from 1 mole of liquid CH_3OH (negligible volume) to 1 mole of gaseous CH_3OH at 65°C, i.e. the volume occupied by 1 mole of gaseous CH_3OH at 65°C.

If we assimilate steam to an ideal gas, we can calculate this volume at 65°C and under 1 atm: PV=nRT,

i.e., at two temperatures, n and P remain constant,

$T_1 = 273\ K$

$T_2 = 333\ K$

$$V_2 = V_1 \frac{T_2}{T_1} = 22,4 * \frac{338}{273} = 27,73\ l$$

Where from:

$$W = -P\Delta V = -671,62\ cal$$

However, internal energy:

$$\Delta U = Q - P\Delta V = 7,74\ kcal/mol$$

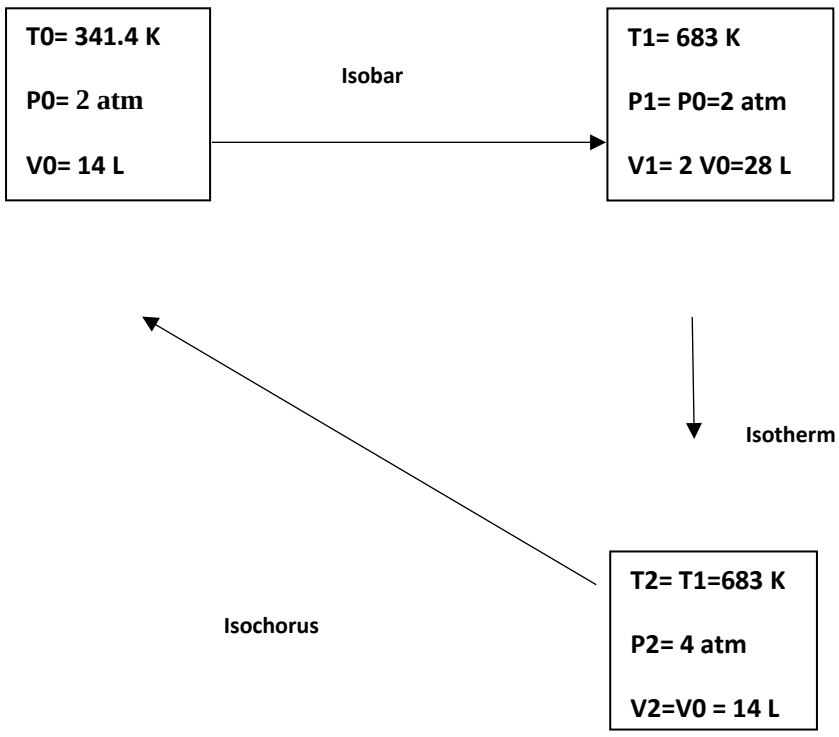
Exercise 25

The initial state of a mole of ideal gas is characterized by P_0 = 2 atm, V_0 = 14 L. This gas is successively subjected to the following reversible transformations:

- An isobaric relaxation that doubles its volume;
- An isothermal compression that brings it back to its initial volume;
- An isochoric cooling that brings it back to the initial state.

We give $\gamma = C_p/C_v = 1.4$; **R= 0.082 atm. L.K^{-1}.mol^{-1}; R=8.314 J.K^{-1}.mol^{-1}**, C_V=5R/2, C_P=7R/2

1. Complete the following thermodynamic states:



2. Complete the table below:

Transformation	**W**	**Q**	**ΔU**	**ΔH**
Isobar	**$-P(V_1-V_0)$ $=-2800$ J**	**$nC_p(T_1-T_0)$ $=9940$ J**	**$nCv(T_1-T_0)$ $=7100$ J**	**$nCp(T_1-T_0)$ $=9940$ J**
Isotherm	**$-nRTLnV_2/V_1$ $=3936$ J**	**$-W$ -3936 J**	**0**	**0**
Isochorus	**0**	**$nCv(T_0-T_2)$ $=-7100$ J**	**$nCv(T_0-T_2)$ $=-7100$ J**	**$nCp(T_0-T2)$ $=-9940$ J**

3. Calculate the internal energy change ΔU of the cycle.

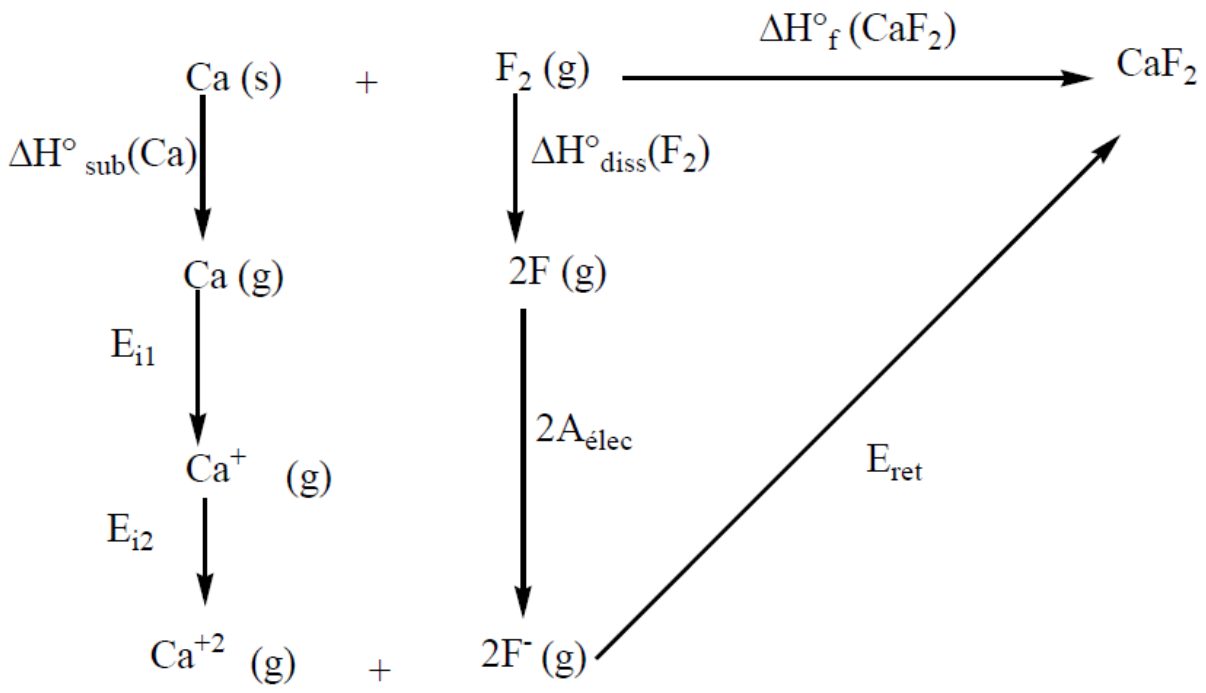
   $\Delta U_{cycle}=0$

<u>Exercise 26</u>

We propose to determine the reticular energy for a mole of (CaF_2) from a number of experimental data at 298 K. This data is:

Enthalpy of sublimation of Ca (solid): $\Delta H_{sublimation}$ (Ca,s)= 177.8 kJ/mol; Ionization energy of Ca (gas): E_i (Ca,g)= 1735 kJ/mol; Dissociation energy of the bond (F-F): $\Delta H_{dissociation}$(F-F)= 157 kJ/mol; Electron affinity of F (gas): A_e(F,g)=- 328 kJ/mol; Enthalpy of formation of CaF_2 (solid): $\Delta H_{formation}$ (CaF_2,s) = -1228 kJ/mole

(1) Represent the Born-Haber cycle.



(2) Calculate the reticular energy Er of cesium chloride (CaF2).

We have: Σ ΔH (cycle) = 0

$\Delta H^0_f (CaF_2) - Er - E_{i1} - E_{i2} - \Delta H_{sub} (Ca) - \Delta H_{diss} (F_2) - 2Aelec = 0$

$E_r = \Delta H0f (CaF_2) - E_{i1} - Ei2 - \Delta H_{sub} (Ca) - \Delta H_{diss} (F_2) - 2A_{elec}$

$E_r = -1220 - 590 - 1145 - 178 - 157 + (328*2)$

$E_r = -2634$ KJ. $^{mol-1}$

Exercise 27

I. A container closed by a moving piston contains 2 g of helium (monoatomic ideal gas) under conditions (P_1, V_1). Adiabatic compression is carried out in a reversible manner which brings the gas into the conditions (P_2, V2). Knowing that P_1=1 bar; V_1 = 10 L; P_2 = 3 bar. Determine:

a) - the final volume V_2

b) - the work exchanged by the gas with the external environment

c) - the variation in the internal energy of the gas

We give: $\gamma = C_p/C_v = 5/3$; R = 8.32 $J.K^{-1}.mol^{-1}$.

II. Calculate the internal energy variation of each of the following systems:

a) - a system absorbs Q = 2 kJ while it provides work for the outside W = 500 J.

b) - a gas maintained at a constant volume yields Q = 5 kJ.

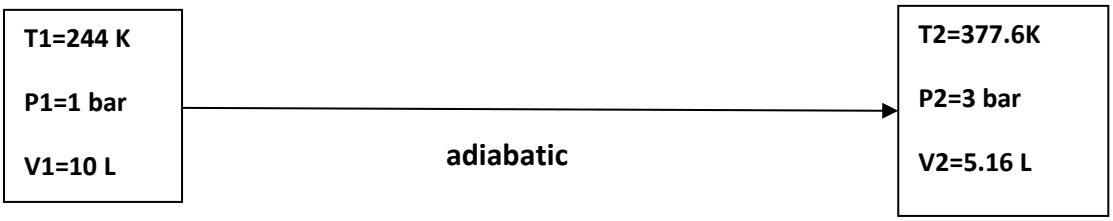
(c) - the adiabatic compression of a gas is accomplished by a work W = 80 J

Exercise 27 Solution

1. Calculation of the number of moles of gas.

n=m/M=2/4=0.5 moles

2. Complete the following thermodynamic states:



The transformation is an adiabatic compression, V2 is calculated by the expression:

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

The work exchanged by the gas with the external environment is given by the expression:

$$W = nC_V(T2-T1)$$

YEAR:

W=834 J

The transformation is adiabatic, the variation of the internal energy of the gas is equal to the work exchanged with the external medium:

ΔU=834J

II. Calculate the internal energy variation of each of the following systems:

a) - a system absorbs Q = 2 kJ while it provides work for the outside world W = 500 J.

According to the 1st law of thermodynamics:

$$\Delta U = W + Q$$

$$\Delta \boldsymbol{U = -500 + 2000 = 1500J}$$

b) - a gas maintained at a constant volume yields Q = 5 kJ.

The gas is kept at a constant volume: W=0, i.e. since the system gives heat to the outside environment.$\Delta U = Q = -5Kj$

c) - the adiabatic compression of a gas is accomplished by a work W = 80 J

The compression is adiabatic; it is done without heat exchange Q=0 so . The system gains energy from the external environment since it is a compression.$\boldsymbol{\Delta U = W = 80J}$

Exercise 28

Calculate by constructing the Born-Haber cycle, the reticular energy of one mole of cesium chloride (CsCl) from the experimental data below at 298 K:

Enthalpy of sublimation of solid Cs: $\Delta H_{sublimation}$ (Cs,s)= 76.58kJ/mol;

Ionization energy of Cs gas

Ei (Cs,g)=275.25 kJ/mol

Bond dissociation energy (Cl-Cl)

ΔHdissociation(Cl-Cl)=242.44 kJ/mol

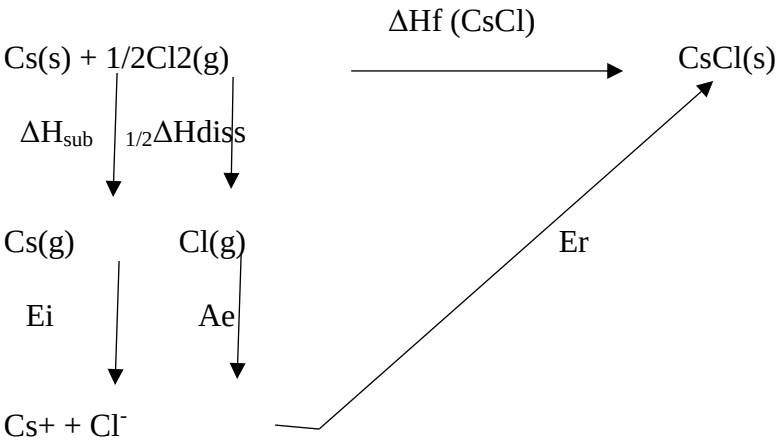
Electronic affinity of Cl gas

Ae(Cl,g)=-348 kJ/mol; Enthalpy of solid CsCl formation

ΔHformation(CsCl,s) = -442.44kJ/mol

Correction of Exercise 28

Calculation of the reticular energy by a cyclic process, which is the Born-Haber cycle



$\Delta Hcycle=0 \leftrightarrow \Delta H_f(CsCl) - E_r - \Delta H_{sub} - 1/2\Delta Hdiss(Cl,g) - E_i(Cs,g) - A_e(Cl,g)=0$

$Er = \Delta Hf(CsCl) - \Delta H_{sub} - 1/2\Delta Hdiss(Cl,g) - E_i(Cs,g) - A_e(Cl,g)$

AN: Er = -567.5 kJ/mol

Some Additional Exercises

Exercise 1

Calculate the enthalpy change when, at a constant pressure of 1 atm, the temperature of two moles of ethanol (M = 4.1 g.mol-1) rises from –117°C (normal melting point) to 100°C. The normal vaporization point is 78°C.

The standard mass enthalpy of vaporization is ($\Delta H°_{vap}$) 854 J.g-1 at 78°C. In the temperature interval considered, the following average values of the molar heat capacities at constant pressure will be accepted:

$C_p^0(C_2H_6OH,l)$ = 112 J.K-1.mol-1 $C_p^0(C_2H_6OH,g)$ = 65 J.K-1.mol-1

Exercise 2

At 25°C, the enthalpy of the reaction: $H_2(g) + 1/2O_2(g) = H_2O(g)$ is –241.8 kJ, each gas being at a pressure of 1atm. What is the thermal effect of the constant pressure reaction Q_p?

What is the standard molar enthalpy of water vapor formation at 25°C?

Exercise 3

One mole of nitrogen N_2 is compressed from an initial state (P_A, V_A, T) to a final state (P_B, V_B, T), with P_A = 1bar, P_B = 200 bars, T = 298 K according to the following processes:

Process 1: Isothermal compression.

Process 2: adiabatic compression from (P_A, T) to (P_B, T_2) followed by isobaric cooling from (P_B, T_2) to (P_B, T).

Process 3: adiabatic compression from (V_A, T) to (V_B, T_3) followed by isobaric cooling from (V_B, T_3) to (V_B, T).

1. Calculate the temperatures T_2 and T_3 reached during processes 2 and 3.
2. Calculate the amount of work required for each process.
3. Calculate, for each process, the amount of heat exchanged.

We give: C_v=5R/2, C_p=7R/2

Exercise 4

Let n moles of nitrogen (ideal gas), being in a state A (P_A, T_A). This system is successively subjected to the following three transformations bringing it back to its initial state A:

1. Reversible isothermal compression (constant temperature) reduces its volume by half.
2. Reversible isochoric transformation (constant volume) up to a temperature $T_A/2$
3. Finally, a reversible isobaric (constant pressure) expansion returning the system to its initial state A (P_A, T_A).
    a) Represent this cycle by a Clapeyron diagram P = f(V);
    b) For each transformation, give the expression of the work and heat exchanged, as well as the variation of the internal energy of the system.
    c) Cite and verify the first law of thermodynamics using this cycle.
    d) Digital applications.

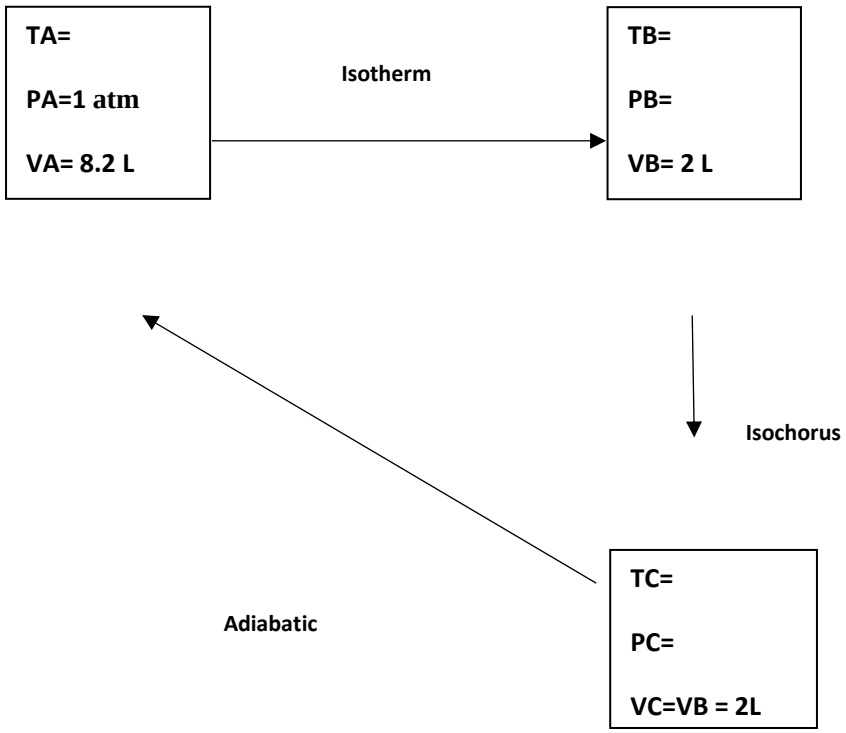
Exercise 5

A mole of nitrogen N_2, assumed to be perfect, initially in state A (V_A=8.2 liters, P_A=1 atm), undergoes the sequence of reversible transformations:

a) AB Isothermal Compression
b) Isochoric transformation BC up to temperature TC
c) Adiabatic transformation AC to the initial state.

We give: R=0.082atm.L. $K^{-1}mol^{-1}$; R=8.314 J.K-1.mol^{-1} ; 1 atm=10^5 Pa; $1m^3=10^3$ liters; γ=1.4

(1) Complete the following thermodynamic states:



(2) Represent the different transformations on a Clapeyron diagram (P,V).

(3) Complete the table below:

Transformation	**W**	**Q**	**ΔU**	**ΔH**
Isotherm				
Isochorus				
Adiabatic				

Exercise 6

It is proposed to determine the reticular energy for one mole of cesium chloride (CsCl) from a number of experimental data at 298 K. This data is:

Enthalpy of sublimation of solid Cs: $\Delta H_{sublimation}$ (Cs,s)= 76.58kJ/mol; Ionization energy of Cs gas: E_i (Cs,g)=275.25 kJ/mol; Dissociation energy of the bond (Cl-Cl): $\Delta H_{dissociation}$(Cl-Cl)=242.44 kJ/mol; Electron affinity of gas Cl: A_e(Cl,g)=-348 kJ/mol; Enthalpy of formation of solid CsCl: $\Delta H_{formation}$(CsCl,s) = -442.44kJ/mol

(3) Represent the Born-Haber cycle.

Exercise 7

We consider hydrogen gas in state 1 defined by: T_1=298 K; P1=1atm; V_1=50 L.

Starting from this state, a succession of reversible transformations is carried out:

- Adiabatic transformation up to T_2=398K
- Isobaric transformation up to T_3=348 K
- Isochoric transformation up to $T_4=T_1$
- Isothermal transformation to state 1.

1. Completing thermodynamic states
2. Represent in Clapeyron coordinates (P, V) the succession of the four transformations.
3. Calculate W, Q, ΔU and ΔH by completing the table below:

Data: γ=1.4; R=0.082 atm. L.K-1.mol-1; R=8.314 $J.K^{-1}.mol^{-1}$

Transformation	W	Q	ΔU	ΔH
Isobar				
Isotherm				
Isochorus				

Exercise 8

The industrial synthesis of vinyl chloride is carried out in two steps: from ethylene:

- First step: addition of dichlorine Cl2 to ethylene in the gas phase at around 90°C under a pressure of 30 bar providing dichloroethane according to the equation:

$$C_2H_4\,(g) + Cl_2(g) \rightleftharpoons C_2H_4Cl_2(g)\ (1)$$

- Second step: elimination of hydrogen chloride in the gas phase at around 500°C under a pressure of 30 bar providing vinyl chloride C2H3Cl(g) according to the equation:

$$C_2H_4Cl_2(g) \rightleftharpoons C2H3Cl(g) + HCl(g)\ (2)$$

All the standard thermodynamic quantities relating to the different species involved in these two reactions are given:

All chemical species are assimilated to ideal gases.

1. Determine:
   - the standard enthalpies of reaction ΔrH°1 and ΔrH°2. Are these reactions exothermal or endothermic?
   - The standard reaction entropies ΔrS°1 and ΔrS°2.
   - The standard free enthalpies of reaction ΔrG°1 and ΔrG°2 as a function of temperature.
2. Calculate numerically the standard free enthalpies of reaction at temperatures T1=363 K and T2=773 K respectively. From this, deduce the values of the equilibrium constants of these two reactions at these two temperatures. Conclude.

Initially, the reactor contains an equimolar mixture of ethylene gas and dichlorine gas at a pressure of 30 bar. The pressure is kept constant.

3. Thermodynamic equilibrium having been reached. To do this, calculate the conversion rate of ethylene to diclhoroethane and the conversion rate of dichloroethane to vinyl chloride at the two temperatures T_1 and T2. It is advisable to make a material assessment presented in the form of clear tables.
4. Is it possible to qualitatively predict the effect of an increase in pressure on reaction (1) at constant temperature?

5. Is it reasonable to carry out reaction (2) under a pressure of 30 bar? Explain why reaction (2) is still carried out under a pressure of 30 bars.

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