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Courses and corrected exercises Of Thermodynamics

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FOREWORD

This handout is intended primarily for all first-year students in the core technical sciences, material sciences, exact sciences, etc. It carries the fundamental and necessary notions of thermodynamics, in order to offer the student a solid base for learning thermodynamics with a view to applications to combustion and thermal machines. It has three chapters, the first chapter deals with general knowledge of thermodynamics and corrected exercises.

The second chapter is described the relations between mechanical phenomena and calorific phenomena and the heats (energies) of the reaction relating to the first law of thermodynamics and as well as corrected exercises to help the best comprehension. The third chapter is devoted to the entropy of reaction, the free enthalpy (Gibbs relation) relating to the second principle of thermodynamics, chemical equilibriums (Le Chatelier's law, Van't Hoff's relation) and as well as corrected exercises.

In conclusion, I am very receptive to any comments or suggestions to improve the content of this handout and I hope that this handout will be of great use to students.

Good luck to you and happy reading

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Chapter (I): *General notions on thermodynamics*

Chapter (II): *First law of thermodynamics*

Abbreviations and symbols

$°C$	*Degree Celsius*
C_i	*Molar concentration of constituent (i)*
C_m	*Specific heat capacity*
C_p	*Molar heat capacity at constant pressure*
C_v	*Molar heat capacity at constant volume*
C^t	*Constant*
E_F	*Final state*
E_I	*Initial state*
E_L	*Binding energy*
G	*Free enthalpy (Gibbs energy)*
s	*Solid*
g	*Gas*
H	*Enthalpy*
K	*Kelvin*
K_T	*Thermodynamic equilibrium constant*
K_p	*Equilibrium constant as a function of partial pressures*
K_c	*Equilibrium constant as a function of molar concentrations*
L	*Latent heat of change of state*
L_{Fus}	*Latent heat of fusion*
L_{Sub}	*Latent heat of sublimation*
L_{Vap}	*Latent heat of vaporization*
l	*Liter*
Ln	*Natural logarithm*
Log	*Decimal logarithm*
M	*Molar mass*
m_i	*Mass of constituent (i)*
n	*Quantity of matter in moles*
n_i	*Number of moles of component (i) in a mixture*
P_{Tot}	*Total pressure in a gas mixture*
P_i	*Partial pressure of constituent (i)*
δQ	*Quantity of heat exchanged during an infinitesimal evolution*

Q	*Quantity of heat exchanged*
Q_P	*Quantity of heat exchanged at constant pressure*
Q_V	*Quantity of heat exchanged at constant volume*
R	*Gas constant*
S	*Entropy*
S_m	*Molar entropy*
ΔS_e	*Entropy variation due to system-external environment heat exchanges*
ΔS_i	*Variation of entropy internal to a system (creation of entropy)*
T	*Temperature*
$T_{éq}$	*Equilibrium temperature*
T_{Fus}	*Fusion temperature*
t	*Time*
U	*Internal energy*
V	*Volume*
V_m	*Molar volume*
δW	*Quantity of work exchanged during an infinitesimal evolution*
W_{rev}	*Work done reversibly*
W_{irr}	*Work done irreversibly*
X_i	*Molar fraction of constituent (i)*
ρ	*Volumic mass*
$\sum$	*Sum*
$\rightarrow$	*Chemical reaction progressing in the forward direction (from left to right)*
$\rightleftharpoons$	Balanced reaction

Chapter (I)
General notions in thermodynamics

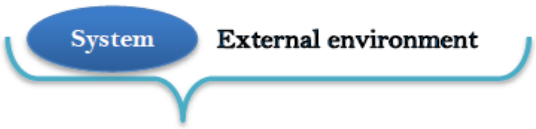
I. Introduction

Thermodynamics is the science of energy transformations which aims to study energy exchanges between systems, or between systems and the external environment. It is not interested in the reaction mechanisms that govern these transformations, or in the speed at which systems evolve. Thermodynamics makes it possible to predict the direction of the evolution of a system and even sometimes the energy balance of a transformation. It is essential in most scientific fields.

I.1 Characteristic quantities, state of a system

I.1.1 Thermodynamic systems: definitions

The system: a portion of space limited by walls or boundaries that we choose to study and to which we apply the laws of thermodynamics. It is defined by the quantity of matter it contains, by the state in which this matter is found and by the parameters which define this state.



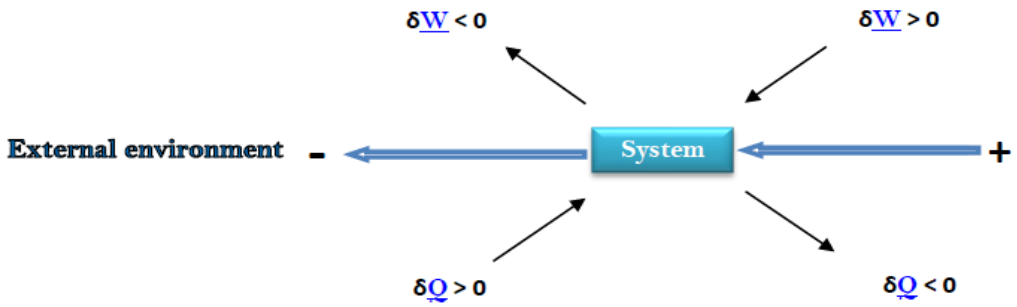
The external environment surrounds the thermodynamic system (Entourage) and everything that is not the system.

I.1.2 Possible transfers between the system and the external environment

The energy that is exchanged during the transformation of closed systems can be in two forms:

- In the form of heat denoted Q.
- In the form of mechanical work denoted W.

By convention, the energy received by the system is counted positively and the energy transferred to the external environment is counted negatively.



I.1.3 Different types of systems

A system takes different names depending on the nature of the boundary between the thermodynamic system and the external environment, we distinguish different thermodynamic systems:

- ✓ **Closed system**: no exchange of matter with its surroundings (external environment).
- ✓ **Isolated system**: no exchange of energy or matter with its surroundings.
- ✓ **Open system**: it exchanges matter and energy with its surroundings.

Note

- *A system can be divided into several parts or subsystems (composite system).*
- *If the walls are non-deformable, there is no exchange of mechanical energy with the outside.*

I.1.4 Balance of a system

A system is in equilibrium if these properties remain constant over time, there is no transfer of matter or energy between the system and the external environment.

- Thermal equilibrium: T constant.
- Mechanical equilibrium: P constant.
- Chemical equilibrium: constant composition.
- Electrical balance: constant potential.

I.1.5 Transformation of a system

A transformation consists of the evolution of a system by modifying at least one state variable.

Different types of transformation are recognized according to the evolution of the state variables, temperature, pressure and volume and according to the heat exchange.

- An isothermal transformation takes place at constant temperature ($T = C^t$).
- An isobaric transformation is carried out at constant pressure ($P = C^t$).
- An isochoric transformation is carried out at constant volume ($V = C^t$).
- A transformation is called adiabatic and takes place without heat exchange with the external environment.

The transformation can be:

- **Reversible:** the system unfolds infinitely slowly and in equilibrium at each stage of its evolution, so it is a succession of infinitely neighboring equilibrium states). An infinitesimal change of a variable allowing the direction of the transformation to be reversed. During the reverse transformation, the system goes through the same intermediate states again.

Note

An invertible reaction can occur in both directions, direct and reverse for example the esterification reaction not to be confused with the reversible transformation.

- **Irreversible:** spontaneous transformation that cannot be reversed.

Note

Natural transformations are generally irreversible. The transformation that takes place without external intervention is spontaneous.

I.1.6 State variables and state functions

The state of a system is defined by the values taken by a set of macroscopic quantities which characterize it. These quantities are called the state variables of the system. These are, for example, the temperature T, the pressure P, the volume V, the number of moles of each of the species present in the system.

- Extensive state variables: are thermodynamic variables obtained by measuring properties that relate to the entire thermodynamic system. They are additive, only being able to be defined across the entire system.

Example: Volume V, mass m, quantity of matter n and electric charge.

- The intensive state variables take well-determined values at every point of the thermodynamic system. They are non-additive.

Example: temperature T and pressure P.

> ***Note***
> *Energy transfer functions depend on the path followed between the initial state (E_I) and the final state (E_F), for example, work W and heat Q which are energy transfer functions.*

In general, state variables depend on each other. A function of state variables is called a **state function**.

The state variables are related to each other by the ideal gas equation of state:

$$P\,V = n\,R\,T$$

Where:

P: pressure of the gas considered in Pascal (Pa).

V: volume occupied by the gas in (m^3).

T: absolute temperature in Kelvin (K).

n: number of moles of gas (mol).

R: ideal gas constant, R = 8.32 J K^{-1} mol^{-1}.

The ideal gas is a simple model which assumes that the intermolecular forces are zero (the molecules have no interaction with each other).

The equation of state of ideal gases: PV = n R T brings together the following three laws:

- **Gas expansion law known as Gay Lussac's law**

At constant pressure, the volume of a given mass of gas is directly proportional to its temperature: $V = K\,T$ with $K = f(n, P)$

- **Law of isothermal compressibility of gases known as Boyle Mariotte's law**

At constant temperature, the volume of a given mass of gas is inversely proportional to its pressure: $V = K / P$ with $K = f(n, T)$

- **Charles' law**

At constant volume, the pressure exerted by a given mass of gas is directly proportional to its absolute temperature: $P = K\,T$ with $K = f(n, V)$

• V/n = ct, at fixed T and P.

The combination of these three laws results in the general ideal gas law:

$$PV = nRT$$

Note

- *Normal conditions of temperature and pressure (CNTP) T= 0°C =273.15K. P = 1bar = 1atm= 1.013 10^5 Pa = 1.013 HPa = 760 mmHg.*
- *At fixed Temperature and Pressure, equal volumes of different gases contain the same number of moles and therefore the same number of molecules (Avogadro Ampère's law).*

I.1.7 Composition of a system

From an extensive quantity, the number of moles or the mass of each constituent, we can describe a system by:

- The mole fraction: $x_i = \frac{n_i}{n_{tot}}$ with $\sum_i x_i = 1$ (dimensionless quantity)
- The mass fraction: $w_i = \frac{m_i}{m_{tot}}$ with $\sum_i w_i = 1$ (dimensionless quantity)
- The molar concentration: $C_i = \frac{n_i}{V}$

Where: n is the number of moles and V is the volume.

The International System (SI) unit of molar concentration is mole per m^3 (mol m^{-3}). In practice we rather use the mole per liter as a unit: mol L^{-1}

I.7.1.1 Law of partial pressures (Dalton's law)

In a mixture of gases, each gas exerts its own pressure (partial pressure), the sum of the partial pressures of each of the gases constituting the mixture gives the total pressure noted (P_{tot}):

$$P_{tot} = \sum_i^n P_i$$
$$= P_A + P_B + P_C + \ldots\ldots\ldots + P_n$$

The partial pressure Pi of any gas forming part of a mixture is equal to its mole fraction multiplied by the total pressure of the mixture:

$$P_i = X_i \, P_{tot}$$

The unit in the international system (SI) of pressure is the pascal (Pa). We also use the bar (1 bar = 10^5 Pa) and sometimes the atmosphere (1 atm = 1.01325. 10^5 Pa).

CORRECTED EXERCISES

Exercise 1:

Commercial C_4H_{10} butane cylinders contain 13 kg of liquid gas. At 25°C, the combustion of butane gas produces liquid water.

a) Write the equation for the combustion of butane.

b) What volume would the gas occupy at 25°C under atmospheric pressure ?

c) What volume of air, taken at 25°C under atmospheric pressure, consumes the complete combustion of the gas cylinder?

d) What mass of liquid water would be obtained following this combustion ?

Given the following data: atomic mass in g mol^{-1}: M_C=12.01 M_O=16.00 M_H=1.008

Air is considered to be an ideal mixture of 20% O_2 and 80% N_2.

Solution

a. The butane combustion equation:

$$C_4H_{10}(g)+\frac{13}{2}O_2(g)\longrightarrow 4CO_2(g)+5H_2O(l)$$

b. Volume would occupy the gas at 25°C under atmospheric pressure

We consider the gas to be perfect:

$$PV = n\,RT = \frac{m}{M_{C_4H_{10}}}RT$$

$$V = \frac{mRT}{PM_{C_4H_{10}}} = \frac{13\times10^3\times8.31\times298.15}{1.013\times10^5\times58.12} = 5.47m^3$$

c. Volume of air consumed by the complete combustion of the gas cylinder:

1 mole of butane consumes (13/2) mole of dioxygen, in 13 Kg of butane there is (13000/58.12) = 233.675 mol of butane.

Hence, (13/2) ×233.675=1453.88 moles of O_2 consumed and consequently 5×1453.88 mol of air consumed.

The volume of air consumed is:

$$V_{Air} = \frac{n_{Air}RT}{P} = \frac{5\times1453.88\times8.31\times298.15}{1.013\times10^5} = 177.88m^3$$

d. Mass of liquid water:

The combustion of one mole of butane gives 5 mol of liquid water, hence 233.675 mol of butane gives $5 \times 233.675 = 1118.36$ mol of liquid water.

So: $m_{Water} = (n \times M_{Water}) = 1118.36 \times 18.016 = 20148.36g = 20.15$ Kg

Exercise 2:

Under a pressure of 2 atmospheres, we know that a mass of 27.3 grams of a gaseous element occupies a volume of 10.5 liters at a temperature equal to 27°C, we also know that this gaseous element follows the ideal gas law.

1) What is this element?

2) Determine its density at 0°C when subjected to a pressure equal to 3 atmospheres.

Solution

1) This involves calculating the molar mass of the gas using the ideal gas law:

n: number of moles, m: mass of the gas and M: molar mass.

From where:

$$M = \frac{mRT}{PV} = \frac{27.3 \times 0.082 \times 300}{2 \times 10.5} = 31.98g/mol$$

$$soit \cong 32g/mol$$

So it's dioxygen.

2- In this case the mass does not change, we determine its volume at P = 3 atm and at a temperature of 0°C = 273 K.

$$V = \frac{mRT}{MP} = \frac{27.3 \times 0.082 \times 273}{32 \times 3} = 6.36Litres$$

Hence the density is:

$$\rho = \frac{m}{M} = \frac{27.3}{6.36} = 4.28g/L$$

Exercise 3:

In a first experiment, a certain mass of gas considered as an ideal gas is enclosed in an enclosure whose volume is V = 11.2 liters, the pressure and temperature measured are respectively p = 1/3 atmosphere and T = 91 K.

1- Calculate the number of moles n of the gas.

2- In a second experiment, we enclose in the same volume a mass equal to twice that of the first experiment, with the same gas, we then raise the temperature until it reaches T_1=350K. Deduce the pressure P_1.

Solution

1- $PV = nRT \Rightarrow n = \frac{PV}{RT} = \frac{0.33 \times 11.2}{0.082 \times 91} = 0.5mol$

2- In the 2nd experiment the mass m_1 is double m, hence the number of moles n_1 is also doubled, hence: n_1= 2n=2(1/2)=1 mole with V_1=V=11.2 liters

$$P_1 V_1 = n_1 RT_1 \Rightarrow P_1 = \frac{n_1 RT_1}{V_1} = \frac{1 \times 0.082 \times 350}{11.2} = 2.56atm$$

Exercise 4:

Calculate the value of the ideal gas constant R, knowing that one mole of gas occupies a volume of 22,414 liters under normal conditions of temperature and pressure (CNTP).

- Give the results in (l atm K^{-1} mol^{-1}), (J K^{-1} mol^{-1}).

Given the following data: Normal Conditions of T and P: T=0°C, P=1atm =1.01325 10^5 Pa

Solution

According to the ideal gas law, under normal conditions of pressure and temperature (P= 1atm, T = 0°C =273K), one mole of ideal gas occupies a volume of 22.414 liters.

PV = n RT with n = 1mol, T = 273K,

P = 1atm = 1.013 105 Pa = 760 mm Hg and V = 22.414 L

- Constant R in (l atm mol^{-1} K^{-1})

$$R = \frac{P \times V}{n \times T} = \frac{1atm \times 22.414l}{1mol \times 273K} = 0.082 \text{l atm mol}^{-1}\text{ K}^{-1}$$

- Constant R in (J mol^{-1} K^{-1})

$$\text{J} = \text{Pa m}^3$$

$$R = \frac{P \times V}{n \times T} = \frac{1.01310^5 Pa \times 22.414 \times 10^{-3} m^3}{1mol \times 273K} = 8.31 \text{J mol}^{-1}\text{ K}^{-1}$$

Exercise 5:

A gas mixture at atmospheric pressure contains 60% dinitrogen, 25% carbon dioxide by volume.

- Calculate the partial pressure of each gas.

Solution

The partial pressure P_i of each gas is:

$$P_{N_2} = 0.6\ P_{tot}$$
$$P_{O_2} = 0.15\ P_{tot}$$

With $P_{tot} = 1$ atm

From where:

$$P_{N_2} = 0.6\,atm$$
$$P_{O_2} = 0.15\,atm$$

Exercise 6:

A gas mixture consists of 0.2 g of H_2; 0.21g of N_2 and 0.51g of NH_3 under the pressure of one atmosphere and at a temperature of 27°C.

Calculate:

1. Mole fractions.
2. The partial pressure of each gas.
3. The total volume.

Given the following data: M(H) = 1g mol^{-1} and M(N) = 14g mol^{-1}

Solution

1. Molar fraction x_i of each gas:

Number of moles of H_2 $$n_{H_2} = \frac{m_{H_2}}{M_{H_2}} = \frac{0.2}{2} = 0.1mol$$

Number of moles of N_2 $$n_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{0.21}{28} = 0.0075mol$$

Number of moles of NH_3 $$n_{NH_3} = \frac{m_{NH_3}}{M_{NH_3}} = \frac{0.51}{17} = 0.03mol$$

Mole fraction of each gas is:

$$x_i = \frac{n_i}{\sum_j n_j} \quad \text{With} \quad \sum_j n_j = n_{H_2} + n_{N_2} + n_{NH_3} = 0.1375mol$$

$$x_{H_2} = \frac{0.1}{0.1375} = 0.727$$
$$x_{N_2} = \frac{0.0075}{0.1375} = 0.055$$
$$x_{NH_3} = \frac{0.03}{0.1375} = 0.218$$

2. The partial pressure of each gas P_i is:

$$P_i = x_i \; P_{tot} \quad \text{With} \quad P_{tot} = \sum P_i = 1 \; atm$$

$$P_{H_2} = x_{H_2} \; P_{tot} = 0.727 atm$$
$$P_{N_2} = x_{N_2} \; P_{tot} = 0.055 atm$$
$$P_{NH_3} = x_{NH_3} \; P_{tot} = 0.218 atm$$

3. The total volume:

Assuming that the mixture is an ideal gas, we have:

$$P_{tot} \, V_{tot} = \sum_j n_j R T$$

From where

$$V_{tot} = \frac{\sum_j n_j RT}{P_{tot}} = \frac{0.1375 \times 0.082 \times 300 \times 15}{15} = 3.38 \; L$$

Exercise 7:

In a container initially filled with air, a vacuum is created until the pressure has dropped to 10^{-3} mm Hg, the temperature of the container being maintained at 300K.

1- Assuming that air can be considered an ideal gas, determine the number of air molecules per unit volume at this pressure.

We give: Avogadro number: $N_A = 6.023 \; 10^{23}$ molecules. ($mole^{-1}$).

Solution

Let X be the number of molecules per unit volume, hence the number of moles of gas is:

$$n = \frac{X \times V}{N_A}$$

We replace this relation in the ideal gas equation:

$$P \, V = n \, R \, T \;\; => P \, V = \frac{X * V}{N_A} \, RT$$

$$X = \frac{PN_A}{RT} = \frac{1.33 \times 10^{-1}\ 6.023 \times 10^{23}}{8.31 \times 300} = 3.2 \times 10^{19}\ molecules\ m^{-3}$$

where: $1\text{Cm Hg} = 1.33 \times 10^{3}\ Pa$

Exercise 8:

We consider two rigid-walled containers containing one Hydrogen, the other methane.

Initially we have:

H_2: P_1=5 atm; T_1=250K; V_1=10 liters.

CH_4: P_2=40 atm; T_2=300K; V_2=40 liters.

1. Calculate the masses of H_2 and CH_4 contained in each container.
2. The two containers are heated to a temperature of 350K. Calculate the pressure of each gas.
3. Using a tap, we then connect the two containers.
   a- What is happening?
   b- Calculate the partial pressures of each gas, deduce the total pressure.
4. Close the tap, calculate the masses of each gas in each container.

Solution

1. The mass of each gas

We apply the equation of state of the ideal gas:

$$P_{H_2} V_{H_2} = n_{H_2} RT$$
$$n_{H_2} = \frac{P_{H_2} V_{H_2}}{RT} = \frac{5 \times 10}{0.082 \times 250} = 2.43mol$$
$$m_{H_2} = M_{H_2} \times n_{H_2} = 2 \times 2.43 = 4.87g$$

$$P_{CH_4} V_{CH_4} = n_{CH_4} RT$$
$$n_{CH_4} = \frac{P_{CH_4} V_{CH_4}}{RT} = \frac{40 \times 40}{0.082 \times 300} = 65.04mol$$
$$m_{CH_4} = M_{CH_4} \times n_{CH_4} = 16 \times 65.04 = 1040.65g$$

2. The pressure of each gas

$$P_{H_2} = \frac{n_{H_2} RT}{V_{H_2}} = \frac{2.43 \times 0.082 \times 350}{10} = 6.97atm$$
$$P_{CH_4} = \frac{n_{CH_4} RT}{V_{CH_4}} = \frac{65.04 \times 0.082 \times 350}{40} = 46.66atm$$

3. a/ If we open the tap we obtain a new pressure of each gas and a total volume. Hence the total volume is:

$$V_T = 40+10 = 50 \text{ liters}$$

The partial pressure of hydrogen is:

$$P_{H_2} = \frac{n_{H_2} RT}{V_T} = \frac{2.43 \times 0.082 \times 350}{50} = 1.39 atm$$

The partial pressure of methane is:

$$P_{CH_4} = \frac{n_{CH_4} RT}{V_T} = \frac{65.04 \times 0.082 \times 350}{50} = 37.33 atm$$

The total pressure is:

$$P_{Tot} = P_{CH_4} + P_{H_2} = 37.33 + 1.39 = 38.72 atm$$

4. If we close the tap, the mass of each gas is:

In the 1st container:

$$n_{H_2} = \frac{P_{H_2} V_{H_2}}{RT} = \frac{1.39 \times 10}{0.082 \times 350} = 0.48 mol$$
$$m_{H_2} = M_{H_2} \times n_{H_2} = 2 \times 0.48 = 0.96 g$$

$$n_{CH_4} = \frac{P_{H_2} V_{H_2}}{RT} = \frac{37.33 \times 10}{0.082 \times 350} = 13.00 mol$$
$$m_{CH_4} = M_{H_2} \times n_{H_2} = 16 \times 13.00 = 208.11 g$$

In the 2nd container:

$$n_{H_2} = \frac{P_{H_2} V_{H_2}}{RT} = \frac{1.39 \times 40}{0.082 \times 350} = 1.93 mol$$
$$m_{H_2} = M_{H_2} \times n_{H_2} = 2 \times 1.93 = 3.86 g$$

$$n_{CH_4} = \frac{P_{H_2} V_{H_2}}{RT} = \frac{37.33 \times 40}{0.082 \times 350} = 52.02 mol$$
$$m_{CH_4} = M_{H_2} \times n_{H_2} = 16 \times 52.02 = 832.44 g$$

Exercise 9:

1- What is the partial pressure of oxygen that reaches the lungs when breathing air at 20°C, under a barometric pressure of 970 hPa (hectopascals)?

2- Physiological disorders can occur if this partial pressure becomes too low (for example at high altitude), or too strong (for example when scuba diving). In the latter case, we consider that it should not exceed 2.3 bars.

- To what depth can a diver breathing air supplied by a compressed air tank descend without risk?

Given the following data:

- A column of water of 1 m exerts a pressure of approximately 0.1 bar.

Solution

1- The hectopascal is the unit used in meteorology:

$$1 \text{ hectopascal} = 100 \text{ Pa.}$$

$$1\text{atm} = 1.01325 \text{ bar} = 1.01325\ 10^5 \text{ Pa} = 1013.25 \text{ hPa}$$

$$\text{So, } 970 \text{ hPa} = 0.97\ 10^5 \text{ Pa} = 0.97 \text{ bar}$$

Air contains approximately (1/5) oxygen (O_2), the partial pressure of oxygen is $P(O_2) = 1/5\ (0.97)$ bar = 0.19 bar.

The total pressure is equal to $5\times P(O_2) = 11.5$ bar.

2- The maximum partial pressure of O_2 must not exceed 2.3 bar therefore the total pressure must not exceed $2.3\times5=11.5$ bar.

This value of 11.5 bar contains a pressure of 1 bar exerted by the atmosphere on the surface of the sea and each column of 1 m of sea water exerts a pressure of 0.1 bar, hence the pressure of 10.5 bar corresponds to a depth of $10.5/0.1=105$ m.

The diver can safely descend to a depth of 105 m.

Chapter (II)
First law of thermodynamics

I. Heat and work

I.1 Heat energy

Heat is a quantity of energy that passes from one system to another because of the temperature difference between these systems.

When we put two objects at different temperatures in contact and isolate them from the rest of the world, their temperatures tend to balance out. Today, we understand this phenomenon by saying that:

Because of the temperature difference, there is a transfer of energy from the hot source to the cold source.

An addition of heat results in heating (rise in temperature) or a change in physical state: fusion, vaporization, sublimation.

A heat subtraction results in cooling (lowering of temperature) or change of physical state: solidification, liquefaction, condensation. The heat symbolized by Q is expressed in J or cal.

The quantity of heat Q to add/subtract from a substance to increase/decrease its temperature by a quantity dT is expressed as:

$$\delta Q = m\ C_m\ dT \text{ , } C_m \text{ in (J K}^{-1}\text{ g}^{-1}\text{)}$$
$$\delta Q = n\ C_n\ dT \text{ , } C_n \text{ in (J K}^{-1}\text{ mol}^{-1}\text{)}$$

Where, C_m is the specific heat capacity of the substance and m its mass in (g) and dT in (K). It is common to express this relationship in mol, C_n is the molar heat capacity and n is the number of moles considered.

The molar heat capacity of a substance represents the quantity of heat that must be supplied to one mole of this substance in order to increase its temperature by one kelvin (K).

When there is a change of state, the quantity of heat received by a system is written:

$$Q = m\ L$$

Where, L is the specific latent heat of change of state.

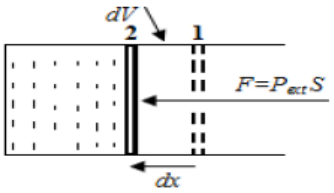
Knowing the heat, we can redefine the walls that separate two systems.

- A diathermy wall is a wall that allows heat to pass through.
- An adiabatic wall is a wall that does not allow heat to pass through.
- Energy communicated through an adiabatic wall is work.

*Zero Principle: If the temperatures T_A and T_B of two systems **A** and **B** are identical and if the temperature T_C of a system **C** is the same as that of **B**, then there is no heat exchange between **A** and **C** when they are brought into contact ($Q_{AC}=0$).*

I.2 Mechanical work

When an external operator exerts a force on a piston which moves to the right without friction in a cylinder containing a gas; the piston has a section S, its mass is negligible.



The gas exerts a pressing force:

$$F = P_{ext} S$$

Where:

P_{ext} is the external pressure.

The elementary work is written:

$$\delta W = -F\,dx = -P_{ext} S\,dx = -P_{ext} dV$$

$$W = -\int_{état\ i}^{état\ f} P_{ext} dV$$

If the volume goes from V_1 to V_2, the work exchanged will be:

$$W = -\int_{V_1}^{V_2} P_{ext}\ dV$$

Special cases:

- If the external pressure remains constant during the transformation:

$$W = -P_{ext}\ (V_2\ -V_1)\ \text{Ou}\ W = -P_{ext}\ \Delta V$$

- If $V_2 < V_1$ then $W > 0$, work has been supplied to the gas, there is heating.

- If the transformation is reversible: T = constant and $P = P_{ext}$ at any time.

For one mole of ideal gas:

$$W = -\int_{V_1}^{V_2} P_{ext}\ dV\ =\ -R\ T \int_{V_1}^{V_2} \frac{dV}{V} =\ -R\ T\ \ln(\frac{V_2}{V_1})$$

- If the isochoric transformation: V = constant or dV = 0 whatever reversible transformation or not. Therefore: W = 0.

The work symbolized by **W** is expressed in **J** or **cal**.

1cal= 4.18 Joules

II. The first law of thermodynamics

II.1 Statement of the first principle

During any transformation, there is conservation of energy, the total quantity of energy remains constant. It cannot therefore be created or destroyed, but converted from one form to another, or transferred from one system to another either in the form of work W, or in the form of heat Q. All energy, whatever its form, lost/gained by the system is recovered/provided by the external environment.

From a mathematical point of view, the first law of thermodynamics is expressed:

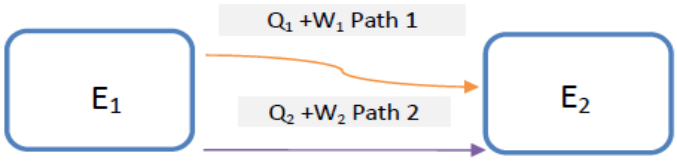
$$\Delta U = Q + W$$

This variation is equal to the sum of the heat and work exchanged, we write:

$$\Delta U = U_2 - U_1 = Q + W$$

The internal energy U is a state function that only depends on the initial state and the final state, therefore does not depend on the path followed.

$$\Delta U = U_2 - U_1 = Q_1 + W_1 = Q_2 + W_2 \text{ Avec } Q_1 \neq Q_2 \text{ et } W_1 \neq W_2$$

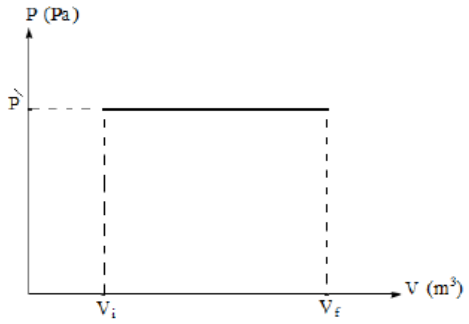


The internal energy U is a state function; dU is an exact total differential (DTE). For a process going from the initial state UI to a final state UF the variation of U is the same whatever the path followed.

II.2 Some transformations for ideal gases

II.2.1 Isobaric transformation: enthalpy function

The isobaric transformation is the transformation during which the gas pressure is kept constant.



When a system evolves at constant pressure with a change in temperature from T_1 to T_2, the quantity of heat received or exchanged by the system with the external environment is equal to its enthalpy variation noted.

The relation $\Delta H = Q_P = \int_{T_1}^{T_2} n\ C_p\ dT$ is always applicable, since H is a state function its variation is independent of the path followed.

C_P is the heat capacity at constant pressure in J $K^{-1}mol^{-1}$. It is the quantity of energy necessary to raise the unit of quantity of matter by one Kelvin, the heat capacity depends on the temperature $C_P = f(T)$, but we can consider $C_P = C^t$ for a small temperature interval.

$$\Delta H = Q_P = n\ C_p \int_{T_1}^{T_2} dT = n\ C_p\ \Delta T = n\ C_p\ (T_2 - T_1)$$

It is important to take into consideration the case of thermodynamic systems subject to phase changes; in this case, we bring into play the variations in enthalpy of change of state (**latent heat**).

- Case of a solid-liquid change:

$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_{Fus}} n\ C_p\ dT + \Delta H_{Fus} + \int_{T_{Fus}}^{T_2} n\ C_p\ dT$$

Where, ΔH_{Fus} represents the latent heat of fusion and T_{Fus} is the melting temperature.

- Case of a Liquid-gas change:

$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_{Vap}} n\ C_p\ dT + \Delta H_{Vap} + \int_{T_{Vap}}^{T_2} n\ C_p\ dT$$

Where, ΔH_{Vap} represents the latent heat of vaporization and T_{Vap} is the temperature of vaporization.

- Case of a Solid-gas change:

$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_{Sub}} n\ C_p\ dT + \Delta H_{Sub} + \int_{T_{Sub}}^{T_2} n\ C_p\ dT$$

Or

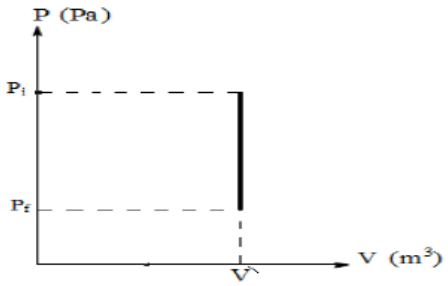
$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_{Fus}} n\ C_p\ dT + \Delta H_{Fus} + \int_{T_{Fus}}^{T_{Vap}} n\ C_p\ dT + \Delta H_{Vap} + \int_{T_{Vap}}^{T_2} n\ C_p\ dT$$

Where:

ΔH_{Sub} represents the latent heat of sublimation and T_{Sub} is the temperature of sublimation.

II.2.2 Isochoric transformation

Isochoric transformations consider constant volume transformations. An illustration is given in the following figure:



For a change of physical state or a chemical reaction at constant volume we have:

$$dV = 0 \text{ et } \delta W = 0$$

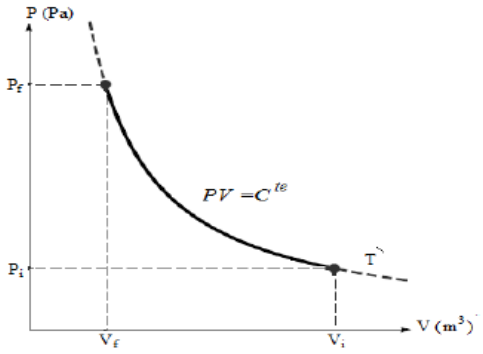
Consequently, if the system evolves at constant V, the heat received (or exchanged by the system with the external environment) is equal to its internal energy variation.

$$\Delta U = (U_f - U_i) = Q_V = \int_{T_i}^{T_f} nC_v\ dT$$

This relationship is always applicable since U is a state function its variation is independent of the path followed.

II.2.3 Isothermal transformation

Isothermal transformations consider transformations at constant temperature. An illustration is given in the following figure:



- Case of a reversible isothermal transformation:

In this case the external pressure is equal to the gas pressure at each moment. It follows:

$$P_1V_1 = P_2V_2 = P_{ext}V = n\ R\ T$$

So:

$$P_{ext} = (P_1V_1)/V$$

$$W = -\int_{V_1}^{V_2} P_{ext}\ dV = -P_1V_1\int_{V_1}^{V_2} dV/V = -P_1V_1[\ln]_{V_1}^{V_2} = -P_1V\ln(\frac{V_2}{V_1}) = nRT\ln(\frac{V_1}{V_2}) = P_1V_1\ln(\frac{P_2}{P_1})$$

$$\Delta U = U_2 - U_1 = Q + W = n\ C_v\ dT = 0$$

Therefore, if the transformation is carried out at constant temperature, the internal energy variation is zero (Joule's law).

$$Q = -W$$

$$Q = nRT\ln(\frac{V_2}{V_1}) = P_1V_1\ln(\frac{P_1}{P_2})$$

$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_2} n\ C_p\ dT = 0 \quad (T_1=T_2=T^{Ct})$$

- Case of an irreversible isothermal transformation:

In this case the gas passes suddenly from (P_1; V_1; T) to (P_2; V_2; T) we have:

$$W = -\int_{V_1}^{V_2} P_2dV = -P_2\int_{V_1}^{V_2} dV = -P_2(V_2 - V_1) = -P_2V_2(1-\frac{V_1}{V_2}) = -nRT(1-\frac{V_1}{V_2})$$

$$\Delta U = U_2 - U_1 = Q + W = n\ C_v\ dT = 0$$

From where,

$$Q = -W$$

$$Q = P_2(V_2 - V_1) = P_2V_2(1-\frac{V_1}{V_2}) = nRT(1-\frac{V_1}{V_2})$$

$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_2} n\, C_p\, dT = 0 \qquad (T_1 = T_2 = T^{Ct})$$

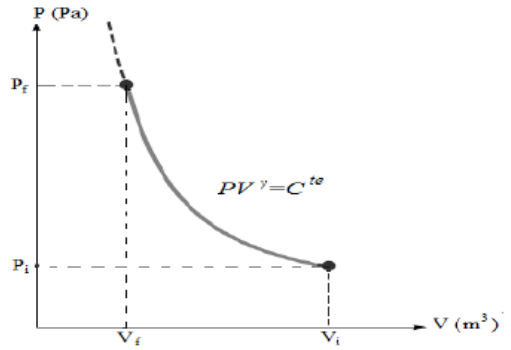
For transformations at constant temperature, the enthalpy variation is zero; (Joule's law).

II.2.4 Adiabatic transformation

It is a transformation that occurs without heat exchange with the external environment $\delta Q = 0$. The variation in internal energy is therefore equal to the exchange work.

- ***Reversible adiabatic transformation.***

An illustration is given in the following figure:



So,

$$dU = \delta W = -PdV = n\, C_v dT$$

As $P = \dfrac{n\, R\, T}{V}$ and $C_v = \dfrac{R}{\gamma - 1}$ and according to Mayer's relation

So: hence

$$\frac{-n\, R\, T}{V} dV = \frac{n\, R}{\gamma - 1} dT, \quad \frac{dT}{T} + (\gamma - 1)\frac{dV}{V} = 0$$

We can rewrite this equation:

$$d(\ln T) + (\gamma - 1) d(\ln V) = 0$$
$$d \ln(TV^{\gamma - 1}) = 0$$

By integrating the equation above, we obtain a relationship between T and V:

$$\ln(TV^{\gamma - 1}) = C^{te} \text{ from where } TV^{\gamma - 1} = T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1} = C^{te}$$

We can find a relationship between P and V, by deriving: $PV = n\ R\ T$

$$P\,dV + V\,dP = nR\,dT\,.$$

We divide the term on the left by PV, and that on the right by nRT.

We obtain:

$$\frac{dV}{V} + \frac{dP}{P} = \frac{dT}{T}$$

We can write this equation as follows:

$$d(\ln P) + \gamma\, d(\ln V) = 0$$

$$d\ln(PV^{\gamma}) = 0$$

By integrating the equation above, we obtain a relationship between P and V:

$$ln = (PV^{\gamma}) = C^{CSTE}$$

From where:

$PV^{\gamma} = P_1V_1^{\gamma} = P_2V_2^{\gamma} = C^{te}$ This is Laplace's law.

$$PV^{\gamma} = P_1V_1^{\gamma} \quad \text{so} \quad P = P_1\ V_1^{\gamma}\ V^{-\gamma}$$

$$\delta W = -PdV$$

We deduce: $\delta W = -P_1\ V_1^{\gamma}\ V^{-\gamma}dV$ in addition $V^{-\gamma}\ dV^{-\gamma} = \frac{d(V^{1-\gamma})}{1-\gamma}$

We can write:

$$\delta W = -P_1\ V_1^{\gamma}\ \frac{d(V^{1-\gamma})}{1-\gamma} = \frac{P_1\ V_1^{\gamma}}{\gamma-1} d(V^{1-\gamma})$$

By integrating each member, we obtain the equation of work and internal energy variation in a reversible adiabatic transformation

$$W = \frac{P_1\ V_1^{\gamma}}{\gamma-1}\int_{V_1}^{V_2} d(V^{1-\gamma}) = \frac{P_1\ V_1^{\gamma}}{\gamma-1}(V_2^{1-\gamma} - V_1^{1-\gamma}) = \frac{1}{\gamma-1}(P_1\ V_1^{\gamma}V_2^{1-\gamma} - P_1\ V_1^{\gamma}V_1^{1-\gamma})$$

$$\text{Or} \quad P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

$$W = \frac{1}{\gamma-1}(P_1\ V_1^{\gamma}V_2^{1-\gamma} - P_1\ V_1^{\gamma}V_1^{1-\gamma}) = \frac{1}{\gamma-1}(P_2\ V_2^{\gamma}V_2^{1-\gamma} - P_1\ V_1^{\gamma}V_1^{1-\gamma})$$

$$= \frac{1}{\gamma-1}(P_2\ V_2 - P_1\ V_1)$$

$$= \frac{nR}{\gamma - 1}(T_2 - T_1) = \int_{T_1}^{T_2} nC_v dT$$

For a monatomic gas: $C_v = \frac{3}{2}R$ and $C_p = \frac{5}{2}R$ from where $\gamma = \frac{C_p}{C_v} = \frac{5}{3}$

For a diatomic gas: $C_v = \frac{5}{2}R$ and $C_p = \frac{7}{2}R$ from where $\gamma = \frac{C_p}{C_v} = \frac{7}{5}$

For a polyatomic gas: $C_v = 3R$ and $C_p = 4R$ from where $\gamma = \frac{C_p}{C_v} = \frac{4}{3}$

- ***Irreversible adiabatic transformation.***

In this case $\delta Q = 0$ therefore $dU = \delta W = -PdV = n\ C_v dT$

The work for the irreversible adiabatic transformation is:

$$W = \Delta U = n\ C_v dT = -PdV = -P_2\ (V_2 - V_1) = -n\ R\ P_2(T_2 / P_2 - T_1 / P_1)$$

$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_2} n\ C_p\ dT$$

CORRECTED EXERCISES

Exercise 1:

Determine the work involved in 2 liters of ideal gas maintained at 25°C under the pressure of 5 atmospheres (State 1) which expands isothermally to occupy a volume of 10 liters (State 2).

1. Reversibly.
2. Irreversibly.

Solution

1. Isothermal reversible transformation:

At each moment ($P_{ext} = P_{gas}$), hence the work involved for the reversible isothermal expansion is:

$$W_{rév} = -\int_{V_1}^{V_2} P_{ext}\, dV = -n\,R\,T \int_{V_1}^{V_2} \frac{dV}{V} = -n\,R\,T\,\ln(\frac{V_2}{V_1}) = -P_1 \times V_1 \ln(\frac{V_2}{V_1})$$

$$W_{rév} = -5 \times 1{,}013 \times 10^5 \times 2 \times 10^{-3} \ln(\frac{10}{2}) = -1630{,}36 \text{Joules}$$

2. Work involved for the irreversible isothermal expansion:

The pressure is constant during the transformation: $P_{ext} = P_{final} = P_2 = C^t$

$$W_{irrév} = -P_{ext}\ (V_2 - V_1) \text{ Ou } W = -P_{ext}\ \Delta V$$

$$W_{irrév} = -1 \times 1{,}013 \times 10^5 \times (10-2) \times 10^{-3} = -810{,}4 \text{ Joules}$$

Exercise 2:

At the constant temperature of 300K, we consider a mole of oxygen O_2 which we compress from V_1=20 l to V_2= 2L according to a reversible process.

- Calculate the work of this compression:

a) If we consider the gas as ideal.

b) If we consider the gas as a real gas whose equation of state follows the Van der Waals relation:

$$(P + \frac{A}{V^2}) = (V - B) = nRT$$

Given the following data: R=8.31 J K^{-1} mol^{-1}; A=0.13 J m^3; B= 3.38 10^{-5} m^3.

Solution

a) The gas is perfect, the work is:

$$W = -\int_{V_1}^{V_2} P_{ext}\ dV\ = -n\,R\,T\int_{V_1}^{V_2}\frac{dV}{V} = -n\,R\,T\ \ln(\frac{V_2}{V_1}) = -8.31\times 300\ln\frac{2}{20} = 5740.34J$$

b) The gas is real:

$$(P+\frac{A}{V^2})=(V-B)=nRT \Rightarrow P=\frac{RT}{V-B}-\frac{A}{V^2}$$

From where:

$$W = -\int_{V_1}^{V_2} P_{ext}\ dV\ = -\int_{V_1}^{V_2}(\frac{RT}{V-B}-\frac{A}{V^2})dV = -RT\int_{V_1}^{V_2}\frac{dV}{V-B}+A\int_{V_1}^{V_2}\frac{dV}{V^2}$$

$$W = -RT\ln\frac{V_2-B}{V_1-B}+A(\frac{1}{V_1}-\frac{1}{V_2})$$

$$W = -8.31\times 300\ln\frac{2-3.8\times10^{-2}}{20-3.8\times10^{-2}}-0.13\times10^{3}(\frac{1}{20}-\frac{1}{2}) = 5724.92J$$

Exercise 3:

The specific heat capacity of solid steel is constant (independent of temperature) and has the value $C_{Steel} = 475\ J\ kg^{-1}\ K^{-1}$.

How much heat is needed to move a 50 kg block of steel from a temperature $T_1 = 5°C$ to a temperature $T_2 = 18°C$?

Solution

The mass and capacity Steel are independent of the temperature T:

$$Q_{T1\to T2} = m_{Steel}\ C_{Steel}\int_{T1}^{T2} dT$$

$$= 50 \times 475 \times (18-5) = 3.0875 \times 10^5\ J = 308.75\ KJ$$

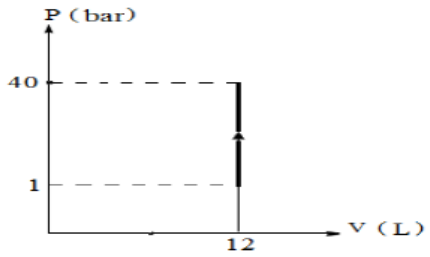
Exercise 4:

A gas enclosed in a sealed tank is heated slowly. Its volume remains stuck at 12 L, and its pressure varies from 1 bar to 40 bar.

- What is the work developed ?

Solution

The pressure-volume diagram can be represented by the following figure:



The volume is constant not changing, hence dV is zero throughout the evolution so the work is zero (no transfer of work).

Exercise 5:

2 moles of ideal gas undergo an isothermal and reversible expansion from 43.2 L to 172.8 L. If the temperature is 25 °C.

- What are the values of Q, heat exchanged and ΔH, enthalpy change ?

We give R= 8.31 J mol^{-1} K^{-1}

Solution

According to Joule's first law the internal energy of an ideal gas only depends on its temperature, therefore: ΔU=0 , Q+W=0

$$Q = -W = \int_{V_1}^{V_2} P\,dV = \int_{V_1}^{V_2} \frac{nRT}{V}\,dV = nRT\ln\frac{V_2}{V_1} = 2\times 8.31\times 298\ln\frac{172.8}{43.2} = 6874J$$

The enthalpy variation is: ΔH=ΔU+Δ(PV)= ΔU+n R ΔT=0 (the enthalpy of an ideal gas only depends on its temperature, this is Joule's second law) .

Exercise 6:

1 g of water at a temperature of 100°C is vaporized under atmospheric pressure.

- Evaluate the total energy exchanged with the external environment.

We give: Volume of 1 g of liquid water at 100°C = 1cm³.

Volume of 1 g of saturated vapor at 1680°C = 1cm³.

Latent heat of vaporization of water: ΔH°_{Vap}= 40.7 KJ mol^{-1}; M=18 g mol^{-1}

Solution

According to the first law of thermodynamics, we have:

$$\Delta U = \Delta H^\circ_{Vap} - \int_{V_1}^{V_2} P\,dV = \Delta H^\circ_{Vap} - P(V_2 - V_1) = \frac{1}{18}\times 40.7\times 10^3 - 10^5\times(1680-1)\times 10^{-6} = 2094.11J$$

Exercise 7:

A mole of ideal gas at an initial temperature of 298K expands from a pressure of 5 atmospheres to a pressure of 1 atmosphere. In each of the following cases:

1. Isothermal and reversible relaxation.
2. Isothermal and irreversible relaxation.
3. Adiabatic and reversible expansion.
4. Adiabatic and irreversible expansion.

Calculate:

a. The final temperature of the gas.

b. The variation of the internal energy of the gas.

c. The work done by the gas.

d. The amount of heat involved.

e. The change in enthalpy of the gas.

We give: $C_V = 3R/2$ and $C_p = 5R/2$

Solution

1. Isothermal and reversible relaxation:

a. Final gas temperature: $T_2 = T_1 = 298K$ isothermal transformation.

b. Variation of the internal energy of the gas during isothermal expansion: $\Delta U = 0$

c. Work done by the gas during isothermal expansion:

$$W_{rév} = -\int_{V_1}^{V_2} P_{ext}\, dV = -n\,R\,T \int_{V_1}^{V_2} \frac{dV}{V} = -n\,R\,T\,\ln(\frac{V_2}{V_1}) = -P_1 \times V_1 \ln(\frac{V_2}{V_1}) = R \times T \ln(\frac{P_2}{P_1})$$

$$W_{rév} = 8.31 \times 298 \ln(\frac{1}{5}) = -3985.6 \text{Joules}$$

d. Quantity of heat Q brought into play during isothermal expansion: $\Delta U = 0$

From where: $Q = -W$, $Q = 3985.6 \text{Joules}$

e. Change in gas enthalpy during isothermal expansion: $\Delta H = 0$

2. Isothermal and irreversible relaxation

a. Final gas temperature is:

Isothermal transformation $T_2 = T_1 = 298K$

b. Variation of the internal energy of the gas during irreversible isothermal expansion:

Isothermal transformation $\Delta H = 0$

c. Work done by the gas during irreversible isothermal expansion:

$$W_{irrév} = -\int_{V_1}^{V_2} P_{ext}\, dV = -\int_{V_1}^{V_2} P_{final}\, dV - P_2(V_2 - V_1) = -P_2\left(\frac{RT}{P_2} - \frac{RT}{P_1}\right) = -1981 \text{Joules}$$

d. Quantity of heat Q brought into play during irreversible isothermal expansion:

$$\Delta U = 0$$

From where:

$$Q = -W,\ Q = 1981 \text{Joules}$$

a. Gas enthalpy variation during irreversible isothermal expansion:

$$\Delta H = 0$$

3. Reversible adiabatic expansion

a. Final gas temperature:

$$PV^{\gamma} = P_1V_1^{\gamma} = P_2V_2^{\gamma} = C^{te}$$ Laplace's law.

Replace V by RT/P in the equation above, we obtain:

$$P_1^{1-\gamma}T_1^{\gamma} = P_2^{1-\gamma}T_2^{\gamma}$$

$$T_2 = T_1(P_1/P_2)^{(1-\gamma/\gamma)}$$

With: $C_V = 3R/2$ and $C_P = 5R/2$ hence $\gamma = 5/3$

$$T_2 = 156.6 \text{ K}$$

b. The variation of the internal energy for reversible adiabatic expansion is:

$$\Delta U = C_v\,(T_2 - T_1)$$

$$\Delta U = 3/2(156.5 - 298)\ 8.31 = -1764 \text{ J mol}^{-1}$$

c. The amount of heat for reversible adiabatic expansion is:

$$Q = 0$$

d. The work involved during the reversible adiabatic expansion is: $\Delta U = W$

$$W = -1764 \text{ J mol}^{-1}$$

e. The enthalpy variation for reversible adiabatic expansion is:

$$\Delta H = C_p\,(T_2 - T_1)$$

$$\Delta H = -2940 \text{ J mol}^{-1}$$

4. Irreversible adiabatic expansion

a. Final gas temperature:

$$Q = 0 \Rightarrow \Delta U = W \Rightarrow C_v\,\Delta T = -P\,\Delta V$$

$$C_v\,(T_2 - T_1) = -P_2\,(V_2 - V_1) = -P_2\,R\,(T_2/P_2 - T_1/P_1)$$

$$T_2 = 203\text{K}$$

b. The variation of the internal energy for the irreversible adiabatic expansion is:

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

$$\Delta U = 3/2\ 8.31\ (203 - 298) = -\ 1184\ J\ mol^{-1}$$

c. The quantity of heat for irreversible adiabatic expansion is:

$$Q = 0$$

d. Work involved for reversible adiabatic expansion: $\Delta U = W + Q$

$$\Delta U = W$$

$$W = -\ 1184\ J\ mol^{-1}$$

e. The enthalpy variation for reversible adiabatic expansion is: $\Delta H = C_p (T_2 - T_1)$

$$\Delta H = -\ 1974\ J\ mol^{-1}$$

II.3 Relationship between ΔU and ΔH

In the case of a chemical reaction at constant temperature T, the relationship between the internal energy variation and the enthalpy variation is given by the following equation:

$$\Delta H = \Delta U + \Delta n_{gas} RT$$

We can also write:

$$Q_P = Q_V + \Delta n_{gas}\, RT$$

With:

Δn_{gas}: variation in the number of gas moles between the initial state and the final state.

R: ideal gas constant.

T: temperature expressed in kelvins (K).

$$\Delta n_{gas} = \sum n_{products} - \sum n_{reactants}$$

II.4 Applications of the first principle

II.4.1 Calculations of heats of reactions

In thermochemistry, we seek to determine the heat of a reaction by different methods, chemical reactions are carried out in a closed reactor but in the general case are carried out in an open reactor.

II.4.1.1 Standard state

From a thermodynamic point of view, the reference or standard state is the most stable physical state of a pure body. In thermodynamic tables, the heats of reaction are reported in the reference state or standard corresponds to a pressure P° called reference pressure, by international convention, it is taken equal to 1 bar (It is slightly less than 1 atm = 1.01324 10^5 Pa) and at the temperature T generally chosen 298 K, for example at 298K the standard state of water is liquid and for carbon is graphite.

Note: *The standard enthalpy of a pure body is noted ΔH°*

II.4.1.2 Enthalpy of formation

By definition, we call the standard enthalpy of formation of a compound (of a body), denoted ΔH_f°, the variation in enthalpy which accompanies its formation from simple

bodies in their most stable physical state at pressure and at the temperature considered.

> ***Note:*** *The standard enthalpies of formation ΔH_f° of simple bodies in the periodic table are zero.*

II.4.1.3 Calorimetry

Calorimetry is an experimental method for accessing reaction heats and heat capacities. This method consists of carrying out a transformation in an adiabatic system and as there is no heat exchange with the outside environment, this implies that the sum of the heat exchanged Q_i within the calorimeter is zero.

$$\Sigma Q_i = 0 \quad \text{From where } \Sigma m_i\, C_i \left(T_F - T_I\right) = 0$$

The heat involved at constant volume Q_v corresponds to a variation in the internal energy of the reaction system. It then makes it possible to calculate the heat at constant pressure Q_P corresponding to an enthalpy variation, using the following relationship:

$$Q_P = Q_V + \Delta n_{gas} RT$$

II.4.1.4 Binding energy or binding enthalpy

Bond energy or bond enthalpy, denoted $\mathbf{\Delta H_{x\text{-}y}}$, is the variation in enthalpy (heat released) which accompanies the formation of a covalent bond between two free atoms, taken in the gaseous state. To form a gaseous chemical compound, the bond enthalpy is expressed in KJ mol^{-1}.

- Case of bond enthalpy:

$$\Delta H^\circ_{reaction} = \Delta H^\circ(bonds)_{products} - \Delta H^\circ(bonds)_{reactants}$$

- Case of dissociation enthalpy:

$$\Delta H^\circ_{reaction} = \Delta H^\circ(dissociation)_{products} - \Delta H^\circ(dissociation)_{reactants}$$

II.4.1.5 Hess's law

Since internal energy and enthalpy are state functions, it is possible to predict ΔU and ΔH by **Hess**'s law, the enthalpy of a reaction (ΔH_r°) is the difference between the sum of the standard enthalpies of formation of products ($\Delta H^\circ_{\text{produits}}$) and the sum of the standard enthalpies of formation of the reactants ($\Delta H^\circ_{\text{réactifs}}$).

We can write Hess's law for the reaction: $a\,A + b\,B \xrightarrow{\Delta H_r^\circ} c\,C + d\,D$

$$\Delta H^\circ_{reaction} = \sum_j v_j \Delta H^\circ_{f\ j}\ (products) - \sum_i v_j \Delta H^\circ_{f\ i}\ (reactants)$$

$$= c\Delta H^\circ_f(C) + d\Delta H^\circ_f(D) - a\Delta H^\circ_f(A) - b\Delta H^\circ_f(B)$$

II.4.1.6 Enthalpy of combustion

Formation enthalpies are not always easily determined by the calorimetric study of formation reactions. It is often easy to determine the reference (standard) enthalpy of the burned body by applying Hess's law to the combustion reaction with dioxygen.

Example:

$$C_2H_6 + \frac{7}{2}O_2 \xrightarrow{\Delta H_r^\circ} 2CO_2 + 3H_2O$$

According to the principle of the initial state and the final state, we can write Hess's law for this reaction:

$$\Delta H_r^\circ = 2\Delta H_f^\circ(CO_2) + 3\Delta H_f^\circ(H_2O) - \Delta H_f^\circ(C_2H_6) - \frac{7}{2}\Delta H_f^\circ(O_2)$$
$$= 2\Delta H_f^\circ(CO_2) + 3\Delta H_f^\circ(H_2O) - \Delta H_f^\circ(C_2H_6)$$

CORRECTED EXERCISES

Exercise 1:

Calculate the change in internal energy of the carbon monoxide combustion reaction:

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$$

We give: ΔH (298K) = -565.68kJ at 298K

Solution

$$\Delta n_{gas} = \sum n_{products} - \sum n_{reactants} = 1 - 1 - \frac{1}{2} = -\frac{1}{2}$$

$$\Delta U = \Delta H - \Delta n_{gaz} RT = \text{-}565.6810^3 \text{ - } (\text{-}\frac{1}{2}) \text{ x } 8.314\text{x}298 = \text{-}563.48\text{kJ}$$

Exercise 2:

The following reaction takes place at 25°C:

$$3Fe_{(S)} + 4H_2O_{(g)} \rightarrow Fe_3O_{4(S)} + 4H_{2(g)}$$

With the standard enthalpies of formation at 298K:

$$\Delta H_f^{\circ}(H_20, g) = -241.8KJ\,mol^{-1}$$

$$\Delta H_f^{\circ}(Fe_30_4, S) = -1117.1KJ\,mol^{-1}$$

Determine the change in internal energy of this reaction at 25°C.

Solution

The internal energy is linked to the enthalpy variation by the relation:

$$\Delta H_r = \Delta U_r + \Delta n_{gas} RT$$

From where

$$\Delta U_r = \Delta H_r - \Delta n_{gas} RT$$

According to **Hess**'s law:

$$\Delta H^{\circ}{}_{reaction} = \sum_j v_j \Delta H^{\circ}{}_{f_j}(products) - \sum_i v_j \Delta H^{\circ}{}_{f_i}(reactants)$$

$$\Delta H_r^{\circ} = \Delta H_f^{\circ}(Fe_3O_4) - 4\Delta H_f^{\circ}(H_2O)$$

$$\Delta H_r^\circ = -117.1 - 4 \times (-241.8) = -149.9 KJ\ mol^{-1}$$

$$\Delta n_g = 0$$

So, the change in the internal energy of the reaction is:

$$\Delta U_r = \Delta H_r = -149.9\ KJ\ mol^{-1}$$

Exercise 3:

A calorimeter contains 75 grams of water (m1) at a temperature of 20 C° (T_1), 200 grams of oil (m_2) are added at a temperature of 50 C° (T_2). The equilibrium temperature reaches a value of 29.43 °C.

- Calculate the value of the mass capacity of oil.

We give: C_{Water}: 1 cal g^{-1} K^{-1}

Solution

We apply the zero principle of thermodynamics:

$$\Sigma Q_i = 0 \quad \text{From where} \quad \Sigma m_i\, C_i\, (T_F - T_I) = 0$$

$$m_1 C_{water}(T_f - T_i) - m_2 C_{oil}(T_f - T_i) = 0$$

$$75.1\ C_{water}(29.43 - 20) - 200\ C_{oil}(29.43 - 50) = 0$$

$$C_{Oil} = 0.172\ cal\ g^{-1} K^{-1}$$

Exercise 4:

Knowing the E_{Cl-Cl} and E_{H-H} bond energies and the standard enthalpy of formation at 298 K of Hydrogen chloride, calculate the E_{H-Cl} bond energy.

We give: E_{Cl-Cl} = -239.7 kJ mol^{-1}; E_{H-H} = -432.0 kJ mol^{-1}; =− 92.3 kJ mol^{-1}.

Solution

It is enough to write the following equations which express two different paths, starting from the same initial state H $_{(g)}$ + Cl $_{(g)}$ and leading to the same final state HCl $_{(g)}$:

$$\frac{1}{2} H_{2\,(g)} + \frac{1}{2} Cl_{2\,(g)} \xrightarrow{\Delta_f H^\circ_{298}(HCl)} HCl_{(g)}$$

$$\frac{1}{2} H_{2\,(g)} + \frac{1}{2} Cl_{2\,(g)} \xrightarrow{-\frac{1}{2}E_{H-H} - \frac{1}{2}E_{Cl-Cl}} H_{(g)} + Cl_{(g)}$$

$$H_{(g)} + Cl_{(g)} \xrightarrow{E_{H-Cl}} HCl_{(g)}$$

Either: $\Delta H_f^\circ(HCl,g) = -\frac{1}{2}(E_{H-H} + E_{H-H}) + E_{H-CL}$

$$E_{H-CL} = \frac{1}{2}E_{H-H} + \frac{1}{2}E_{H-H} + \Delta H_f^\circ(HCl,g)$$

$$E_{H-CL} = \frac{1}{2}(-432 - 239.7) - 92.3 = -428.1 KJ mol^{-1}$$

Exercise 5:

Calculate the enthalpy of the reaction:

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

We give the bond dissociation energies:

$$H_2 \longrightarrow 2H_{(g)}$$

$$\Delta_{diss}H^\circ_{298K}(H_2) = 436 KJ mol^{-1}$$

$$O_{2\,(g)} \longrightarrow 2O_{(g)} \qquad \Delta_{diss}H^\circ_{298K}(O_2) = 498 KJ mol^{-1}$$

$$H_2O_{(g)} \longrightarrow 2H_{(g)} + O_{(g)} \qquad \Delta_{diss}H^\circ_{298K}(H_2O) = 463 KJ mol^{-1}$$

Solution

By forming two different paths, starting from the same initial state $H_{2\,(g)} + O_{2\,(g)}$ and ending at the same final state H_2O (g), it comes:

$$2H_{2\,(g)} + O_{2\,(g)} \xrightarrow{\Delta_r H^\circ} 2H_2O_{(g)} \qquad 2H_{2\,(g)} \xrightarrow{2\Delta_{diss}H^\circ(H_2)} 4H_{(g)}$$

$$O_{2\,(g)} \xrightarrow{\Delta_{diss}H^\circ(O_2)} 2O_{(g)} \qquad 4H_{(g)} + O_{2\,(g)} \xrightarrow{-4\Delta_{diss}H^\circ(OH)} 2H_2O_{(g)}$$

So the enthalpy of reaction is:

$$\Delta_r H^\circ_{298K}(réaction) = 2\Delta_{diss}H^\circ_{298K}(H_2) + \Delta_{diss}H^\circ_{298K}(O_2) - 4\Delta_{diss}H^\circ_{298K}(OH) = -482 KJ mol^{-1}$$

Exercise 6:

Calculate the $\Delta H_r°$ of the following reaction:

$$C_3H_8(g) + 5O_2(g) \xrightarrow{\Delta H_r^\circ} 3CO_2(g) + 4H_2O(l)$$

We give: $\Delta H_f°\,(C_3H_8) = -103.8$ KJ mol^{-1}

$\Delta H_f°\,(CO_2) = -393.5$ KJ mol^{-1}

$\Delta H_f°\,(H_2O) = -285.8$ KJ mol^{-1}

Solution

$$\Delta H_r^\circ(C_3H_8) = 3\Delta H_f^\circ(CO_2) + 4\Delta H_f^\circ(H_20) - \Delta H_f^\circ(C_3H_8) - 5\Delta H_f^\circ(O_2)$$
$$\Delta H_r^\circ(C_3H_8) = 3(-393.5) + 4(-285.8) - (-103.8) - 5(0)$$
$$= -2219.9\ KJ\ mol^{-1}$$

Hess's law also states that the values of $\Delta H_r°$ relating to chemical equations are additive, which means that chemical equations can be treated as mathematical equations.

Exercise 7:

Calculate the enthalpy of the chemical reaction of hydrogenation of benzene:

$$C_6H_6(l) + 3H_2(g) \xrightarrow{\Delta H_r^\circ} C_6H_{12}(g)$$

The combustion reactions of the reactants and the product of this reaction are given.

(1) $C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$ $\quad \Delta H_{298}^\circ(réa1) = -3270KJ\ mol^{-1}$

(2) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\quad \Delta H_{298}^\circ(réa2) = -258.8\,KJ\ mol^{-1}$

(3) $C_6H_{12}(l) + 9O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$ $\quad \Delta H_{298}^\circ(réa3) = -3923KJ\ mol^{-1}$

Solution

By combining the three reactions, (rea 1) + 3 (rea 2) - (rea 3) we find the hydrogenation reaction of benzene:

$$\Delta H_r^\circ = \Delta H_{298}^\circ(1) + 3\Delta H_{298}^\circ(2) - \Delta H_{298}^\circ(3)$$
$$\Delta H_r^\circ = -3270 + 3(-285.8) - (-3923) = -204.4\ KJ\ mol^{-1}$$

Exercise 8:

Consider the combustion reaction of carbon (graphite) resulting in the formation of CO_2:

(1) $C_{(graphite)} + O_2(g) \longrightarrow CO_2(g)$ avec $\Delta H^\circ(1) = -393.5\,KJ$

This reaction can also be carried out in two successive steps:

(2) $C_{(graphite)} + \frac{1}{2}O_2(g) \longrightarrow CO(g)$ avec $\Delta H^\circ(2) = -393.5\,KJ$

and

$$(3) \quad \text{avec } \Delta H^{\circ}(3) = X\,KJ$$

Total: $C_{(graphite)} + O_2(g) \longrightarrow CO_2(g)$ avec $\Delta H^{\circ} = -393.5\,KJ$

Solution

Equation (1) is obtained by combining equations (2) and (3):

According to *Hess*'s law:

$$\Delta H°(1)=\Delta H°(2) + \Delta H°(3)$$

$$-393.5 \text{ KJ} = -110.5 \text{ KJ} + X$$

This exercise asserts that the ΔH of any reaction has a well-defined and constant value, regardless of whether it occurs in a single step or in several steps.

Kirchhoff's law then allows the calculation of the standard enthalpy at a different temperature T.

$$\Delta H_r^{\circ} = \Delta H_{298}^{\circ} + \int_{298}^{T} (\sum_j \vartheta_j C_{P,j}(\text{products}) - \sum_i \vartheta_i C_{P,i}(\text{reactants}))dT$$

Exercise 9:

The oxidation of SO_2 (g) leads to the reaction:

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g) \qquad \Delta H_{298K}^{\circ} = -198\,KJ\,mol^{-1}$$

Knowing the heat capacities at constant pressure (which we will assume to be constant over the temperature interval):

- Calculate the standard enthalpy at 598 K.

We give: C_p (SO_2, g) = 39.9 J K^{-1} mol^{-1}, C_p (SO_3, g) =50.7 J K^{-1} mol^{-1}, C_p (O2, g) = 29.4 J K-1 mol^{-1}.

Solution

By applying **Kirchhoff**'s law:

$$\Delta H_r^{\circ} = \Delta H_{298}^{\circ} + \int_{298}^{T} (\sum_j \vartheta_j C_{P,j}(\text{products}) - \sum_i \vartheta_i C_{P,i}(\text{reactants}))dT$$

$$\Delta H_r^{\circ}(598K) = \Delta H_{298}^{\circ} + \int_{298}^{598} (2C_P(SO_3) - 2C_P(SO_2) - C_P(O_2))\,dT$$

$$\Delta H_r^{\circ}(598K) = -198 + (598-298)\left[2(-50{,}7) - 2(39.9) - (29.4)\right]$$

$$\Delta H_r^{\circ}(598K) = -200.34\,KJ\,mol^{-1}$$

Note: *If there is a change in the physical state of one of the bodies involved in the reaction, the latent heat* ***Lx*** *must be taken into account.*

- If ΔH <0 or ΔU<0, the reaction is exothermic, it releases heat.
- If ΔH >0 or ΔU >0, the reaction is endothermic, it absorbs heat.
- If ΔH = 0 or ΔU = 0, the reaction is athermal, there is no heat exchange.

Exercise 10:

The latent heat of vaporization of water at 100°C under 1 atm is 40.5 KJ mol^{-1}.

- What is its value at 25°C.

We give: C_P ($H_2O_{(l)}$)=75.3 KJ mol^{-1}, C^P ($H_2O_{(g)}$)=33.6 KJ mol^{-1} under 1 atm.

The heat capacities are constant in the temperature range.

Solution

Applying Kirchhoff's law:

$$298.15K \quad H_2O_{(l)} \dashrightarrow H_2O_{(g)} \quad \Delta H_V(25\,^\circ C)$$

$$\Delta H_1 = \int_{29815}^{37315} C_P(H_2O,l)dT \qquad \Delta H_2 = \int_{29815}^{37315} C_P(H_2O,l)dT$$

$$\grave{a} \quad 373.15K \quad H_2O_{(l)} \longrightarrow H_2O_{(g)} \quad \Delta H_V(100^\circ C)$$

$$\Delta H_V(25^\circ C) = \Delta H_1 + \Delta H_V(100^\circ C) + \Delta H_2 = \int_{298}^{37315} C_P(H_2O,l)dT + \Delta H_V(100^\circ C) + \int_{37315}^{29815} C_P(H_2O,g)dT$$

$$\Delta H_V(25^\circ C) = \Delta H_V(100^\circ C) + \int_{37315}^{29815} [C_P(H_2O,g) - C_P(H_2O,l)]dT = \Delta H_V(100^\circ C) + [C_P(H_2O,g) - C_P(H_2O,l)]\Delta T$$

$$\Delta H_V(25^\circ C) = 40500 - (33.6 - 75.3) \times 75 = 43627\, J\, mol^{-1}$$

Exercise 11:

At 25°C, the standard enthalpy of combustion of ethane is given by:

$$C_2H_6 + \frac{7}{2}O_2 \xrightarrow{\Delta H_C^\circ} 2CO_2 + 3H_2O \qquad \Delta H_C^\circ = -1562.5 KJ\, mol^{-1}$$

a. Calculate the standard internal energy of this reaction.
b. Calculate the enthalpy of formation of ethane.
c. Calculate the standard enthalpy of combustion of ethane under the same pressure of 1 bar but at 75°C.

We give at 25°C:

$C_P^\circ(H_2O\ l) = 75.2\ J mol^{-1}K^{-1}$ $\Delta H_f^\circ(H_2O\ l) = -285.5 J mol^{-1}$

$C_P^\circ(CO_2\ g) = 36.8\ J mol^{-1}K^{-1}$ $\Delta H_f^\circ(CO_2\ g) = -392.9 J mol^{-1}$

$C_P^\circ(C_2H_6\ g) = 50.6\ J mol^{-1}K^{-1}$

$C_P^\circ(O_2\ g) = 29.3\ J mol^{-1}K^{-1}$

Solution

a. $\Delta U_C^\circ = \Delta H_C^\circ - \Delta n(gaz)RT = -156.5 - (2 - \frac{9}{2}) \times 8.31 \times 10^{-3} \times 298 = -1556.3\ KJ\ mol^{-1}$

b. According to the principle of the initial state and the final state, we can write Hess' law for this reaction:

$$\Delta H_C^\circ(C_2H_6) = 3\Delta H_f^\circ(CO_2) + 2\Delta H_f^\circ(H_2O) - \Delta H_f^\circ(C_2H_6) - \frac{7}{2}\Delta H_f^\circ(O_2)$$

D'où

$$\Delta H_f^\circ(C_2H_6) = 3\Delta H_f^\circ(CO_2) + 2\Delta H_f^\circ(H_2O) - \Delta H_C^\circ(C_2H_6)$$
$$= 15625 - 3 \times 285.5 - 2 \times 392.9 = -79.8\ KJ\ mol^{-1}$$

c. We apply Kirchhoff's law:

$$\Delta H_r^\circ = \Delta H_{298}^\circ + \int_{298}^{T} (\sum_j \vartheta_j C_{P,j}(products) - \sum_i \vartheta_i C_{P,i}(reactants))dT$$

$$\Delta H_r^\circ(348K) = \Delta H_{298}^\circ + \int_{298}^{348} \Delta C_P^\circ\ dT$$

$$\Delta C_P^\circ = 2C_P^\circ(CO_2, g) + 3C_P^\circ(H_2O, l) - C_P^\circ(C_2H_6, g) - \frac{7}{2}C_P^\circ(O_2, g)$$

$$\Delta C_P^\circ = 2C_P^\circ(CO_2, g) + 3C_P^\circ(H_2O, l) - C_P^\circ(C_2H_6, g) - \frac{7}{2}C_P^\circ(O_2, g)$$

$$\Delta C_P^\circ = 2 \times 36.8 + 3 \times 75.2 - 50.6 - \frac{7}{2} \times 29.3 = 146.05 J mol^{-1}\ K^{-1}$$

So : $\Delta H_r^\circ = -1562.5 + 146.05 \times 10^{-3}(348 - 298) = -1555.2 KJ\ mol^{-1}$

Exercise 12:

Calculate the combustion of methane we give:

$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$ $\Delta H_r^\circ(298) = -839.5 KJ mol^{-1}$

$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$ $\Delta H_r^\circ(1298) = ...KJ mol^{-1}$

Calculate $\Delta H_r^\circ(1298)$ knowing that the standard enthalpy of vaporization of water is and that the average values of the molar heat capacities between 298K and 1298K in J mol^{-1} K^{-1} are:

$C_P^\circ(CH_{4(g)}) = 55.2$ $C_P^\circ(O_{2(g)}) = 31.8$ $C_P^\circ(CO_{2(g)}) = 46.8$ $C_P^\circ(H_2O_{(g)}) = 38.5$

Solution

By applying Kirchhoff's law:

$$\Delta H_r^{\circ}(1298) = \Delta H_r^{\circ}(298) + 2\Delta H_{Vap}^{\circ}(298) + \int_{298}^{1298} \Delta C_P dT$$

$$\Delta C_P = 2C_P(H_2O_{(g)}) + C_P(CO_{2(g)}) - 2C_P(O_{2(g)}) - C_P(CH_{4(g)})$$

$$\Delta C_P = 2\times 38.5 + 31.8 - 2\times 31.8 - 55.2 = -10 J\, mol^{-1}K^{-1}$$

$$\Delta H_r^{\circ}(1298) = -839.5 + 2\times 43.9 - 10\times 10^{-3}(1298 - 298) = -761.7 KJ\, mol^{-1}.$$

Chapter (III)
Second law of thermodynamics

I. Introduction

The second principle of thermodynamics makes it possible to predict the direction of spontaneous evolution of systems using a new extensive state function which is called **entropy** denoted **S**. Entropy is a measure of disorder (the distribution of the constituents of the system in space) and the dispersion of energy.

I.1 Statement of the second principle

The entropy of an isolated system can only increase; it increases to a maximum value which corresponds to a state of stable equilibrium of the system (state in which the system is no longer likely to evolve without the intervention of the external environment).

Entropy is defined by:

$$dS_{system} = S_{final} - S_{initial} = \delta S_{\text{exchanged}} + \delta S_{\text{created}}$$

$$= \frac{\delta Q_{echanged}}{T} + \delta S_{\text{created}}$$

Where $\delta S_{\text{exchanged}}$ is the heat exchanged with the outside, $\delta S_{\text{created}}$ is the heat created by the system.

The entropy of an isolated system:

$dS_I = S_{final} - S_{initial} = \delta S_{\text{created}} \geq 0$ ($\delta Q_{\text{exchanged}} = 0$ From where $\delta S_{\text{exchanged}} = 0$).

The second law of thermodynamics can be expressed mathematically by:

$$\Delta S_I \geq 0$$

- $\Delta S_I = 0$ for a reversible process.
- $\Delta S_I > 0$ for an irreversible process.

The entropy of the universe is only increasing:

$$dS_{Univ} = S_{final} - S_{initial} = dS_{System} + dS_{External}$$

$$= \delta S_{\text{exchanged}} + \delta S_{\text{created}} + \delta S'_{\text{exchanged}}$$

$$\frac{\delta Q_{echanged}}{T} + \delta S_{\text{created}} + \frac{-\delta Q_{echanged}}{T}$$

$$= \delta S_{\text{created}} \geq 0$$

> ***Note:*** *the amount of heat released from the external environment is the opposite of what the system receives.*

$$\delta Q_{System} = -\delta Q_{external\ environment}.$$

I.2 Calculation of the variation of entropy in certain transformations of ideal gases

What we measure is the difference ΔS between the final state and the initial state of the system since entropy is a function of state.

I.2.1 Adiabatic and reversible transformation

During an adiabatic transformation δQ =0 which gives:

$$\Delta S = S_{final} - S_{initial} = \int_{T1}^{T2} \frac{\delta Q_{echanged}}{T} = 0$$

I.2.2 Isothermal and reversible transformation

An isothermal transformation is carried out at a constant temperature dT = 0 which gives:

$$dU = \delta Q + \delta W = 0 \text{ therefore: } -\delta Q = \delta W$$

The change in entropy is:

$$\Delta S = S_{final} - S_{initial} = \int_{T1}^{T2} \frac{\delta Q_{echanged}}{T} = \int_{T1}^{T2} \frac{-\delta W_{echanged}}{T} = -nRln\frac{V_f}{V_i}$$

I.2.3 Isochoric and reversible transformation

An isochoric transformation is carried out at a constant volume $dV = 0$ which gives:

$$dU = \delta Q = nC_V dT$$

We consider that the C_V value is constant in the temperature interval $[T_i - T_f]$.

The change in entropy is:

$$\Delta S = S_{final} - S_{initial} = \int_{Ti}^{Tf} \frac{\delta Q_{echanged}}{T} = \int_{Ti}^{Tf} \frac{nC_V}{T} dT = nC_V ln\frac{T_f}{T_i}$$

I.2.4 Isobaric and reversible transformation

An isobaric transformation is carried out at a constant pressure $dP = 0$ which gives:

$$dH = \delta Q_P = nC_P dT$$

We consider that the value of C_P is constant in the temperature interval $[T_i - T_f]$.

The change in entropy is:

$$\Delta S = S_{final} - S_{initial} = \int_{Ti}^{Tf} \frac{\delta Q_{echanged}}{T} = \int_{Ti}^{Tf} \frac{nC_P}{T} dT = nC_P ln \frac{T_f}{T_i}$$

I.3 Calculation of entropy in the event of a change of physical state

If the thermodynamic system subjected to changes in physical state, solid-liquid, liquid-gas or solid-gas, entropy can be expressed mathematically by:

- $\Delta S = S_{final} - S_{initial} = n\, C_P \ln \frac{T_{Fus}}{T_i} + \frac{\Delta H_{Fus}}{T_{Fus}} + n\, C_P \ln \frac{T_f}{T_{Fus}}$, $\boldsymbol{solid - Fusion \rightarrow liquid}$
- $\Delta S = S_{final} - S_{initial} = n\, C_P \ln \frac{T_{Vap}}{T_i} + \frac{\Delta H_{Vap}}{T_{Vap}} + n\, C_P \ln \frac{T_f}{T_{Vap}}$, $\boldsymbol{liquid - Vaporization \rightarrow gas}$
- $\Delta S = S_{final} - S_{initial} = n\, C_P \ln \frac{T_{Sub}}{T_i} + \frac{\Delta H_{Sub}}{T_{Sub}} + n\, C_P \ln \frac{T_f}{T_{Sub}}$, $\boldsymbol{solid - Sublimation \rightarrow gas}$

II. Calculation of the standard entropy variation of chemical transformations

To calculate the standard entropy variation ΔS° of a chemical reaction we use the standard molar entropies which are listed in thermodynamic tables.

For a general chemical reaction: $a\,A + b\,B \xrightarrow{\Delta S_r^\circ} c\,C + d\,D$

The entropy variation is written:

$$\Delta S_r^\circ = \sum_j \vartheta_j S_j^\circ(products) - \sum_i \vartheta_i S_i^\circ(reactants)$$
$$= cS^\circ(C) + dS^\circ(D) - aS^\circ(A) - bS^\circ(B)$$

Kirchhoffs law allows us to calculate the standard entropy variation of a chemical reaction at a different temperature T.

$$\Delta S_r^\circ(T) = \Delta S_{298}^\circ + \int_{298}^{T} \frac{\Delta C_P}{T} dT = \int_{298}^{T} \frac{C_P(products) - C_P(reactants)}{T} dT$$

III. Nernst's theorem

Nernst's theorem is also called the third law of thermodynamics which states that at the temperature zero kelvin (0 K) the entropy of any body is zero (there is no longer any vibration). This means that there is no disorder at this temperature (0 K).

IV. Free enthalpy G and free energy F

The second principle of thermodynamics makes it possible to predict the direction of evolution of isolated systems, but for many transformations, the systems are not isolated, they exchange energy with the outside. Then we define two new state functions which are the free enthalpy **G** (**Gibbs energy**) and the free energy **F** (**Helmholtz energy**).

For a chemical reaction carried out at constant temperature and pressure we have:

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

The free enthalpy variation ΔG is written:

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= \Delta U + P\Delta V - T\left(\Delta S_{echanged} - \Delta S_{created}\right) \\ &= Q + W + P\Delta V - T\left(\frac{Q}{T} + \Delta S_{created}\right) \\ &= -T\Delta S_{created}\end{aligned}$$

- If ΔG > 0, the system can evolve spontaneously.
- If ΔG = 0, the system is in equilibrium.
- If ΔG < 0, the system cannot evolve spontaneously without external intervention.

> ***Note:*** *free enthalpy is a state function, we can apply the same rules to it as to other state functions such as enthalpy or entropy.*

For a chemical reaction carried out at constant volume the free energy **F** is:

$$F = U - T\,S$$

The variation of the free energy ΔF at constant volume is written:

$$\Delta F = \Delta U - T\,\Delta S$$

- If ΔF> 0, the system can evolve spontaneously.
- If ΔF= 0, the system is in equilibrium.
- If ΔF<0, the system cannot evolve spontaneously without external intervention.

The two functions **G** and **F** are functions of states, we can calculate the variation of the standard free enthalpy and the standard free energy of a chemical reaction from the values of the enthalpies/free energies of formation using the law from ***Hess***:

For a general chemical reaction: $a\,A + b\,B \xrightarrow{\Delta G_r^\circ} c\,C + d\,D$

The free enthalpy variation is written:

$$\Delta G_r^\circ = \sum_j \vartheta_j G_j^\circ(products) - \sum_i \vartheta_i G_i^\circ(reactants)$$
$$= c\Delta G^\circ(C) + d\Delta G^\circ(D) - a\Delta G^\circ(A) - b\Delta G^\circ(B)$$

We can also calculate the free enthalpy of reaction using the following relationship:

$$\Delta G_r^\circ = \Delta H_r^\circ - T\,\Delta S_r^\circ$$

With:

$$\Delta H^\circ{}_{reaction} = \sum_j v_j\,\Delta H^\circ{}_f{}_j\ (products) - \sum_i v_j\,\Delta H^\circ{}_f{}_i\ (reactants)$$

$$= c\Delta H^\circ{}_f(C) + d\Delta H^\circ{}_f(D) - a\Delta H^\circ{}_f(A) - b\Delta H^\circ{}_f(B)$$

And

$$\Delta S_r^\circ = \sum_j \vartheta_j S_j^\circ(products) - \sum_i \vartheta_i S_i^\circ(reactants)$$
$$= cS^\circ(C) + dS^\circ(D) - aS^\circ(A) - bS^\circ(B)$$

Note: *the standard free enthalpies of simple bodies in the periodic table are zero.*

V. Equilibrium constant K and gas phase equilibrium law

In order to know the sign of ΔGr it is necessary to determine ΔGr° and the equilibrium constant noted K.

We consider that the reactants and products are gases: a gas A reacts with a gas B:

$$a\,A_{(g)} + b\,B_{(g)} \xrightarrow{\Delta G_r^\circ} c\,C_{(g)} + d\,D_{(g)}$$

We have:

During the evolution of this reaction the partial pressures are modified and the variation of the free enthalpy is written:

$$\Delta G_T = \Delta G^\circ + RT\,Ln\left[\frac{P_C^c\ P_D^d}{P_A^a\ P_B^b}\right]$$

With $K_p(T) = \left[\frac{P_C^c\ P_D^d}{P_A^a\ P_B^b}\right]$ is the equilibrium constant as a function of partial pressures at temperature T.

Equilibrium is characterized by zero free enthalpy $\Delta G_T = 0$

From where $\frac{-\Delta G^{\circ}}{RT} = Ln\ K_P$

$\Delta G^{\circ} = -RT\,Ln\,K_P$

The criterion for spontaneous evolution of the reaction is: ΔGT < 0, the reaction occurring from left to right; $\Delta G_T = \Delta G^{\circ} + RT\,Ln\,K_P < 0$

From where $Ln\,K_P < \frac{-\Delta G^{\circ}}{RT}$.

If $Ln\,K_P > \frac{-\Delta G^{\circ}}{RT}$, the reaction spontaneously evolves to the left.

Notes

- *If $\Delta G°_T$ is small (negative but large in absolute value) this means that the equilibrium constant is very large and in this case the reactants tend to transform almost completely into products, we can say that the reaction is complete .*
- *If $\Delta G°_T$ is large (positive and large in absolute value) this means that the equilibrium constant is very small and in this case the reactants practically do not react or there are very few products formed, we can say that the reaction does not take place.*

It is possible to express the equilibrium constant as a function of concentrations or with mole fractions.

Either $P_i = [X_i]RT$

$$K_P = \left[\frac{X_C^c\ X_D^d}{X_A^a\ X_B^b}\right](RT)^{(c+d)-(a+b)} = K_C\,(RT)^{(c+d)-(a+b)}$$

If we put: (c+d)-(a+b)=h et $K_C = \left[\frac{X_C^c\ X_D^d}{X_A^a\ X_B^b}\right]$

We obtain $K_P = K_C\,(RT)^h$

From where $K_C = K_P\,(RT)^{-h}$

LE CHATELIER's law makes it possible to predict the direction of movement of the balance when one of the balance factors is varied; a modification of one of the balance factors leads to a movement of the balance in the meaning which opposes this modification.

By deriving with respect to the temperature the relation:

$$\Delta G_T^\circ = -RT\,Ln\,K_P$$

We obtain the Van't ***Hoff*** relation:

$$\Delta G_T^\circ = -RT\,Ln\,K_P = \Delta H^\circ - T\Delta S^\circ$$

$$Ln\,K_P = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$\frac{d(Ln\,K_P)}{dT} = \frac{\Delta H}{R\,T^2}$$

Van't Hoff's law is written:

$$\frac{d(Ln\,K)}{dT} = \frac{\Delta H}{R\,T^2}$$

- If $\Delta H < 0$, $d(\text{Ln } K) / dT < 0$, the reaction occurring in the direction from right to left is favored.
- If $\Delta H > 0$, $d(\text{Ln } K) / dT > 0$, the reaction is favored in the direction from left to right.

CORRECTED EXERCISES:

Exercise 1:

1 kg of ice taken at -10°C is brought into contact with an external environment at 25°C, Calculate the entropy variation of:

a- This mass of water

b- The source

c- The universe

We give:

C_P (H_2O) (solid) = 2090 J kg^{-1} K^{-1}; CP (H_2O) (liquid) = 4180 J kg^{-1} K^{-1}

L_f (latent heat of melting of ice at 273 °C) = 333 KJ kg^{-1}

Solution

a- The variation in entropy of this mass of water:

$$H_2O_{(S)} \xrightarrow{\Delta S_1} H_2O_{(S)} \xrightarrow{\Delta S_2} H_2O_{(l)} \xrightarrow{\Delta S_3} H_2O_{(l)}$$
$$263K \qquad 273K \qquad 273K \qquad 298K$$

$$\Delta S_{eau} = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\Delta S_{eau} = \int_{263}^{273} \frac{mC_P(H_2O_{(s)})}{T} dT + \frac{m\Delta H_{fus}}{273K} + \int_{273}^{298} \frac{mC_P(H_2O_{(l)})}{T} dT$$

$$= 1\times 2090\times \ln\frac{273}{263} + \frac{333\times 10^3}{273} + 1\times 4180\times \ln\frac{298}{273} = 166403 JK^{-1}$$

b- The enthalpy variation of the source:

The source releases a quantity of heat Q at a constant temperature (Ts=298K)

$$Q = -\left[mC_P(H_2O_{(s)})(T_2 - T_1) + mLf + mC_P(H_2O_{(l)})(T_3 - T_2)\right]$$

$$= 1\times 2090\times (273-263) + 333\times 10^3 + 1\times 4180\times (298-273) = -458400J$$

$$\Delta S_2 = \frac{Q}{T_3} \frac{-458400}{298} = -153825 JK^{-1}$$

c- The enthalpy variation of the universe:

$$\Delta S = \Delta S_{Source} + \Delta S_{water} = 1664.03 - 125.78 JK^{-1}$$

Exercise 2:

What is the change in entropy when we transform a mole of ice at -10°C into water vapor at 100°C and under a pressure of one bar?

We give for one gram of material:

C_P (H_2O, s) = 2.1J K^{-1} mol^{-1}

C_P (H_2O, l) = 75.33 J K^{-1} mol^{-1}

Enthalpy of fusion of ice L_f = 0.33 KJ.

Enthalpy of vaporization of water L_v = 2.25 KJ.

Solution

Water goes through several stages:

$$\underset{-10°C}{H_2O_{(S)}} \xrightarrow{\Delta S_1} \underset{0°C}{H_2O_{(S)}} \xrightarrow{\Delta S_2} \underset{0°C}{H_2O_{(l)}} \xrightarrow{\Delta S_3} \underset{100°C}{H_2O_{(l)}} \xrightarrow{\Delta S_4} \underset{100°C}{H_2O_{(g)}}$$

The change in total entropy will be the sum of all changes in entropy ΔS_i.

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$$

$$\Delta S_r = \int_{263}^{273} \frac{C_P(H_2O_{(s)})}{T} dT + \frac{\Delta H_{fus}}{273K} = \int_{273}^{373} \frac{C_P(H_2O_{(l)})}{T} dT + \frac{\Delta H_{Vap}}{373K}$$

$$\Delta S_r = \int_{263}^{273} \frac{C_P(H_2O_{(s)})}{T} dT + \frac{\Delta H_{fus}}{273K} + \int_{273}^{373} \frac{C_P(H_2O_{(l)})}{T} dT + \frac{\Delta H_{Vap}}{373K}$$

$$\Delta S_r = 2.11\ln\frac{273}{263} + \frac{330}{273K} + 75.33\ln\frac{373}{273} + \frac{2250}{373K}$$

$$\Delta S_r = 30.83 JK^{-1}mol^{-1}$$

The change in total entropy will be the sum of all changes in entropy ΔS_i.

Exercise 3:

At 27°C and under 1 atm, the standard enthalpies of formation $\Delta H°_f$ of solid urea (CH_4N_2O) and urea in aqueous solution are respectively -332.85 KJ mol^{-1} and -318.93 KJ mol^{-1}.

1- Calculate the quantity of heat absorbed during the dissociation of a mole of urea in water.

2- What must be the sign of the free enthalpy variation for dissolution to occur spontaneously?

3- Deduce the minimum value of the entropy variation associated with this dissociation, justify the sign of this value.

4- At 27°C and under 1 atm, the standard free enthalpies of formation $\Delta G°_f$ of solid urea and urea in aqueous solution are respectively -196.96 KJ K-1 mol-1 and -203.64 KJ K^{-1} mol^{-1}.

Solution

1- The urea dissociation reaction is written:

$$CO(NH_2)_{2(S)} \longrightarrow CO(NH_2)_{2(aq)}$$

ΔH_r of the reaction is:

2- A spontaneous reaction its free enthalpy variation is negative: $\Delta G_r < 0$

3- We have $\Delta G_r < 0 \Rightarrow \Delta H_r^\circ - T\Delta S_r^\circ < 0$

$$\text{SO: } \Delta S_r^\circ > \frac{\Delta H_r^\circ}{T} = \frac{13920}{300} = 46.4\ J K^{-1} mol^{-1}$$

4- $\Delta G_r = \Delta G_f^\circ(\text{urea}_{(aq)}) - \Delta G_f^\circ(\text{urea}_{(l)}) = -6.68\ KJ\ mol^{-1}$

$$\text{We have: } \Delta G_r = \Delta H_r^\circ - T\Delta S_r^\circ$$

$$\text{So: } \Delta S_r^\circ = \frac{\Delta H_r^\circ - \Delta G_r}{T} = 68.66 KJ\ K^{-1} mol^{-1}$$

Exercise 4:

Calculate the change in entropy when one mole of iodine solid at 25°C vaporizes at 184°C, the pressure being 1 atm.

We give: C_p (solid I_2) = 54.6 J K-1 mol-1

C_p (I_2 liquid) = 81.5 J K-1 mol-1

ΔH_{fus}= 15633 J mol-1 Melting temperature 113.6 °C

ΔH_{vap}= 25498 J mol-1 Vaporization temperature 184°C

Solution

Iodine goes through several stages:

$$I_{2(S)} \xrightarrow{\Delta S_1} I_{2(S)} \xrightarrow{\Delta S_2} I_{2(l)} \xrightarrow{\Delta S_3} I_{2(l)} \xrightarrow{\Delta S_4} I_{2(g)}$$

$$25°C \qquad 113.6°C \qquad 113.6°C \qquad 184°C \qquad 184°C$$

ΔS_1: Passage of a mole of solid iodine from 298K to 386.6 K

$$\Delta S_1 = n\ C_P(s) \ln \frac{T_f}{T_i} = 54.6 \ln \frac{386.6}{298} = 14.2 J mol^{-1}$$

ΔS_2: Fusion of a mole of solid iodine at 386.6 K

$$\Delta S_2 = \frac{\Delta H_{Fus}}{T_{Fus}} = \frac{15633}{386.6} = 40.4 J mol^{-1}$$

ΔS_3: Passage of a mole of liquid iodine from 386.6 K to 457 K

$$\Delta S_3 = n\ C_P(l) \ln \frac{T_f}{T_i} = 81.5 \ln \frac{457}{386.6} = 13.6 J mol^{-1}$$

ΔS_4: Vaporization of a mole of solid iodine at 457 K

$$\Delta S_4 = \frac{\Delta H_{Vap}}{T_{Vap}} = \frac{25498}{457} = 55.8\, J\, mol^{-1}$$

Hence, the variation in entropy when a one mole of solid iodine at 25°C vaporizes at 184°C, the pressure being 1 atm is the sum of all the variations in entropy ΔS_i.

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$$

$$= 14.2 + 40.4 + 13.6 + 55.8$$

$$= 124 \text{ J mol}^{-1}$$

Exercise 5:

Calculate the value of the equilibrium constant K_{eq} relating to the reaction taking place at 298 K and which is described by the following equation:

$$H_{2(g)} + CO_{2(g)} \leftrightarrow H_2O_{(g)} + CO_{(g)}$$

Knowing that:

	$\Delta H^{\circ}_f (KJ\, mol^{-1})$	$S^{\circ} (KJ\ K^{-1}\, mol^{-1})$
$H_2(g)$	0	130.6
$CO_2(g)$	-393.6	213.7
$H_2O(g)$	-241.9	188.8
$CO(g)$	-110.5	198.8

Solution

To calculate the equilibrium constant K_{eq} we apply the Van't Hoff relation:

$$\Delta G^{\circ}_{reaction} = -RTLnK_P = \Delta H^{\circ}_{reaction} - T\Delta S^{\circ}_{reaction}$$

$$K_P = e^{\left(\frac{-\Delta G^{\circ}_{reaction}}{RT}\right)}$$

$$\Delta H^{\circ}{}_{reaction} = \sum_j v_j\, \Delta H^{\circ}{}_f\ (products) - \sum_i v_j\, \Delta H^{\circ}{}_f\ (reactants)$$

$$= \Delta H^{\circ}_f(H_2O) + \Delta H^{\circ}_f(CO) - \Delta H^{\circ}_f(H_2) - \Delta H^{\circ}_f(CO_2)$$

$$= -241.9 - 110.5 = 41.1\ KJ\ K^{-1}\, mol^{-1}$$

$$\Delta S^{\circ}{}_{reaction} = \sum_j v_j\, S^{\circ}{}_j\ (products) - \sum_i v_j\, S^{\circ}{}_i\ (reactants)$$

$$= S^{\circ}(H_2O) + S^{\circ}(CO) - S^{\circ}(H_2) - S^{\circ}(CO_2)$$

$$= 188.8 + 198.8 = 43.3\ KJ\ K^{-1}\, mol^{-1}$$

From where:

$$\Delta G^{\circ}_{reaction} = -RTLnK_P = \Delta H^{\circ}_{reaction} - T\Delta S^{\circ}_{reaction}$$

$$= 41100 - 298 \times 43.3 = 28196.6\, J\, mol^{-1}$$

$$K_P = e^{-\frac{28196.6}{8.31\times298}}$$

$$K_P = 1.1 \times 10^{-5}$$

Exercise 6:

Two liters of Ethylamine ($C_2H_5NH_2$) gas are introduced into a container at 500K, under an initial pressure of 2 atm. The equilibrium of dissociation of Ethylamine into Ethylene $C_2H_{4\,(g)}$ and Ammonia $NH_{3\,(g)}$ is established and the final pressure is 3.2 atm.

1- Write the decomposition reaction.

2- Give the expression for the variation of the free enthalpy as a function of the partial pressures.

3- Write the equilibrium condition and give the expression for the equilibrium constant K of the reaction.

4- Calculate K at a temperature of 500 K, we give R=2 cal $K^{-1}mol^{-1}$.

5- Determine the composition in numbers of moles of the system at equilibrium.

We give at 298K.

	$\Delta H_f^\circ (Kcal\,mol^{-1})$	$S^\circ (cal\ K^{-1}\,mol^{-1})$
$C_2H_5NH_2(g)$	-11.60	71.17
$NH_2\,(g)$	-11.04	46.01
$C_2\,H_4\,(g)$	12.50	52.45

Solution

1- We consider that ideal gases and we neglect the influence of heat capacities, the dissociation reaction is:

$$C_2H_5NH_{2(g)} \leftrightarrow C_2H_{4(g)} + NH_{3(g)}$$

2- The expression of the variation of the free enthalpy as a function of the partial pressures is:

$$\Delta G_T = \Delta G^\circ + RT\,Ln\left[\frac{P_{C_2H_4}\ P_{NH_3}}{P_{C_2H_5NH_2}}\right]$$

3- The equilibrium condition is: $\Delta G_T = 0$

Hence the equilibrium constant:

$$K = \frac{P_{C_2H_4}\ P_{NH_3}}{P_{C_2H_5NH_2}} = e^{\frac{-\Delta G^\circ}{RT}}$$

4- First we calculate at 500 K using variations in enthalpy and entropy

$$\Delta H^{\circ}_{reaction} = \Delta H^{\circ}_f(C_2H_4) + \Delta H^{\circ}_f(NH_3) - \Delta H^{\circ}_f(C_2H_5NH_2) = 213.06\ Kcal$$

$$\Delta S^{\circ}_{reaction} = S^{\circ}(C_2H_4) + S^{\circ}(NH_3) - S^{\circ}(C_2H_5NH_2) = 213.06\ Kcal$$

$$\Delta G^{\circ}_{500K} = \Delta H^{\circ} - 500\ \Delta S^{\circ} = -585\ cal$$

$$\text{So, } K = e^{585/(500\times 2)} = 1.79$$

5- Calculation of the composition in numbers of moles of the system at equilibrium

We have:

Etat	$C_2H_5NH_{2(g)} \leftrightarrow C_2H_{4(g)} + NH_{3(g)}$		
Etat initial	n_0	0	0
Etat final	n_0-x	x	x

The initial number of moles is:

$$n_0 = PV/RT = (2\times 2)/(0.082\times 500) = 0.1mol$$

$$K = \frac{P_{C_2H_4}\ P_{NH_3}}{P_{C_2H_5NH_2}} = \frac{X_{C_2H_4}P_{tot}\times X_{NH_3}P_{tot}}{X_{C_2H_5NH_2}\times P_{tot}} = \frac{X^2\times P_{tot}}{X_{C_2H_5NH_2}} = \frac{(\frac{x}{n_0+1})^2\times P_{tot}}{(\frac{n_0-1}{n_0+1})}$$

$$1.79 = \frac{3.2\times x^2}{(0.1+x)(0.1-x)} \Rightarrow x = 0.059mol$$

The composition in numbers of moles of the system at equilibrium: 0.059, 0.059 and 0.041mol for C_2H_4, NH3 and $C_2H_5NH_2$ respectively.

Exercise 7:

What is the influence?

a- An increase in temperature.

b- An increase in pressure on the following balances?

$$SO_{2\,(g)} + \frac{1}{2}O_{2\,(g)} \underset{2}{\overset{1}{\rightleftharpoons}} SO_{3(g)} \qquad \Delta H_1 = -98.23KJ\,mol^{-1}$$

$$Fe_3O_{4(S)} + 4C_{(s)} \underset{2}{\overset{1}{\rightleftharpoons}} 3Fe_{(s)} + 4CO_{(g)} \qquad \Delta H_2 = 674.48KJ\,mol^{-1}$$

$$N_{2(g)} + O_{2(g)} \underset{2}{\overset{1}{\rightleftharpoons}} 2NO_{(g)} \qquad \Delta H_3 = 179.74KJ\,mol^{-1}$$

Solution

a- Based on Van't Hoff's law which links the equilibrium constant Ln K_P to the temperature T:

$$\frac{d(Ln\,K_P)}{dT} = \frac{\Delta H}{R\,T^2}$$

$$SO_{2\,(g)} + \frac{1}{2}O_{2\,(g)} \underset{2}{\overset{1}{\rightleftharpoons}} SO_{3(g)} \qquad \Delta H_1 = -98.23 KJ\,mol^{-1}$$

$\Delta H_1 < 0$ this reaction is exothermic, the term $d(Ln\ K_P)/dT < 0$ this means that the derivative of ln K_P with respect to T is negative.

From where:

The function $\ln K_P = f(T)$ is decreasing, if T increases ln K_P decreases, the equilibrium moves in the direction from right to left (direction 2) this means that in the endothermic direction.

$$Fe_3O_{4(S)} + 4C_{(s)} \underset{2}{\overset{1}{\rightleftharpoons}} 3Fe_{(s)} + 4CO_{(g)} \quad \Delta H_2 = 674.48 KJ\,mol^{-1}$$

$\Delta H_2 < 0$ this reaction is endothermic, the term $d(Ln\ K_P)/dT < 0$ this means that the derivative of ln K_P with respect to T is positive.

From where:

The function $\ln K_P = f(T)$ is increasing, if T increases ln K_P increases, the equilibrium moves in the direction from left to right (direction 1) this means that in the exothermic direction.

Equilibrium 3 moves in direction (1).

a- The increase in pressure has the same effect on the equilibrium as an increase in the number of gas moles, according to Le Chatelier's principle the equilibrium will move in the direction of the decrease in the number of gas moles.

- Balance (1): moves in direction 1 since $\Delta n = -1/2$
- Balance (2): moves in direction 2 since $\Delta n = 1$
- Balance (1): no influence on balance since $\Delta n = 0$.

Exercise 8:

How does the following balance evolve?

$$CH_{4(g)} \underset{2}{\overset{1}{\rightleftharpoons}} C_{(s)} + 2H_2O_{(g)} \quad \Delta H > 0$$

a- If we raise the temperature?

b- If we increase the pressure?

c- If we add methane at constant volume?

d- If we add carbon?

e- If we add an inert gas (argon for example) at constant volume?

f- If we add an inert gas (argon for example) at constant pressure?

Solution

a- Movement to the right in the direction which decreases the temperature of the system (in the endothermic direction of the transformation).

b- Movement to the left in the direction which decreases the number of moles of gaseous compounds.

c- Movement to the right in the direction of disappearance of a compound participating in the chemical reaction.

d- No influence, carbon in the solid phase its title is 1 whatever its mass.

e- No influence (no variation in partial pressures).

Exercise 9:

We consider the following reaction possibly leading to equilibrium:

$$2H_2O_{2(l)} + N_2H_{4(l)} \underset{2}{\overset{1}{\rightleftharpoons}} N_{2\,(g)} + 4H_2O_{(l)}$$

a- Calculate the enthalpy change and the standard entropy change of this reaction.

What remark(s) can justify the sign of the entropy change?

b- Calculate the standard free energy variation of this reaction.

We give:

T=298K, R= 8.32 J K^{-1} mol^{-1}

	$\Delta H_f^\circ (KJ\,mol^{-1})$	$S^\circ (J\ K^{-1}\ mol^{-1})$
H_2O_2 (l)	-187.43	101.87
N_2H_4 (l)	50.63	121.05
H_2O (l)	-285.58	70.18
N_2 (g)	0	191.44

Solution

a- We apply Hess's law for the meaning (1)

$$\Delta H^\circ_{reaction} = 4\Delta H_f^\circ(H_20)_{(l)} - \Delta H_f^\circ(N_2H_4)_{(l)} - 2\Delta H_f^\circ(H_2O_2)_{(l)}$$

$$= -817.82\ KJ\ K^{-1}mol^{-1}$$

$$\Delta S^\circ_{reaction} = 4S^\circ(H_20)_{(l)} + S^\circ(N_2)_{(g)} - S^\circ(N_2H_4)_{(l)} - 2S^\circ(H_2O_2)_{(l)}$$

$$= 147.37\ KJ\ K^{-1}mol^{-1}$$

The variation in the entropy of the reaction is positive which is explained by the increase in disorder since the system passes from a liquid state to another liquid and gaseous state.

We have:

$$\Delta G_r = \Delta H_r^\circ - T\Delta S_r^\circ = -817.82 - 298\times 147.37\times 10^{-3} = -861.74 KJ\,mol^{-1}$$

Exercise 10:

The decomposition of dinitrogen monoxide in the gas phase at high temperature is an irreversible reaction which can be written:

$$N_2O_{(g)} \longrightarrow N_{2\ (g)} + \frac{1}{2}O_{2\ (g)}$$

a- Calculate the enthalpy change $\Delta H°_{298}$ and the entropy change $\Delta S°_{298}$ of this reaction.

b- Is the reaction thermodynamically possible at 298K? justify.

c- Is the reaction thermodynamically possible in the temperature range 600-1000 K. Justify ? (we will assume that the values of $\Delta H°_r$ and $\Delta S°_r$ do not depend on the temperature).

We give:

T=298K, R= 8.32 J K^{-1} mol^{-1}

	$\Delta H_f^\circ (KJ\,mol^{-1})$	$S^\circ (J\ K^{-1}\ mol^{-1})$
N_2O (g)	82.1	219.9
O_2 (g)	0	191.6
N_2 (g)	0	205.2

Solution

a- The variation in the enthalpy of the reaction is the opposite of the enthalpy of formation of N_2O (gas):

$$\Delta H_{réaction}^\circ = -\Delta H_{f(298K)}^\circ (N_2O_{(g)}) = -82.1 KJ\,mol^{-1}$$

To calculate the change in entropy using ***Hess***'s law:

$$\Delta S^\circ{}_{reaction} = \sum_j v_j\, S^\circ{}_{j\ (products)} - \sum_i v_j\, S^\circ{}_{i\ (reactants)}$$

$$= \frac{1}{2}S_{298}^\circ(O_2)_{(g)} + S_{298}^\circ(N_2)_{(g)} - S^\circ(N_2O_4)_{(g)}$$

$$= \frac{1}{2}\times(191.6) + 205.2 - 2019.9 = 81.1\ J\ K^{-1}\ mol^{-1}$$

b- To know whether the reaction is spontaneous or not, we calculate the free enthalpy at 298K.

$$\Delta G^{\circ}_{r(298)} = \Delta H^{\circ}_{r(298)} - T\Delta S^{\circ}_{r(298)} = -82.1 - 298 \times 81.1 \times 10^{-3} = -106.3\, KJ\, mol^{-1}$$

The variation in free enthalpy at 298K is negative which means that the decomposition of N_2O (gas) is spontaneous at 298K.

c- In the temperature interval 600-1000K, the free enthalpy variation is always negative ($\Delta G^{\circ}_{r(T)} < 0$), hence the decomposition of the decomposition of N_2O (gas) is spontaneous in the interval 600-1000K.

Exercise 11:

At 298K, the following equilibrium of the two tautomeric forms of vitamin C, schematized by:

$$A \longleftrightarrow B \qquad K = 10^{-9}$$

1- Determine the standard free enthalpy variation of this reaction, in the forward direction.

We give: RT ln=$10^3 \times 5.7$log

2- Under these conditions, which is the most stable species (A or B), from a thermodynamic point of view? Justify.

3- Or, at 298K, 100 mL of vitamin C solution, in form A, containing 10^{-2} mol. Calculate the concentrations of tautomeric forms A and B at equilibrium.

4- At 353K, with initial conditions similar to equilibrium, the concentration of species B is 10^{-8} mol L^{-1}. Deduce the equilibrium constant at this temperature.

5- By justifying, indicate whether the equilibrium in the forward direction is exothermic.

Solution

1- The variation of the standard enthalpy is:

$$\Delta G^{\circ} = -RT\,Ln\,K = -10^3 \times 5.7 \log 10^{-9} = 51.3 \times 10^3\, J\, mol^{-1}$$

2- The spontaneous direction of the reaction corresponds to a variation in negative free enthalpy, $\Delta G^{\circ} = +51.3 \times 10^3\, J\, mol^{-1}$, therefore in the opposite direction leading to the formation of A; hence the species A is the most stable.

3- We use the progress table:

	$A \longleftrightarrow B$		$K = 10^{-9}$
t_0	10^{-2}	0	
$t_{éq}$	$10^{-2} - x$	x	

The equilibrium constant is therefore written:

$$K = [B]_{éq} / [A]_{éq} = x/(10^{-2} - x) = 10^{-9}$$

The value of the equilibrium constant is very low which means that $[A]_{éq} << [B]_{éq}$ we therefore formed few B, that means, x << 10-2. We therefore neglect x in front of the initial concentration.

From where: $K = x/10^{-2} \Rightarrow x = 10^{-2} \times K = 10^{-2} \times 10^{-9} = 10^{-11}$

The equilibrium concentrations are:

$$[B]_{éq} = x/V = 10^{-11}/10^{-1} = 10^{-10} molL^{-1}$$
$$[A]_{éq} = (10^{-2} - x)/V = (10^{-2} - 10^{-11})/10^{-1} = 10^{-1} molL^{-1}$$

4- In the same way, the equilibrium concentrations are:

$$[B]_{éq} = x/V \Rightarrow x = 10^{-1} \times 10^{-8} = 10^{-9}$$
$$[A]_{éq} = (10^{-2} - x)/V = (10^{-2} - 10^{-9})/10^{-1} = 10^{-1} molL^{-1}$$

From where:

$$K = 10^{-8}/10^{-1} = 10^{-7}$$

5- According to the values of the equilibrium constant, we see that K increases with the temperature and according to ***Van't Hoff***'s law the equilibrium constant K varies as a function of the temperature T:

$$\frac{d(Ln\,K)}{dT} = \frac{\Delta H}{R\,T^2}$$

RT^2 is positive so $\Delta H°$ has a sign of, which is positive since the function $lnK = f(T)$ is an increasing function, hence the reaction is not exothermic, it is endothermic.

VI. Conclusion

The first law of thermodynamics is a valuable guide allowing us to predict the relationships between mechanical phenomena and calorific phenomena and to calculate the heat (energies) of the reaction but insufficient, it does not allow us to predict the direction in which natural phenomena take place. , this requires the introduction of a second principle and the definition of a new function which makes it possible to predict the direction of a reaction and subsequently to be able to determine the proportions of the products formed.

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