

**People's Democratic Republic of Algeria**  
**Ministry of Higher Education and Scientific Research**  
**Mohamed Khider University- Biskra**  
**Faculty of sciences and technology**



**COLLECTION OF SOLVED EXERCISES AND  
PROBLEMES IN CHEMICAL THERMODYNAMICS.**

**1<sup>st</sup> year Science and Technology LMD**

Presented by :

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### Foreword:

- ✓ This handout is specifically intended for first-year university students.
- ✓ It is of particular interest to students in technical sciences LMD.
- ✓ This handout can be considered as a reference for students in the study of thermodynamics.
- ✓ It includes exercises and problems for each chapter, along with a model solution.

Recommended prior knowledge:

The student must have prior knowledge before solving the exercises in order to facilitate the process, we mention the following:

- Basic concepts in mathematics, including derivation and integration ...
- Basic concepts in thermodynamics: thermodynamic systems and the external environment, states of matter, sublimation, condensation, evaporation, liquefaction, melting, freezing, expansion, compression, physical change, chemical change, state functions, path functions, Extensive, intensive variables, reversible and irreversible process, isothermal and isochoric and isobaric and adiabatic transformations, Meyer's relationship, Boyle-Mariotte's law, Gay-Lussac's law, Charle's law, and Avogadro's law, first principle of thermodynamics, the work (W), the amount of heat (Q), the change in internal energy ( $\Delta U$ ), the change in enthalpy ( $\Delta H$ ), the heat capacity and standard molar enthalpy of formation  $\Delta H^\circ_f$ , the standard enthalpy of a reaction  $\Delta H^\circ_R$ , Hess's law, Kirchhoff's law, bond energy, cycle method.

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**CHAPTER I: GENERALITIES OF THERMODYNAMICS:****LEARNING OBJECTIVES:**

The learning objectives of first chapter “generalities of thermodynamics” involve understanding fundamental concepts of thermodynamics including:

The states of matter and its transformations as freezing, evaporation, condensation...

The difference between the physical and chemical changes.

The extensive and intensive state variables.

State function and how to prove that it is a state function and not a path function.

The concept of thermodynamic system.

The different types of thermodynamic systems “open, closed or isolated”

The difference between the reversible and irreversible thermodynamic process.

Temperature and pressure conversion methods.

How to use the ideal gas law to solve exercises.

The concept of partial pressure.

**EXERCISES OF CHAPTER I:****A. THE STATES OF MATTER AND STATE FUNCTIONS:****EXERCISE I.A.1 :**

- 1- Explain the physical and chemical changes.
- 2- Select the type of change in each case :
  - During digestion, starch is converted into glucose.
  - Freezing of water.
  - Sugar caramelizes when heated.
  - Phosphorus burns in air.
  - Casting silver in a mold.
  - Rusting of iron.
  - Crumpling a sheet of aluminum foil.
  - Digesting food.

**EXERCISE I.A.2 :**

- 1- What is the freezing and melting point?
- 2- What is the condensation process?

- 3- Find the type of process when the matter changes its state from gas to solid?  
 4- What is the process in the formation of ice, and formation of clouds?

**EXERCISE I.A.3:**

1. Define the extensive and intensive state variables, using some examples.
2. Classify in the following table :
  - The temperature T.
  - The volume V.
  - The density D.
  - The pressure P.
  - The mass M.
  - The energy E.
  - The moles number n.
  - The internal energy U.
  - viscosity, velocity V.

Intensive variables:	Extensive variables :

**EXERCISE I.A.4 :**

- a. Prove that these functions are state functions :

1-  $f(x,y) = \frac{x}{x^2+y^2} dx + \frac{y}{x^2+y^2} dy.$

- 2- The pressure P an ideal gas.

- b. If atmospheric air is assumed to be an ideal gas under normal pressure and temperature conditions (T=273,15 K, and P = 1,013 bar )

calculate the coefficient :

1-  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)$

2-  $\beta = \frac{1}{P} \left( \frac{\partial P}{\partial T} \right)$

3-  $\chi = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)$

- 4- Demonstrate the following equality :  $\alpha = P \beta \chi$

**B. THERMODYNAMIC SYSTEMS, EXTERNAL ENVIRONMENT,**  
**POSSIBLE TRANSFERS, TRANSFORMATIONS OF STATE OF A SYSTEM,**  
**CONCEPT OF TEMPERATURE:**

**EXERCISE I.B.1 :**

- 1- Give a definition of the thermodynamic system “open, closed and isolated”
- 2- Select in a table the type of the thermodynamic system “open, closed or isolated” in each case:

Air fryer, solution of NaCl in a thermos flask, a pressure cooker.

A plant, Air inside a car tire, refrigerator, planet earth.

A bottle of orange juice, a calorimeter containing a mixture of water and ice.

Perfume bottle, a care engine, a student in lecture hall.

Open system	Closed system	Isolated system

**EXERCISE I.B.2 :**

Classify the following processes in the table as reversible or irreversible:

- a leak of natural gas.
- mixing of salt in water.
- burning of a paper.
- freezing of water.
- compression of an ideal gas.
- sour milk.
- bomb explosion.
- the mixture of water and small pieces of glass.
- swing without air resistance.

Reversible process:	Irreversible process:

**EXERCISE I.B.3:**

- A-
- 1- Convert the following temperatures to Kelvin and Fahrenheit :
  - 1- Melting point of gold (1064 °C).
  - 2- Boiling point of Nitrogen ( -195,8 °C ).

- 3- Freezing point and evaporation point of pure water.
- B- Find the temperature at which we get the same reading on both Kelvin and Fahrenheit scales.
- C- If you know that the butane  $C_4H_{10}$  gas cylinder pressure is 10 barr , calculate that pressure in atm then Pas and mmHg, and torr .

**C. REMINDER OF IDEAL GAS LAWS:**

**EXERCISE I.C.1 :**

Calculate the value of the ideal gas constant R, knowing that 1 mol of ideal gas occupies a volume of 22,4 l, under normal conditions of temperature and pressure (1 atm and 0°C) by:

- 1- L.atm /K.mol.
- 2- j/ /K.mol.
- 3- l.mm Hg /K.mol.
- 4- Cal/K.mol.

**EXERCISE I.C.2 :**

A- 3,062 g of a gas occupies a volume of 1,224 liters at 10 °C and a pressure of 2 atm, under wich pressure P will 0,436 g of the same gas occupy a volume of 300 ml, at 25 °C. It is assumed that this gas is ideal.

B- A helium gas cylinder has a volume of 4.60 L and a pressure of 150 atm at 23.0°C. How many balloons can be filled if each balloon has a volume of 1.35 L and a pressure of 1.20 atm at 23.0°C?

C- A 0,6 m<sup>3</sup> rigid bottle contains 500g of ethane  $C_2H_6$  1,2 atm and 60°C.

The bottle is cooled to 0°C, calculate the new pressure P.

**EXERCISE I.C.3 :**

The composition of a dry air at sea level is approximately as follows (mass percentage) :

- $N_2 = 75,52 \%$
- $O_2 = 23,15 \%$
- $Ar = 1,28 \%$
- $Co_2 = 0,046 \%$

What will be the partial pressure of each constituent when the total pressure is 1 atm .

Data:  $M_N = 14g$   $M_O = 16g$   $M_{Ar} = 40g$   $M_C = 12g$  .

**SOLUTIONS OF EXERCISES OF CHAPTER I :****A. THE STATES OF MATTER AND STATE FUNCTIONS:****EXERCISE I.A.1:**

1- The physical and chemical changes:

- The physical change:

The material involved is the same before and after the change, and it can be reversed, for example the change in the state of matter.

- The chemical change:

Take place when the composition of a substance is changed, in this case the chemical bonds are broken, and new substances are formed, and cannot be reversed.

2- Select the type of change in each case :

- During digestion, starch is converted into glucose “*chemical change*”.
- Freezing of water “*physical change*”.
- Sugar caramelizes when heated “*chemical change*”.
- Phosphorus burns in air “*chemical change*”.
- Casting silver in a mold “*physical change*”.
- Rusting of iron “*chemical change*”.
- Crumpling a sheet of aluminum foil “*physical change*”.
- Digesting food “*chemical change*”.

**EXERCISE I.A.2:**

1- What is the freezing and melting point?

- The freezing point:

Is the temperature at which the liquid is converted to solid.

- The melting point:

Is the temperature at which the solid is converted to liquid.

2- What is the condensation process?

The condensation:

Is the change of state from a gas to a liquid.

3- Find the type of process when the matter changes its state from gas to solid?

The process when the matter changes its state from gas to solid is called “deposition process”

4- What is the process in the formation of ice? and formation of clouds?

The process in the formation of ice is freezing.

The process in the formation of clouds is condensation.

### **EXERCISE I.A.3:**

1. Define the extensive and intensive state variables, using some examples:

- The intensive state variables: are independent of the amount of substance (n)  
example: P, T, and Density...
- The extensive state variables: are dependent of the amount of substance (n)  
example: V, m, n...

2. Classify in the table:

The temperature T, the volume V, the density D, the pressure P, the mass M, the energy E, the moles number n, the internal energy U, viscosity, the velocity V.

Intensive variables:	Extensive variables :
the temperature T	the mass M
the density D	the moles number n
the pressure P	the volume V
viscosity	the energy E
the velocity V	the internal energy U

### **EXERCISE I.A.4:**

A- Prove that these functions are state functions:

$$1- f(x,y) = \frac{x}{x^2+y^2} dx + \frac{y}{x^2+y^2} dy.$$

f(x,y) is a state function if :  $(d/dy (df/dx)_y)_x = (d/dx (df/dy)_x)_y$

$$f(x,y) = \frac{x}{x^2+y^2} dx + \frac{y}{x^2+y^2} dy = (df/dx)_y dx + (df/dy)_x dy$$

$$(d/dy (df/dx)_y)_x = d/dy (x/x^2+y^2)_x = x d/dy (x^2+y^2)^{-1} = -2 xy/(x^2+y^2)^2$$

$$(d/dx (df/dy)_x)_y = d/dx (y/x^2+y^2)_y = x d/dx (x^2+y^2)^{-1} = -2 xy/(x^2+y^2)^2$$

We find that the equality is true:

$$(d/dy (df/dx)_y)_x = (d/dx (df/dy)_x)_y$$

so the function  $f$  is a state function.

2- The function of pressure  $P$  of an ideal gas:  $P = nRT/V$ .

$P(V,T)$  is a state function if :

$$(d/dT (dP/dV)_T)_V = (d/dV (dP/dT)_V)_T.$$

$$(d/dT (dP/dV)_T)_V = d/dT (-nRTV^{-2})_V = -nR/V^2 .$$

$$\text{And } (d/dV (dP/dT)_V)_T = d/dV (nR/V)_T = -nR/V^2 .$$

The equality is true so the pressure  $P$  of an ideal gas is a state function.

B- Calculate the coefficient:

$$1- \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right) \text{ with } PV=nRT \text{ so } V=nRT/P$$

$$\alpha = \frac{1}{V} \left( \frac{\partial nRT/P}{\partial T} \right) = nR/PV = 1/T = 1/ 273,15K = 3,66 \cdot 10^{-3} \text{ K}^{-1} .$$

$$2- \beta = \frac{1}{P} \left( \frac{\partial P}{\partial T} \right) = 1/P (d/dT(nRT/V)) = nR/PV \\ = 1/T = 3,66 \cdot 10^{-3} \text{ K}^{-1} .$$

$$3- \chi = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right) = -1/V(d/dP(nRT/P)) = -1/V(-nRT/P^2) \\ = nRT/P(PV) = 1/P = 1/ 1,013 = 0,987 \text{ bar}^{-1} .$$

4- Demonstrate the following equality :  $\alpha = P \beta \chi$

$$\alpha = P (1/T) (1/P) = 1/T \text{ so this equality is true .}$$

## **B. THERMODYNAMIC SYSTEMS, EXTERNAL ENVIRONMENT,**

### **POSSIBLE TRANSFERS, TRANSFORMATIONS OF STATE OF A SYSTEM:**

#### **EXERCISE I.B.1:**

1- Give a definition of the thermodynamic system “open, closed and isolated”

- Open system:

Can exchange both matter and energy.

- Closed system:

Exchange energy, and not matter.

- Isolated system:

Cannot exchange either matter or energy.

2- Select in a table the type of the thermodynamic system “open, closed or isolated” in each case:

Air fryer, solution of NaCl in a thermos flask, a pressure cooker,

a plant, Air inside a car tire, refrigerator, planet earth,  
 a bottle of orange juice, a calorimeter containing a mixture of water and ice ,  
 perfume bottle, a care engine, student in lecture hall.

Open system	Closed system	Isolated system
- a plant.	- Air fryer.	- solution of NaCl
- planet earth.	- a pressure cooker.	- in a thermos flask.
- a care engine.	- air inside a car tire.	- a calorimeter
- a student in lecture hall.	- Refrigerator.	- containing a
	- a bottle of orange juice.	- mixture of water and ice.
	- perfume bottle.	

### **EXERCISE I.B.2:**

Classify the following processes in the table as reversible or irreversible:

- a leak of natural gas.
- mixing of salt in water.
- burning of a paper.
- freezing of water.
- compression of an ideal gas.
- sour milk.
- bomb explosion.
- the mixture of water and small pieces of glass.
- swing without air resistance.

Reversible process:	Irreversible process:
- freezing of water	- a leak of natural gas.
- compression of an ideal gas.	- mixing of salt in water.
- the mixture of water and small pieces of glass.	- burning of a paper.
	- sour milk.
	- bomb explosion.

- swing without air resistance	
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**EXERCISE I.B.3:**

**A-** Convert temperature to Kelvin and Fahrenheit:

$$T_K = T_c + 273,15$$

$$T_F = 1,8 T_c + 32$$

1- Melting point of gold  $T_c = 1064 \text{ }^\circ\text{C}$ :

$$T_K = 1064 + 273,15 = 1337,15 \text{ K.}$$

$$T_F = 1,8 (1064) + 32 = 1947,2 \text{ F.}$$

2- Boiling point of nitrogen  $T_c = -195,8 \text{ }^\circ\text{C}$ :

$$T_K = -195,8 + 273,15 = 77,35 \text{ K.}$$

$$T_F = 1,8(-195,8) + 32 = -320,44 \text{ F.}$$

3- Freezing point and evaporation point of pure water:

- Freezing point  $T_c = 0 \text{ }^\circ\text{C}$ :

$$T_K = 0 + 273,15 = 273,15 \text{ K.}$$

$$T_F = 1,8 (0) + 32 = 32 \text{ F.}$$

- Evaporation point  $T_c = 100 \text{ }^\circ\text{C}$ :

$$T_K = 100 + 273,15 = 373,15 \text{ K.}$$

$$T_F = 1,8 (100) + 32 = 212 \text{ F.}$$

**B-** Find the temperature at which we get the same reading on both Kelvin and Fahrenheit scales:

To find this temperature we put  $T_K = T_F$  so:

$$T_c + 273,15 = 1,8 (T_c) + 32$$

After solving the equation, we get the following result:

the temperature at which  $T_K=T_F$  is  $T_c= 301,437\text{ }^\circ\text{C}$ .

**C-** Calculate the pressure:

“1 atm=1,013  $10^5$  Pa = 1,013 bar =760 mmHg =760 torr”

$P = 10\text{ bar} = 10/1,013 = 9,87\text{ atm}$

=7501,2 mmHg

=7501,2 torr

=  $10^6$  Pa

### **C. REMINDER OF IDEAL GAS LAWS :**

#### **EXERCISE I.C.1:**

Calculate the constant R:

The ideal gases law is:  $PV= nRT$

so  $R= (PV/nT) = 1\text{atm} (22,4\text{L})/1\text{mol}(273,15\text{K}) = 0,082\text{ l.atm /K.mol}$ .

$R= 1 \times 1,013 \times 10^5\text{ Pa} (22,4 \times 10^{-3}\text{ m}^3) / 1\text{mol} (273,15\text{K}) = 8,314\text{ j/K.mol}$ .

$R= 760\text{ mmHg} (22,4\text{L})/1\text{mol} (273,15\text{K}) = 62,36\text{ l.mmHg/K.mol}$ .

1 cal=4,186j we find  $R=1,98\text{ cal/ K.mol}$ .

#### **EXERCISE I.C.2:**

**A-** Calculate the pressure  $P_2$  :

Data:  $m_1=3,062\text{g}$   $m_2=0,435\text{g}$

$V_1=1,224\text{L}$   $\rightarrow$   $V_2=0,3\text{L}$

$T_1= 283,15\text{K}$   $T_2=298,15\text{K}$

$P_1= 2\text{ atm}$   $P_2= \dots?$

For ideal gas :  $PV=nRT$

$P_1V_1=nRT_1$   $\rightarrow$   $P_1V_1=(m_1/M)RT_1$  (1) with  $n=m/M$

$P_2V_2=nRT_2$   $P_2V_2=(m_2/M)RT_2$  (2)

Dividing the first equation by the second:

$(P_1V_1)/ P_2V_2 = (m_1/m_2) \times (T_1/T_2)$

$P_2= (V_1/V_2) \times (m_2/m_1) \times (T_2/T_1) \times P_1$  we find :  $P_2= 1.22\text{ atm}$  .

**B-** Calculate the number of balloons:

$V_1= 4,6\text{ L}$   $V_2= ?$

$T_1= 23\text{ }^\circ\text{C}$   $\rightarrow$   $T_2=23\text{ }^\circ\text{C}$

$$P_1 = 150 \text{ atm}$$

$$P_2 = 1,2 \text{ atm}$$

The temperature is constant so  $P_1 V_1 = P_2 V_2$  *Boyl-Mariotte* law

$$V_2 = (P_1 V_1) / P_2 = (150 \times 4,6) / 1,2 = 575 \text{ L}$$

Number of balloons =  $V_2 / V_{\text{balloon}} = 575 / 1,35 = 426$  balloon.

**C-** Calculate the new pressure  $P_2$ :

$$V_1 = 0,6 \text{ m}^3$$

$$V_1 = 0,6 \text{ m}^3$$

$$T_1 = 333,15 \text{ K}$$

→

$$T_2 = 273,15 \text{ K}$$

$$P_1 = 1,2 \text{ atm}$$

$$P_2 = \dots ?$$

The volume  $V$  is constant so:  $(P_1/P_2) = (T_1/T_2)$  *Gay-Lussac* Law

$$P_2 = (P_1 T_2) / T_1 = (1,2 \times 273,15) / 333,15 = 0,984 \text{ atm}$$

### **EXERCISE I.C.3:**

Calculate the partial pressure of each constituent:

- First we must calculate the amount of substance :

$$n = m/M$$

$$n_{N_2} = m_{N_2} / M_{N_2} = 75,52 / 28 = 2,7 \text{ mol.}$$

$$n_{O_2} = m_{O_2} / M_{O_2} = 23,15 / 32 = 0,723 \text{ mol.}$$

$$n_{Ar} = m_{Ar} / M_{Ar} = 1,28 / 40 = 0,032 \text{ mol.}$$

$$n_{CO_2} = m_{CO_2} / M_{CO_2} = 0,046 / 44 = 0,001 \text{ mol.}$$

- Calculate the mol fractions :

$$X_i = n_i / n_t \text{ with } n_t = \sum n_i = 3,456 \text{ mol}$$

$$X_{N_2} = n_{N_2} / n_t = 2,7 / 3,456 = 0,782.$$

$$X_{O_2} = n_{O_2} / n_t = 0,723 / 3,456 = 0,209.$$

$$X_{Ar} = n_{Ar} / n_t = 0,032 / 3,456 = 0,0093.$$

$$X_{CO_2} = n_{CO_2} / n_t = 0,001 / 3,456 = 0,0003.$$

- Partial pressure  $P_i$  :

$$P_i = X_i \times P_T \text{ with } P_T = 1 \text{ atm.}$$

$$P_{N_2} = X_{N_2} / P_T = 0,782 / 1 = 0,782 \text{ atm.}$$

$$P_{O_2} = X_{O_2} / P_T = 0,209 / 1 = 0,209 \text{ atm.}$$

$$P_{Ar} = X_{Ar} / P_T = 0,0093 / 1 = 0,0093 \text{ atm.}$$

$$P_{CO_2} = X_{CO_2} / P_T = 0,0003 / 1 = 0,0003 \text{ atm.}$$

**CHAPTER II: THE CONCEPT OF HEAT AND WORK:****LEARNING OBJECTIVES:**

The learning objectives of second chapter “the concept of heat and work” involve understanding:

- Knowing the concept of heat or heat quantity Q.
- Knowing the different forms of energy transfer (work and heat).
- Learn the difference between Heat capacity, and Specific heat as: specific heat at constant volume,  $C_v$  and specific heat at constant pressure,  $C_p$ .
- Calculate the equilibrium temperature between two mixed substances in a system.
- Get to know the Latent heat.
- Understanding the process of Calorimetry.
- Knowing the work W, for a reversible and irreversible process.
- Learn to draw a Clapeyron diagram.

**EXERCISES OF CHAPTER II:****A. THE CONCEPT OF HEAT:****EXERCISE II.A.1:**

A mole of diode is heated from 300K to 500K under the pressure of one atmosphere.

Calculate the amount of heat Q, knowing that:

$$C_p(\text{I2, solide}) = 5,4 \text{ cal. mol}^{-1}\text{K}^{-1}$$

$$C_p(\text{I2, liquide}) = 19,5 \text{ cal. mol}^{-1}\text{K}^{-1}$$

$$C_p(\text{I2, gaz}) = 9,0 \text{ cal. mol}^{-1}\text{K}^{-1}$$

The molar enthalpies of changing state (latent heats):

$$\Delta H^\circ_{\text{vaporisation, 457 K}} = L_v = 6,10 \text{ kcal.mol}^{-1}$$

$$\Delta H^\circ_{\text{fusion, 387 K}} = L_f = 3,74 \text{ kcal.mol}^{-1}$$

**EXERCISE II.A.2:**

A mole of  $\text{N}_2$  (g), considered as an ideal gas, is raised from 20°C to 100°.

Calculate the amount of heat (Q) received by this system in the following two cases:

- a- when the process is isochoric
- b- when the process is isobaric.

Data:  $C_{p(N_2, g)} = 29,08 \text{ J. mol}^{-1} .\text{K}^{-1}$  and  $R = 8,31 \text{ J. mol}^{-1} .\text{K}^{-1}$

## **B. THE CALORIMETRY :**

### **EXERCISE II.B.1:**

In an experiment, a student introduced a quantity of hot water “ $T_2 = 90^\circ\text{C}$ ” to a calorimeter that contained cold water “ $T_1 = 10^\circ\text{C}$ ”.

As a result, the temperature and the mass of this mixture were:  $m=90\text{g}$  water and  $T_f = 50^\circ\text{C}$ .

Deduce the mass of both hot and cold water.

Data :  $C_{p(H_2O,L)} = 75 \text{ J/K.mol}$ .  $C_{cal} = 338 \text{ j/K}$ .

### **EXERCISE II.B.2:**

A calorimeter contains a mass  $m_1= 350\text{g}$  of water at a initial temperature  $T_1= 23^\circ\text{C}$  , an ice cube with a mass  $m_2 = 45\text{g}$  with a temperature  $T_2 = 0^\circ\text{C}$  is placed inside the calorimeter, the final temperature is  $T_f=15^\circ\text{C}$

- 1- Deduce the Heat capacity of calorimeter  $C_{cal}$ .
- 2- Calculate the water equivalent of the calorimeter  $M_{cal}$ .

Data:  $C_{p(H_2O,l)} = 4190 \text{ J/K.Kg}$  ; and  $L_{fusion}= 3,35 \times 10^5 \text{ J/Kg}$ .

## **C. THE WORK :**

### **EXERCISE II.C.1:**

A mole of an ideal gas is irreversibly compressed, at a constant temperature of  $25^\circ\text{C}$ , from 1 to 10 atm, calculate:

- 1- The minimum work ( $W_{irr}$ ) thus involved.
- 2- The work ( $W_{rev}$ ) wich for the inverse transformation, would be involved under ideal conditions of reversibility.

Present the work in both cases on the Clapeyron diagram  $P = f(V)$ .

### **EXERCISE II.C.2:**

The volume of a quantity of Nitrogen is expanded 4 times and provides a work of  $- 600$  Joules against a constant external pressure equal to the final pressure of the gas.

Find the initial pressure of this gas if the heat received by the gas in this process is 1350 Joules

Data:  $V_{initial} = 10^{-3} \text{ m}^3$  ,  $R= 8.31 \text{ J/K.mol}$  ,  $C_p= 29,08 \text{ J/K.mol}$

### **EXERCISE II.C.3:**

Consider 1.2 moles of an ideal gas in a piston at 298 K and 0.2 MPa and at volume  $V_1$ , this gas is :

- a- expanded isothermally to twice its original volume,
- b- cooled isobarically to  $V_1$ .
- c- heated at constant volume back to  $T_1$ .

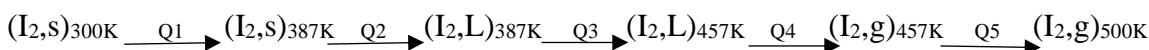
Demonstrate that the net work is non-zero, and that the work depends on the path and is not a state function.

## SOLUTIONS OF EXERCISES OF CHAPTER II:

### A. THE CONCEPT OF HEAT:

#### EXERCISE II.A.1:

Calculate the amount of heat  $Q$  of iode:



The amount of heat  $Q_T$  of iode :  $Q_T = \sum Q_i$

$$Q_1 = nC_{p,s}(\Delta T) = 1 \times 5,4 (387-300) = 0,469 \text{ K cal.}$$

$$Q_2 = nL_f = 1 \times 3,74 = 3,74 \text{ K cal.}$$

$$Q_3 = nC_{p,L}(\Delta T) = 1 \times 19,5 (457-387) = 1,365 \text{ K cal.}$$

$$Q_4 = nL_v = 1 \times 6,10 = 6,10 \text{ K cal.}$$

$$Q_5 = nC_{p,g}(\Delta T) = 1 \times 5,4 (387-300) = 0,469 \text{ K cal.}$$

$$Q_T = \sum Q_i = 12,062 \text{ K cal.}$$

#### EXERCISE II.A.2:

Calculate the amount of heat ( $Q$ ) received by the system:

- a- When the process is isochoric: Volume is constant so  $Q = Q_v = nC_v \Delta T$

$$\text{With: } C_p - C_v = R \text{ so } C_v = C_p - R = (29,08 - 8,31) = 20,77 \text{ j/K.mol.}$$

$$\text{So } Q_v = 1 \times 20,77 (100-20) = 1661,6 \text{ j} = \Delta U \text{ " the internal energy" .}$$

- b- when the process is isobaric: Pressure is constant so  $Q = Q_p = nC_p \Delta T$

$$Q_p = 1 \times 29,08 (100-20) = 2326,4 \text{ j} = \Delta H \text{ " enthalpy" .}$$

### B. THE CALORIMETRY :

#### EXERCISE II.B.1:

In the calorimeter, the system is isolated :  $\sum Q_i = 0$  .

$$Q_1 + Q_2 + Q_{cal} = 0 \text{ so : } n_1 C_{p,H_2O(L)} (T_f - T_1) + n_2 C_{p,H_2O(L)} (T_f - T_2) + C_{cal} (T_f - T_1) = 0$$

With the amount of substance is:

$$n_T = m_T / M_{H_2O} = 90/18 = 5 \text{ mol. } n_1 + n_2 = 5 \text{ mol.}$$

From the previous equation:

$$n_1 C_{pH_2O(L)} (T_f - T_1) + (5 - n_1) C_{pH_2O(L)} (T_f - T_2) + C_{cal} (T_f - T_1) = 0$$

$$n_1 75 (50 - 10) + (5 - n_1) 75 (50 - 90) + 338 (50 - 10) = 0$$

After solving the previous equation:

$$n_1 = 0,25 \text{ mol and } n_2 = 5 - n_1 = 4,75 \text{ mol.}$$

The mass of cold water:

$$m_1 = n_1 \times M_{H_2O} = 0,25 \times 18 = 4,5 \text{ g}$$

The mass of hot water:

$$m_2 = n_2 \times M_{H_2O} = 4,75 \times 18 = 85,5 \text{ g}$$

### **EXERCISE II.B.2:**

1- Deduce the Heat capacity of calorimeter  $C_{cal}$ .

In the calorimeter, the system is isolated:  $\sum Q_i = 0$ .

$Q_{water} + Q_{cal} + Q_{ice} + Q_{fusion} = 0$  so:

$$m_1 C_{pH_2O(L)} (T_f - T_1) + C_{cal} (T_f - T_1) + m_2 C_{pH_2O(L)} (T_f - T_2) + m_2 \times L_{fusion} = 0$$

$$C_{cal} = - [m_1 C_{pH_2O(L)} (T_f - T_1) + m_2 C_{pH_2O(L)} (T_f - T_2) + m_2 \times L_{fusion}] / (T_f - T_1)$$

$$= [m_1 C_{pH_2O(L)} (T_f - T_1) + m_2 C_{pH_2O(L)} (T_f - T_2) + m_2 \times L_{fusion}] / (T_1 - T_f)$$

$$= [0,35 \times 4190 (-8) + 0,045 \times 4190 (15) + 0,045 (3,35 \times 10^5)] / (8)$$

Finally:  $C_{cal} = 799,75 \text{ J/K.}$

2- Calculate the water equivalent of the calorimeter  $M_{cal}$ :

$$C_{cal} = M_{cal} \times C_{pH_2O(L)} \text{ so: } M_{cal} = C_{cal} / C_{pH_2O(L)}$$

$$M_{cal} = (799,75 \text{ J/K}) / (4190 \text{ J/K.Kg}) = 0,191 \text{ Kg.}$$

so the water equivalent of the calorimeter  $M_{cal}$  is 0,191 Kg.

### **C. THE WORK :**

#### **EXERCISE II.C.1:**

$$P_1 = 1 \text{ atm}$$

$$P_2 = 10 \text{ atm}$$

$$T_1 = 25^\circ \text{C}$$

→

$$T_2 = 25^\circ \text{C}$$

$$V_1 = \dots ?$$

$$V_2 = \dots ?$$

1- Calculate the minimum work ( $W_{irr}$ ) thus involved:

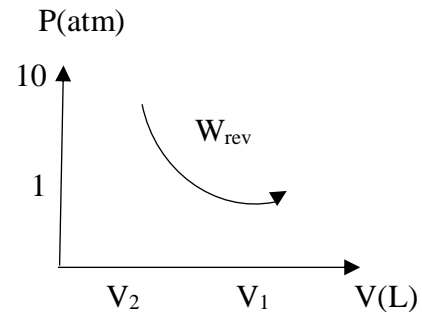
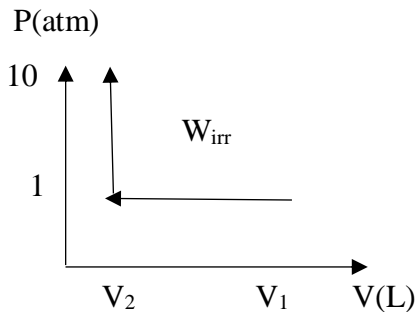
$$W_{\text{irr}} = -P_{\text{ext}} \int dV = -P_2 (V_2 - V_1) = -P_2 (nRT/P_2 - nRT/P_1) = -P_2 nRT (1/P_2 - 1/P_1) = -10 (1,013 \times 10^5) (8,314) (298) [1/10(1,013 \times 10^5) - 1/(1,013 \times 10^5)] \text{ so } W_{\text{irr}} = 22298 \text{ J.}$$

2- Calculate the work ( $W_{\text{rev}}$ ) which for the inverse transformation:

$$W_{\text{rev}} = \int -P_{\text{ext}} dV = \int (-nRT/V) dV = -nRT \ln (V_1/V_2) \\ = -nRT \ln (P_2/P_1) \text{ so } W_{\text{rev}} = -5705 \text{ J } W_{\text{rev}} < 0$$

The negative value of  $W_{\text{rev}}$  which is consistent with expansion 'the gas provides work to the outside'.

3- Clapeyron diagram  $P=f(V)$ :



### EXERCISE II.C.2:

Calculate the initial pressure of nitrogen ( $N_2$ ) gas :

The constant external pressure equal to the final pressure of the gas so this process is irreversible.

With  $W = -600 \text{ J}$  and  $Q = 1350 \text{ J}$ ,  $V_i = 10^{-3} \text{ m}^3$  and  $V_f = 4V_i$ .

$$W_{\text{irrev}} = -P_f (V_f - V_i) = -P_f (4V_i - V_i) = -3P_f V_i$$

the final pressure

$$P_f = -W_{\text{irrev}} / 3V_i = -(-600) / (3 \times 10^{-3}) = 2 \times 10^5 \text{ Pa} = 2 \text{ bar.}$$

$$P_f V_f = nRT_f \quad (1)$$

$$P_i V_i = nRT_i \quad (2)$$

After subtracting the second equation from the first, we find:

$$P_f V_f - P_i V_i = nR (T_f - T_i)$$

$$P_i = (4P_f V_i - nR (T_f - T_i)) / V_i \text{ with:}$$

$$n (T_f - T_i) = Q / C_p$$

$$P_i = 4P_f - (RQ) / (C_p V_i) = 4 \times 2 \times 10^5 - 8,31 \times 1350 / (29,08 \times 10^{-3}) \\ = 4,1 \times 10^5 \text{ Pa} = 4 \text{ bar.}$$

**EXERCISE II.C.3:**

Demonstrate that the net work is non-zero, and that the work depends on the path and is not a state function:

First we must calculate the initial volume  $V_i$ :

$$P_i V_i = nRT \text{ so } V_i = nRT/P = 1,2(8,31) (298)/0,2 \times 10^6 = 0,0148 \text{ m}^3 .$$

A- Isothermally expand:

$$W_1 = -\int P dV = -nRT \ln(V_2/V_1) = -1,2(8,314)(298) \ln 2 = -2060 \text{ J}.$$

B- Isobarically cool down to  $V_1$ :

$$W_2 = -\int P dV = -P_2(V_1 - V_2) = -0,1 \times 10^6 (-14,865 \times 10^{-3}) = 1487 \text{ J}.$$

$P_2$  is calculated from first process "isothermally expand"

$$P_1 V_1 = P_2 V_2 \text{ so: } P_2 = (P_1 \times V_1)/V_2 = (P_1 \times V_1)/ 2V_1 = P_1/2 = (0,2 \text{ Mpa}) /2 = 0,1 \text{ Mpa}.$$

C- heated at constant volume back to  $T_1$ :

$$W_3 = -\int P dV = 0.$$

We have returned the system to its original state :

$$W_T = \sum W_i = W_1 + W_2 + W_3 = -573 \text{ J}.$$

➤ We conclude that the work "W" is a path function, not a state function.

**CHAPTER III: THE FIRST PRINCIPLE OF THERMODYNAMICS:****LEARNING OBJECTIVES:**

The learning objectives of third chapter “the first principle of thermodynamics” involve understanding:

- Equivalence between Heat and Work.
- Statement of the First Law of Thermodynamics.
- Definition of Internal Energy (U).
- Calculation of the Change in Internal Energy  $\Delta U$ .
- Joule's Law: Change in Internal Energy of an Ideal Gas.
- Relationship Between  $Q_P$  and  $Q_V$ .
- Concept of Enthalpy (H).
- Second Law of Joule: Variation of Enthalpy of Ideal Gases.

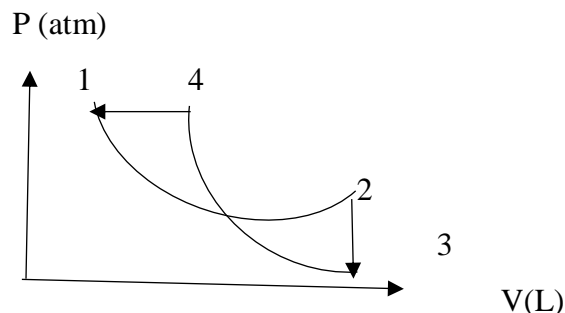
**EXERCISES OF CHAPTER III:****A. THE FIRST PRINCIPLE AND THE INTERNAL ENERGY:****EXERCISE III.A.1:**

Consider  $O_{2(g)}$  as an ideal gas occupying a volume of 8 liters at  $27^\circ C$  under 1 atmosphere.

- 1- This gas is compressed isothermally to a volume of 5 liters, calculate:
  - The pressure  $P_2$ .
  - The amount of heat  $Q$ .
  - The work  $W$ .
  - The internal energy  $\Delta U$ .
- 2- This gas from its initial state is compressed reversibly and adiabatically to a volume of 5 liters, calculate:
  - The pressure  $P_2$ .
  - The temperature  $T_2$ .
  - The amount of heat  $Q$ .
  - The work  $W$ .
  - The internal energy  $\Delta U$ .

**EXERCISE III.A.2:**

The Clapeyron diagram represent the series of reversibles transformations of an ideal gas with the data recorded in the table :



	P (atm)	V (L)	T (K)
1	10	1	600
2	2	5	600
3	1	5	300
4	10	1,25	750

with:  $C_v = 3,03 \text{ cal/K.mol}$ .

- Calculate the amount of substance n.
- Identify the type of transformation in each case.
- Complete the table:

	W (cal)	Q(cal)	$\Delta U(\text{cal})$
1→2	....	....	.....
2→3	....	....	....
3→4	....	....	....
4→1	....	....	....

**B. THE CONCEPT OF ENTHALPY :****EXERCISE III.B.1:**

Consider  $\text{Cl}_{2(g)}$  as an ideal with:  $V=10\text{L}$  and  $T=25^\circ\text{C}$  and  $P=1$  atmosphere.

This gas is transformed isobarically to a volume  $V= 4\text{L}$  deduce:

- The temperatue T2.
- The amount of heat Q.

- The work  $W$ .
- The internal energy  $\Delta U$ .
- The change in enthalpy  $\Delta H$ .

**EXERCISE III.B.2:**

(1/8,32) mol of an diatomic ideal gas, initially at a temperature of 200 K, It undergoes several transformations :

- ❖ A-B: isochoric heating from  $T_A$  to  $T_B=2T_A$  .
- ❖ B-C: isothermal expansion with an increase in gas heat of 230 joules
- ❖ C-A: isobaric compression

The net work done during this thermodynamic cycle is : -30 joul.

1- Calculate for each process :

the work  $W$ , and the mount of heat  $Q$ , the internal energy  $\Delta U$ , the enthalpy  $\Delta H$ .

2- Is the isothermal transformation B-C reversible? justify your answer.

**EXERCISE III.B.3:**

An ideal gas initially in state A ( $T_A=293K$ ,  $P_A=1$  atm,  $V_A=12$  L) with  $C_v=3R$ , undergoes the following transformations:

- a- reversible adiabatic compression up to  $T_B = 400$  K (state B)
  - b- reversible isothermal compression up to  $V_C = 1$  L (state C)
  - c- reversible adiabatic expansion up to  $T_D = T_A$  (state D)
  - d- reversible isothermal expansion up to state A.
- 1- Calculate the variables:  $P$ ,  $V$ ,  $T$  for all states A, B, C, D.
  - 2- Represent the different transformations on a Clapeyron diagram ( $P,V$ ).
  - 3- Complete the table below:

Process:	Type of process:	$W$ (J) :	$Q$ (J) :	$\Delta U$ (J):	$\Delta H$ (J):
A→B					
B→C					
C→D					
D→A					
Cycle					

**EXERCISE III.B.4 :**

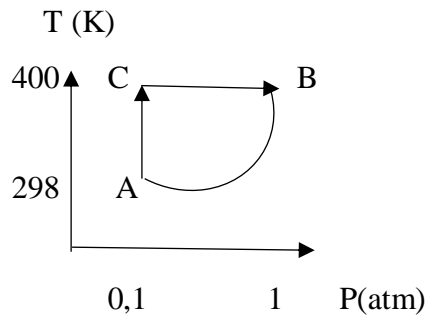
The transformation of 1 mole of ideal gas from an initial (state A) to final (state B) takes place along two paths in the diagram:

Path 1 (A-B): isobaric heating followed by isothermal compression.

Path 2 (A-B): compression to state (C) verifying the equation  $PV^\gamma = \text{constant}$  followed by isobaric cooling.

Calculate for each path the work  $W$ , the amount of heat  $Q$  and the internal energy  $\Delta U$ , and conclude.

$$C_p = 37,69 \text{ J/mol.K} \quad \gamma = 1,283$$

**SOLUTIONS OF EXERCISES OF CHAPTER III:****A. THE FIRST PRINCIPLE AND THE INTERNAL ENERGY:****EXERCISE III.A.1:**

First we must calculate the amount of substance:

$$PV = nRT \text{ so } n = PV/RT \text{ so: } n = 0,325 \text{ mol.}$$

1- This gas is compressed isothermally to a volume of 5 liters:

$$P_1 = 1 \text{ atm, } V_1 = 8 \text{ L, } T_1 = 27^\circ\text{C} = 300 \text{ K, and } V_2 = 5 \text{ L, isothermally so } T_2 = 27^\circ\text{C} = 300 \text{ K.}$$

- The pressure  $P_2$ :

$$P_2 = (nRT_2/V_2) = 1,6 \text{ atm.}$$

- The amount of heat and the work and the internal energy  $\Delta U$ :

This gas is compressed isothermally so

$$\Delta U = nC_v(T_2 - T_1) = 0$$

$$\Delta U = W + Q = 0 \text{ and } W = -nRT \ln(V_2/V_1) = -381 \text{ j}$$

$$\text{And } Q = -W = 381 \text{ j.}$$

2- This gas from its initial state is compressed reversibly and adiabatically to a volume of 5 liters:

- Calculate the pressure  $P_2$  :

$$P_1 V_1^\gamma = P_2 V_2^\gamma \text{ with } \gamma = (C_p/C_v), \text{ this gas is a diatomic gas so}$$

$$C_p = (7/2)R \text{ and } C_v = (5/2)R \text{ finally: } \gamma = (C_p/C_v) = 1,4 \text{ so } P_2 = 1,93 \text{ atm.}$$

- The temperature  $T_2$  :

$$T_2 = (P_2 V_2)/(nR) = 362 \text{ K.}$$

- The amount of heat  $Q$ :

This gas is compressed reversibly and adiabatically ( $Q=0$ ).

- The work  $W$  and the internal energy  $\Delta U$ :

$$\Delta U = Q + W \text{ and } Q = 0 \text{ so } \Delta U = W \text{ and } \Delta U = nC_v(T_2 - T_1) = 419,49 \text{ j.}$$

### EXERCISE III.A.2:

- Calculate the amount of substance  $n$ :

$$PV = nRT \text{ so } n = P_1 V_1 / RT_1 = 0,203 \text{ mol.}$$

- Identify the type of transformation in each case.

- Complete the table:

$$C_v = 3,03 \text{ cal/K.mol and } C_p = C_v + R = 5,03 \text{ cal/K.mol}$$

$$\text{Also } \gamma = C_p/C_v = 1,66$$

		W (cal)	Q(cal)	$\Delta U$ (cal)
1→2	Isothermal Process	$-nRT \ln(V_2/V_1)$ = -392,06 cal	= -W = 392,06 cal	= Q+W = 0
2→3	Isochoric Process	= 0	= $nC_v (T_3 - T_2)$ = - 184,53 cal	= $nC_v (T_3 - T_2)$ = - 184,53 cal
3→4	Adiabatic Process	= $(P_4 V_4 - P_3 V_3)/(\gamma - 1)$ = 272,73 cal	= 0	= $nC_v (T_4 - T_3)$ = W = 272,73 cal
4→1	Isobaric process	= $-P_1(V_1 - V_4)$ = 60,55 cal	= $nC_p (T_1 - T_4)$ = - 153,163 cal	= $nC_p(T_1 - T_4)$ Q+W = -92,61 cal

**A. THE CONCEPT OF ENTHALPY :****EXERCISE III.B.1:**

Consider  $\text{Cl}_{2(g)}$  as an ideal with:  $V=10\text{L}$  and  $T=25^\circ\text{C}$  and  $P=1$  atmosphere.

This gas is transformed isobarically to a volume  $V=4\text{L}$ :

First we must calculate the amount of substance:

$$PV=nRT \text{ so } n=(PV)/(RT) \quad n=0,409 \text{ mol .}$$

- The temperature  $T_2$ :

$$P_2V_2=(nRT_2) \text{ and } T_2= P_2V_2/nR=119,267\text{K.}$$

- The amount of heat  $Q$ :

$$Q=n C_p \times \Delta T \text{ with } C_p = (7/2)R \text{ finally } Q= -20,98 \text{ l.atm} = - 2125,29\text{j.}$$

- The work  $W$ :

$$W= -P_2(V_2-V_1) = 6 \text{ l.atm} = 607,8\text{j.}$$

- The internal energy  $\Delta U$ :

$$\Delta U=Q+W= -1517,5 \text{ j.}$$

- The change in enthalpy  $\Delta H$ :

This gas is transformed isobarically so:

$$\Delta H=Q_p=nC_p \times \Delta T \text{ with } C_p = (7/2)R \text{ finally } \Delta H = -1517,5 \text{ j.}$$

**EXERCISE III.B.2:**

1- Calculate for each process, the work  $W$ , and the amount of heat  $Q$ , the internal energy  $\Delta U$ , the enthalpy  $\Delta H$ :

- Process A-B: isochoric heating from  $T_A$  to  $T_B=2T_A$

Volume is constant so  $W_{A-B}=0$

$$\Delta U_{A-B} = nC_v \Delta T \text{ with } n=1/R \text{ and } C_v=(5/2)R \text{ we find : } \Delta U_{A-B} = n (5/2) R (2T_A-T_A) \\ = 1/R (5/2) R (T_A) = (5/2) T_A = (5/2) 200 = 500\text{j.}$$

$$Q_{A-B} = \Delta U_{A-B} - W_{A-B} = 500-0 = 500\text{j.}$$

$$\Delta H_{A-B} = \Delta U_{A-B} + \Delta(PV) = \Delta U_{A-B} + V(P_2-P_1) = \Delta U_{A-B} + V(nRT_B/V - nRT_A/V)$$

$$= \Delta U_{A-B} + V(2nRT_A/V - nRT_A/V) = \Delta U_{A-B} + nRT_A \text{ with } n=1/R \text{ so: } \Delta H_{A-B}$$

$$= \Delta U_{A-B} + 1/R (R) T_A = \Delta H_{A-B} = \Delta U_{A-B} + T_A = 500+200 = 700\text{j.}$$

- Process B-C: isothermal expansion: the temperature is constant so

$$\Delta U_{B-C} = 0 \text{ j and } \Delta H_{B-C} = 0 \text{ j}$$

$$Q_{B-C} = \Delta U_{B-C} - W_{B-C} = -W_{B-C}$$

increase in heat of system by 230j so  $Q_{B-C} = Q_{A-B} + 230 = 500 + 230 = 730j$ .

and  $W_{B-C} = -Q_{B-C} = -730j$ .

- Process C-A: isobaric compression:

$\Delta U$  and  $\Delta H$  are state functions so:

$$\Delta U_{\text{cycl}} = \Delta H_{\text{cycl}} = 0.$$

$$\Delta U_{C-A} = \Delta U_{\text{cycl}} - \Delta U_{A-B} - \Delta U_{B-C} = 0 - 500 - 0 = -500j.$$

the second method:

$$\Delta U_{C-A} = nC_v \Delta T = 1/R (5/2)R (200 - 400) = -500j.$$

$$\Delta H_{C-A} = \Delta H_{\text{cycl}} - \Delta H_{A-B} - \Delta H_{B-C} = 0 - 700 - 0 = -700j.$$

the second method:

$$\Delta H_{C-A} = nC_p \Delta T = 1/R (7/2)R (200 - 400) = -700j.$$

the net work done during this cycle is (-30 Joule) so  $W_{\text{cycl}} = -30j$

$$W_{C-A} = W_{\text{cycl}} - W_{A-B} - W_{B-C} = -30 - 0 - (-730) = 700j.$$

$$Q_{C-A} = \Delta U_{C-A} - W_{C-A} = -500 - 700 = -1200j.$$

Process:	Q (j)	W (j)	$\Delta U$ (j)	$\Delta H$ (j)
Process A-B:	500	0	500	700
Process B-C:	730	-730	0	0
Process C-A:	-1200	700	-500	-700

- 2- Is the isothermal transformation B-C reversible:

We must calculate the work  $W_{B-C}$  in a reversible way and compare it with that  $W_{B-C}$  in the table  $W_{B-C} = -730j$ .

$W_{B-C \text{ reversible}} = -nRT_B \ln(V_C/V_B) = nRT_B \ln(V_B/V_C)$ , to calculate the value of  $(V_B/V_C)$ :

Process A-B isochoric :  $V_B = V_A$  so:  $V_B/V_C = V_A/V_C$

Process C-A isobaric :  $V_A/V_C = T_A/T_C$

Process B-C isothermal :  $T_A/T_C = T_A/T_B$

Finally  $T_A/T_B = T_A/2T_A = 1/2$  so :  $W_{B-C \text{ reversible}}$

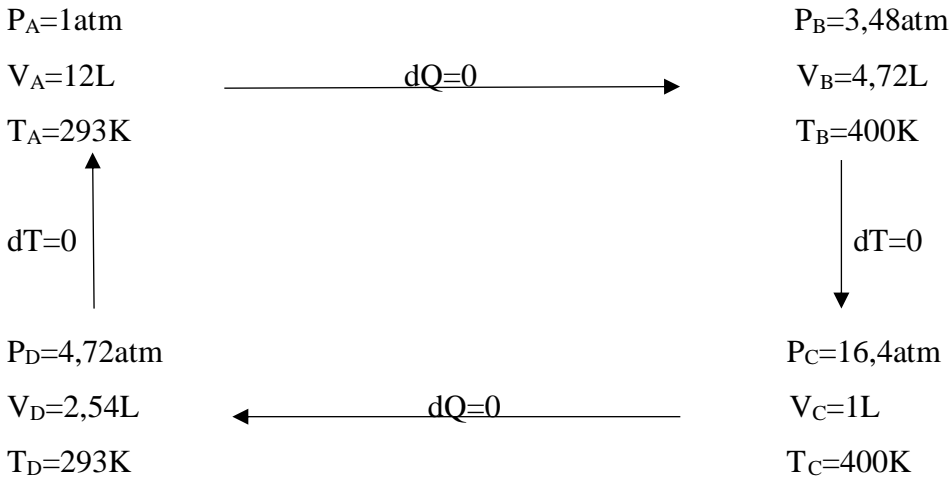
$$= nRT_B \ln(1/2) = (1/R) R(2) (200) \ln 1/2$$

$W_{B-C \text{ reversible}} = -277,26j$ . the value  $W_{B-C \text{ reversible}} = -277,26j \neq W_{B-C \text{ irreversible}} = -730j$

So the process B-C is irreversible.

**EXERCISE III.B.3:**

1- Calculate the variables: P, V, T for all states A, B, C, D:



The amount of substance:  $P_A V_A = n R T_A$  so  $n = P_A V_A / R T_A = 0,5 \text{ mol}$ .

Calculate the variables in each case:

$$T_A V_A^{\gamma-1} = T_B V_B^{\gamma-1} \text{ so } V_B = 4,72 \text{ L.}$$

$$P_B V_B = n R T_B \text{ so } P_B = 3,48 \text{ atm.}$$

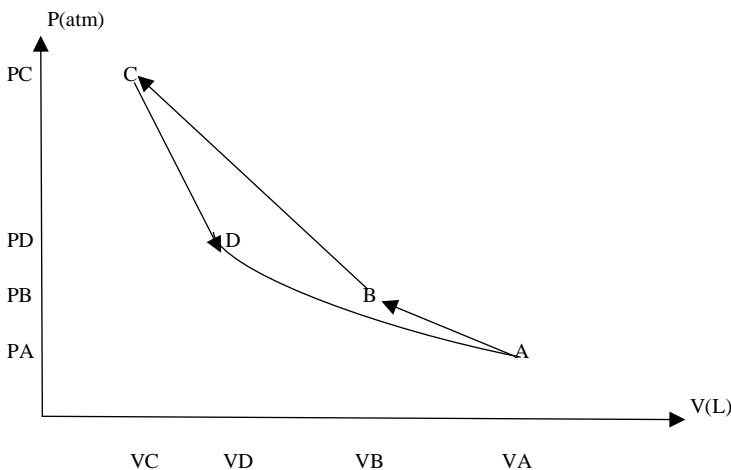
$$P_C V_C = P_B V_B \text{ so } P_C = 16,4 \text{ atm.}$$

$$P_C V_C = n R T_C \text{ so } T_C = 400 \text{ K.}$$

$$T_C V_C^{\gamma-1} = T_D V_D^{\gamma-1} \text{ so } V_D = 2,54 \text{ L.}$$

$$P_D V_D = n R T_D \text{ so } P_D = 4,72 \text{ atm.}$$

2- Represent the different transformations on a Clapeyron diagram (P,V)



3- Complete the table below:

Process A-B: adiabatic so  $Q=0$  so  $W=\Delta U = nC_v(T_B-T_A)$  and  $\Delta H = nC_p(T_B-T_A)$ .

Process B-C: isothermal so  $\Delta T=0$   $\Delta U=0$  and  $\Delta H=0$  and  $Q=-W$ , and  $W=-nRT \ln(V_C/V_B)$ .

Process C-D: adiabatic so  $Q=0$  so  $W=\Delta U = nC_v(T_B-T_A)$  and  $\Delta H = nC_p(T_B-T_A)$ .

Process D-A: isothermal so  $\Delta T=0$  ;  $\Delta U=0$  and  $\Delta H=0$  and  $Q=-W$ ,

and  $W = -nRT \ln(V_A/V_D)$

Process:	Type of process:	W (J) :	Q (J) :	$\Delta U$ (J):	$\Delta H$ (J):
A→B	Adiabatic	1334	0	1334	1779
B→C	Isothermal	2580	-2580	0	0
C→D	Adiabatic	-1334	0	-1334	-1779
D→A	Isothermal	-1891	1891	0	0
Cycle		689	-689	0	0

- $\Delta U_{cycl.} = 0$  and  $\Delta H_{cycl.} = 0$  so:  $\Delta U$  and  $\Delta H$  are state functions.
- $Q_{cycl.} \neq 0$  and  $W_{cycl.} \neq 0$  so:  $\Delta U$  and  $\Delta H$  are path functions.

#### **EXERCISE III.B.4 :**

Calculate for each path:

**Path 1 (A-B):** isobaric heating followed by isothermal compression:

$$\begin{array}{ccccc}
 P_1=0.1 \text{ atm} & & P_2=0.1 \text{ atm} & & P_3=1 \text{ atm} \\
 T_1=298 \text{ K} & \xrightarrow{\text{isobar}} & T_2=400 \text{ K} & \xrightarrow{\text{isotherm}} & T_3=400 \text{ K} \\
 V_1=244.36 \text{ L} & & V_2=328 \text{ L} & & V_3=32.8 \text{ L}
 \end{array}$$

$$W_{1-2} = -P(V_2-V_1) = -0.1 \times 1.013 \times 10^5 (328-244.36) \times 10^{-3} = -848 \text{ J.}$$

$$Q_{1-2} = Q_p = n C_p (T_2-T_1) = 37,69 (400-298) = 3844,38 \text{ J.}$$

$$\Delta U_{1-2} = W_{1-2} + Q_{1-2} = -848 \text{ J} + 3844,38 \text{ J} = 2996,38 \text{ J.}$$

$$W_{2-3} = -nRT \ln V_3/V_2 = -8,314 \times 400 \ln (32,8/328) = 7657,48 \text{ J.}$$

$$\Delta U_{2-3} = 0$$

$$Q_{2-3} = \Delta U_{2-3} - W_{2-3} = -W_{2-3} = -7657,48 \text{ J.}$$

$$W_T = W_{1-2} + W_{2-3} = -848 + 7657,48 = 6809,48 \text{ J.}$$

$$Q_T = Q_{1-2} + Q_{2-3} = 3844,38 + (-7657,48) = -3813,10 \text{ J.}$$

$$\Delta U_T = \Delta U_{1-2} + \Delta U_{2-3} = 2996,38 + 0 = 2996,38 \text{ J.}$$

**Path 2 (A-B):** compression to state (C) verifying the equation  $PV^\gamma = \text{constant}$

followed by isobaric cooling:

$$\begin{array}{ccccc}
 P_1=0.1 \text{ atm} & & P_2=1 \text{ atm} & & P_3=1 \text{ atm} \\
 T_1=298 \text{ K} & \xrightarrow{\text{adiabatic}} & T_2=495,28 \text{ K} & \xrightarrow{\text{isobar}} & T_3=400 \text{ K} \\
 V_1=244,38 \text{ L} & & V_2=40,61 \text{ L} & & V_3=32,8 \text{ L}
 \end{array}$$

$$P_1 V_1^\gamma = P_2 V_2^\gamma \text{ so } V_2 = (P_1/P_2) V_1^{1/\gamma} = 244,38,38(0,1)^{1/1,283} = 40,61 \text{ L.}$$

$$P_2 V_2 = nRT_2 \text{ so } T_2 = P_2 V_2 / nR = 495,28 \text{ K.}$$

$$Q_{1-2} = 0$$

$$\Delta U_{1-2} = Q_{1-2} + W_{1-2} = W_{1-2} = nC_v (T_2 - T_1) = 5795,44 \text{ J. with } C_v = C_p / \gamma = 29,37 \text{ J/K.mol.}$$

$$W_{2-3} = -P_3(V_3 - V_2) = 791,86 \text{ J.}$$

$$Q_{2-3} = Q_p = nC_p(T_3 - T_2) = -3591,1 \text{ J.}$$

$$\Delta U_{2-3} = W_{2-3} + Q_{2-3} = 791,86 - 3591,1 = -2799,24 \text{ J.}$$

$$W_T = W_{1-2} + W_{2-3} = 6587,31 \text{ J.}$$

$$Q_T = Q_{1-2} + Q_{2-3} = -3591,1 \text{ J.}$$

$$\Delta U_T = \Delta U_{1-2} + \Delta U_{2-3} = 2996,38 \text{ J.}$$

Conclusion:  $W_T$  and  $Q_T$  have different values depending on the path 1 or 2, so  $W$  and  $Q$  are path functions.

$\Delta U_T$  has the same value according to the two paths 1 or 2, so  $\Delta U$  is a state function, only depend on the initial state and the final state and not on the path followed.

**CHAPTER IV: APPLICATION OF THE FIRST PRINCIPLE OF  
THERMODYNAMICS TO THERMOCHEMISTRY:**

**LEARNING OBJECTIVES:**

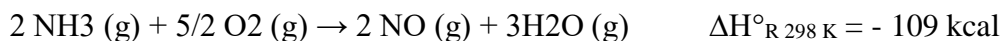
The learning objectives of fourth chapter “Application of the first principle of thermodynamics to thermochemistry” involve understanding:

- Knowing the concept of heat of formation.
- Knowing the standard state.
- Learn the difference between enthalpy of formation and enthalpy of dissociation.
- Knowing the enthalpy of change of physical state.
- Understanding the concept of enthalpy of chemical reaction.

**EXERCISES OF CHAPTER IV:**

**A. STANDARD ENTHALPY OF FORMATION:**

**EXERCISE IV.A.1:**



Calculate the standard enthalpy of formation of  $\text{NH}_3(\text{g})$ .

$$\Delta H_{\text{f } 298 \text{ K NO}(\text{g})} = 21,5 \text{ kcal} ; \Delta H_{\text{f } 298 \text{ K H}_2\text{O}(\text{g})} = -58,0 \text{ kcal.}$$

**EXERCISE IV.A.2:**

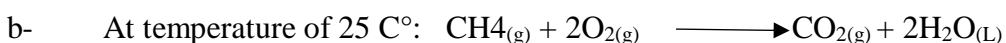
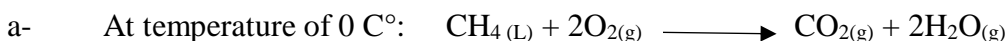
Knowing that the combustion of 1,2 g of acetic acid  $\text{C}_2\text{H}_4\text{O}_2$  under constant pressure  $10^5$  Pa in a calorimetric bomb immersed in a container containing 20 kg of water at  $T_i = 298\text{K}$ , after reaction the temperature of water in this container increased by 0,209 K.

- Calculate the enthalpy of formation of acetic acid

$$\Delta H_{\text{f CO}_2(\text{g})} = -393,5 \text{ KJ/mol} ; \Delta H_{\text{f H}_2\text{O}(\text{l})} = -285,8 \text{ KJ/mol} ; C_{\text{H}_2\text{O}(\text{l})} = 1 \text{ cal/g} .$$

**EXERCISE IV.A.3:**

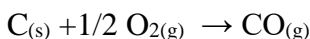
Calculate the difference between the heat of combustion at constant volume and the heat of combustion at constant pressure in the following two cases:



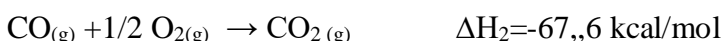
**B. THE ENTHALPY OF CHEMICAL REACTION, ENTHALPY OF DISSOCIATION, THE ENTHALPY OF CHANGE OF PHYSICAL STATE:**

**EXERCISE IV.B.1:**

Determine the change in the enthalpy for the following reaction:



If you know:



**EXERCISE IV.B.2:**

Calculate the enthalpy of reaction  $\Delta H_R$ :



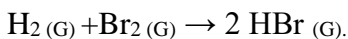
Knowing that:  $\Delta H_{f \text{H}_2\text{O}(g)} = -285,84 \text{ kJ/mol}$  ;  $\Delta H_{f \text{CO}_2(g)} = -393,51 \text{ kJ/mol}$

$$\Delta H_{\text{com CH}_4(g)} = -890,35 \text{ kJ/mol} ; \Delta H_{\text{com C}_2\text{H}_6(g)} = -1559,88 \text{ kJ/mol}$$

**EXERCISE IV.B.3:**

The mixture  $\text{H}_2(g) + \text{Br}_2(g)$  is reacted at constant pressure 1 atm and  $63^\circ\text{C}$ .

Calculate under these conditions, the enthalpy of the reaction :



$$\Delta H_{f \text{HBr}(g)} = -36,2 \text{ kJ/mol (at 298 K)}$$

$$\Delta H_{\text{vap Br}_2} = 29,3 \text{ kJ/mol (at 336 K)}$$

Compound :	HBr (g)	H <sub>2</sub> (g)	Br <sub>2</sub> (l)
Cp: J/mol .K	27,8	28,5	71,6

**EXERCISE IV.B.4:**

Determine at  $25^\circ\text{C}$  and  $500^\circ\text{C}$  the heat of formation of methane  $\text{CH}_4$ .

Deduce the internal energy of formation of methane  $\Delta U_{f \text{CH}_4(g)}$  at  $500^\circ\text{C}$ .

Knowing that:



$$C_p \text{C}(s) = 1,1 + 48 \times 10^{-4} T + 12 \times 10^{-7} T^2 \text{ cal/mol. K}$$

$$C_p \text{H}_2(g) = 6,5 + 9 \times 10^{-1} T \text{ cal/mol. K}$$

$$C_p_{\text{CH}_4(\text{g})} = 5,34 + 1140 \times 10^{-4} T \text{ cal/mol. K}$$

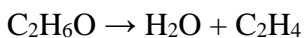
**EXERCISE IV.B.5:**

Calculate the bond energy (C-H) and (C-C) and (C=C) and (C≡C) using the following if you know the enthalpy of formation of:

$$\begin{aligned} \text{CH}_4 &= -74,85 \text{ KJ/mol} & \text{C}_2\text{H}_6 &= -84,67 \text{ KJ/mol} \\ \text{C}_2\text{H}_4 &= 52,88 \text{ KJ/mol} & \text{C}_2\text{H}_2 &= 226,75 \text{ KJ/mol} \\ \Delta H_{\text{diss H}_2(\text{g})} &= 436 \text{ KJ/mol} & \Delta H_{\text{sub C}} &= 715 \text{ KJ/mol} \end{aligned}$$

**EXERCISE IV.B.6:**

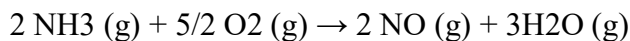
Consider the following reaction:



The value of enthalpy of reaction is  $\Delta H_R = 40,5 \text{ KJ}$

Using the data, calculate the bond energy  $E_{(\text{O-H})}$ :

$$\begin{aligned} E_{(\text{C}=\text{C})} &= -605,2 \text{ KJ/mol} & E_{(\text{C}-\text{O})} &= -351 \text{ KJ/mol} \\ E_{(\text{C}-\text{H})} &= -410 \text{ KJ/mol} & E_{(\text{C}-\text{C})} &= -347 \text{ KJ/mol} \end{aligned}$$

**SOLUTIONS OF EXERCISES OF CHAPTER IV:****A. STANDARD ENTHALPY OF FORMATION:****EXERCISE IV.A.1:**

By direct application of Hess's law, we find that:

$$\Delta H_R = \sum \Delta H_{f \text{ prod}} - \sum \Delta H_{f \text{ react}} = 2\Delta H_{f \text{ NO}(\text{g})} + 3\Delta H_{f \text{ H}_2\text{O}(\text{g})} - 2\Delta H_{f \text{ NH}_3(\text{g})} - 5/2\Delta H_{f \text{ O}_2(\text{g})}$$

$$\text{with: } \Delta H_{f \text{ O}_2(\text{g})} = 0$$

The standard enthalpy of formation of the chemical elements is equal to zero:

$$\Delta H_{f \text{ O}_2(\text{g})} = 0$$

$$\Delta H_{f \text{ NH}_3(\text{g})} = (2\Delta H_{f \text{ NO}(\text{g})} + 3\Delta H_{f \text{ H}_2\text{O}(\text{g})} - 5/2\Delta H_{f \text{ O}_2(\text{g})} - \Delta H_R) / 2$$

$$\Delta H_{f \text{ NH}_3(\text{g})} = ((2 \times 21,5) + (3 \times (-58)) + 109) / 2$$

$$\Delta H_{f \text{ NH}_3(\text{g})} = -11 \text{ Kcal}$$

We find that the standard enthalpy of formation of  $\text{NH}_3(\text{g})$  is:  $-11 \text{ Kcal}$

**EXERCISE IV.A.2:**

In this case, the heat of combustion is the same heat absorbed by the water.

$$\Delta H_{\text{comb}} = -\Delta H_{\text{water}}$$

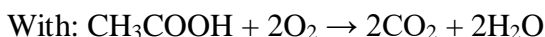
$$\Delta H_{\text{water}} = mC_p\Delta T = 20 \times 10^3 \times 1 \times (0,209) = 4180 \text{ cal} = 17,5 \text{ kJ.}$$

So  $\Delta H_{\text{comb}} = -17,5 \text{ kJ}$  for 1,2 g of acetic acid, with an amount of substance of  $n=m/M = (1,2)/60 = 0,02 \text{ mol}$ .

So the heat of one mol of acetic acid  $\text{C}_2\text{H}_4\text{O}_2$  is :

$$\Delta H_{\text{comb CH}_3\text{COOH (1mol)}} = -17,5 \text{ kJ}/0,02 \text{ mol}$$

=  $-873,5 \text{ kJ/mol}$  for 1 mol of acetic acid.



$$\Delta H_{\text{comb}} = \sum \Delta H_{\text{f prod}} - \sum \Delta H_{\text{f react}}$$

$$\Delta H_{\text{comb CH}_3\text{COOH (1mol)}} = 2\Delta H_{\text{f CO}_2(\text{g})} + 2\Delta H_{\text{f H}_2\text{O}(\text{g})} - 2\Delta H_{\text{f O}_2(\text{g})} - \Delta H_{\text{f CH}_3\text{COOH}(\text{g})}$$

with:  $\Delta H_{\text{f O}_2(\text{g})} = 0$  and  $\Delta H_{\text{f CO}_2(\text{g})} = -393,5 \text{ KJ/mol}$  and  $\Delta H_{\text{f H}_2\text{O}(\text{l})} = -285,8 \text{ KJ/mol}$

We find:  $\Delta H_{\text{f CH}_3\text{COOH}(\text{g})} = -485,1 \text{ kJ/mol}$ .

### **EXERCISE IV.A.3:**

Calculate the difference between the heat of reaction at constant volume and the heat of reaction at constant pressure in the following two cases:



The difference between the heat of reaction at constant volume and the heat of reaction at constant pressure is:  $\Delta U_{\text{R}} - \Delta H_{\text{R}}$

$$\Delta U_{\text{R}} = \Delta H_{\text{R}} - P\Delta V = \Delta H_{\text{R}} - \Delta n_{(\text{g})}RT \text{ so } \Delta U_{\text{R}} - \Delta H_{\text{R}} = -\Delta n_{(\text{g})}RT$$

$$\Delta n_{(\text{g})} = \sum n_{i(\text{g})} \text{ prod} - \sum n_{i(\text{g})} \text{ react}$$

In this case:  $\Delta n_{(\text{g})} = (1+2) - 2 = 1 \text{ mol}$ .

$$\Delta U_{\text{R}} - \Delta H_{\text{R}} = -(1) \times 8,31 \times 273 = -2268,63 \text{ j.}$$



$$\Delta U_{\text{R}} = \Delta H_{\text{R}} - P\Delta V = \Delta H_{\text{R}} - \Delta n_{(\text{g})}RT \text{ so } \Delta U_{\text{R}} - \Delta H_{\text{R}} = -\Delta n_{(\text{g})}RT$$

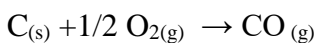
In this case:  $\Delta n_{(\text{g})} = 1 - (1+2) = -2 \text{ mol}$ .

$$\Delta U_{\text{R}} - \Delta H_{\text{R}} = -(-2) \times 8,31 \times 298 = 4952,76 \text{ j.}$$

In this case, the difference between the heat of reaction at constant volume and the heat of reaction at constant pressure is:  $4952,76 \text{ j}$ .

### **A. THE ENTHALPY OF CHEMICAL REACTION, ENTHALPY OF DISSOCIATION, THE ENTHALPY OF CHANGE OF PHYSICAL STATE:**

#### **EXERCISE IV.B.1:**



$$\Delta H_R = \sum \Delta H_{f \text{ prod}} - \sum \Delta H_{f \text{ react}} = \Delta H_{f \text{ CO (g)}} - \frac{1}{2} \Delta H_{f \text{ O}_2 \text{ (g)}} - \Delta H_{f \text{ C (s)}} \text{ with: } \Delta H_{f \text{ C (s)}} = \Delta H_{f \text{ O}_2 \text{ (g)}} = 0 \text{ "elements" so : } \Delta H_R = \Delta H_{f \text{ CO (g)}} \quad (1)$$

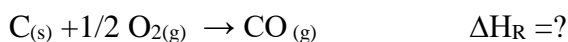
$$\text{With: } \Delta H_2 = \Delta H_{f \text{ CO}_2 \text{ (g)}} - \Delta H_{f \text{ CO (g)}} \quad (2)$$

$$\Delta H_1 = \Delta H_{f \text{ CO}_2 \text{ (g)}} \quad (3)$$

From the previous equations we conclude that:  $\Delta H_2 = \Delta H_1 - \Delta H_R$ .

$$\text{So: } \Delta H_R = \Delta H_1 - \Delta H_2 = -26,4 \text{ kcal.}$$

- Second method:



Finally:

$$\Delta H_R = \Delta H_1 - \Delta H_2 = -26,4 \text{ kcal.}$$

### **EXERCISE IV.B.2:**

Calculate the enthalpy of reaction  $\Delta H_R$ :  $2\text{CH}_4 \text{ (g)} \rightarrow \text{C}_2\text{H}_6 \text{ (g)} + \text{H}_2 \text{ (g)}$

$$\Delta H_R = \sum \Delta H_{f \text{ prod}} - \sum \Delta H_{f \text{ react}}$$

$$\Delta H_R = \Delta H_{f \text{ C}_2\text{H}_6 \text{ (g)}} + \Delta H_{f \text{ H}_2 \text{ (g)}} - 2\Delta H_{f \text{ CH}_4 \text{ (g)}} \text{ with: } \Delta H_{f \text{ H}_2 \text{ (g)}} = 0 \text{ "element"}$$

First we must calculate  $\Delta H_{f \text{ CH}_4 \text{ (g)}}$  and  $\Delta H_{f \text{ C}_2\text{H}_6 \text{ (g)}}$ :

- The reaction of combustion of  $\text{CH}_4$  is :  $\text{CH}_{4(g)} + 2\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(g)}$

$$\Delta H_{\text{com CH}_4 \text{ (g)}} = \Delta H_{f \text{ CO}_2} + 2\Delta H_{f \text{ H}_2\text{O}} - \Delta H_{f \text{ CH}_4} - 2\Delta H_{f \text{ O}_2}$$

$$\text{So } \Delta H_{f \text{ CH}_4} = 2\Delta H_{f \text{ H}_2\text{O}} + \Delta H_{f \text{ CO}_2} - \Delta H_{\text{com CH}_4 \text{ (g)}} = 2(-285,84) + (-393,51) - (-890,35)$$

we find:  $\Delta H_{f \text{ CH}_4} = -74,84 \text{ kJ/mol}$ .

- The reaction of combustion of  $\text{C}_2\text{H}_6$  is :  $\text{C}_2\text{H}_{6(g)} + \frac{7}{2} \text{O}_{2(g)} \rightarrow 2\text{CO}_{2(g)} + 3\text{H}_2\text{O}_{(g)}$

$$\Delta H_{\text{com C}_2\text{H}_6 \text{ (g)}} = 2\Delta H_{f \text{ CO}_2} + 3\Delta H_{f \text{ H}_2\text{O}} - \Delta H_{f \text{ C}_2\text{H}_6} - \frac{7}{2}\Delta H_{f \text{ O}_2}$$

$$\text{So } \Delta H_{f \text{ C}_2\text{H}_6} = 2\Delta H_{f \text{ CO}_2} + 3\Delta H_{f \text{ H}_2\text{O}} - \Delta H_{\text{com C}_2\text{H}_6 \text{ (g)}} = 2(-393,51) + 3(-285,84) - (-1559,88)$$

we find:  $\Delta H_{f \text{ C}_2\text{H}_6} = -84,66 \text{ kJ/mol}$ .

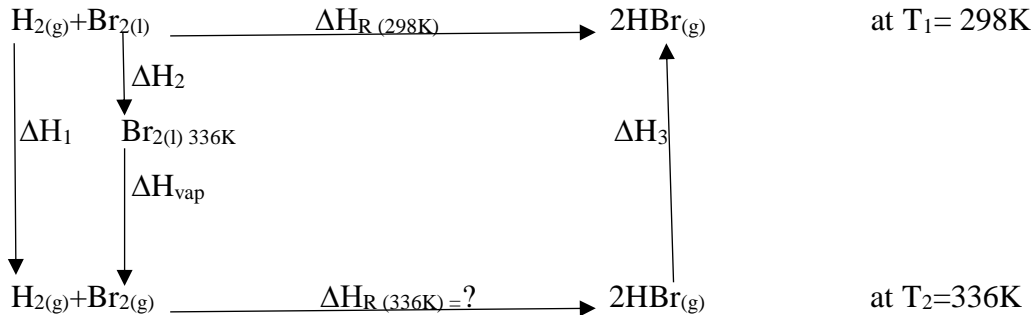
- Finally :  $\Delta H_R = \Delta H_{f \text{ C}_2\text{H}_6 \text{ (g)}} - 2\Delta H_{f \text{ CH}_4 \text{ (g)}} = -84,66 - 2(-74,84)$

we find:  $\Delta H_R = 65,02 \text{ kJ}$  for 2 mol of  $\text{CH}_4$ .

The positive value of enthalpy  $\Delta H_R$  indicates that this reaction is "endothermic".

**EXERCISE IV.B.3:**

Calculate the enthalpy of the reaction :



With:

$$\Delta H_1 + \Delta H_2 + \Delta H_{\text{vap}} + \Delta H_{\text{R}(336\text{K})} + \Delta H_3 - \Delta H_{\text{R}(298\text{K})} = 0$$

$$\Delta H_{\text{R}(336\text{K})} = \Delta H_{\text{R}(298\text{K})} - \Delta H_2 - \Delta H_{\text{vap}} - \Delta H_1 - \Delta H_3$$

$$\Delta H_3 = n C_{\text{pHBr}} (T_1 - T_2) = 2(27,8) (25 - 63) = -2112,8 \text{ J}$$

$$\Delta H_{\text{R}(298\text{K})} = 2 \Delta H_{\text{fHBr}(298\text{K})} = 2(-36,2 \times 10^3) = -72,4 \times 10^3 \text{ J}$$

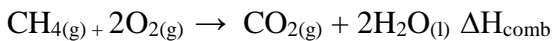
$$\Delta H_2 = n C_{\text{pBr}_2} (T_2 - T_1) = 1(71,6) (63 - 25) = 2720,8 \text{ J}$$

$$\Delta H_1 = n C_{\text{pH}_2} (T_2 - T_1) = 1(28,5) (63 - 25) = 1083 \text{ J}$$

$$\text{Finally : } \Delta H_{\text{R}(336\text{K})} = (-72,4 \times 10^3) - 2720,8 - (-29,3 \times 10^3) - 1083 - (-2112,8) = -103,4 \text{ KJ}$$

**EXERCISE IV.B.4:**

- Calculate  $\Delta H_{\text{fCH}_4(\text{g})}$  at 293 K:



$$\Delta H_{\text{comb}} = \sum \Delta H_{\text{f prod}} - \sum \Delta H_{\text{f react}}$$

$$\Delta H_{\text{comb}} = \Delta H_{\text{f CO}_2(\text{g})} + 2\Delta H_{\text{f H}_2\text{O}(\text{l})} - 2\Delta H_{\text{f O}_2(\text{g})} - \Delta H_{\text{f CH}_4(\text{g})} \quad \text{with } \Delta H_{\text{f O}_2(\text{g})} = 0$$

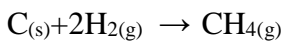
$$\Delta H_{\text{f CH}_4(\text{g})} = \Delta H_{\text{f CO}_2(\text{g})} + 2\Delta H_{\text{f H}_2\text{O}(\text{l})} - \Delta H_{\text{comb}}$$

$$= -94,2 + 2(-68,35) - (-212,98) \text{ so: } \Delta H_{\text{f CH}_4(\text{g})} = -17,92 \text{ kcal/mol at } 293 \text{ K}$$

- Calculate  $\Delta H_{\text{fCH}_4(\text{g})}$  at 773 K:

$$\Delta H_{\text{f CH}_4(\text{g})} 773\text{K} = \Delta H_{\text{f CH}_4(\text{g})} 293\text{K} + \int \Delta C_{\text{p}} dT \quad \text{Kirchoff law.}$$

The reaction of formation of CH<sub>4</sub> is:



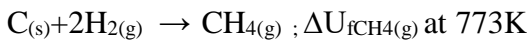
$$\Delta C_{\text{p}} = \sum C_{\text{p prod}} - \sum C_{\text{p react}} = C_{\text{pCH}_4(\text{g})} - C_{\text{pC}(\text{s})} - 2C_{\text{pH}_2(\text{g})}$$

$$\Delta C_{\text{p}} = -8,76 - 16908 \times 10^{-4} T - 12 \times 10^{-7} T^2$$

$$\Delta H_{\text{f CH}_4(\text{g})} 773\text{K} = -17,92 \times 10^3 - 8,76 [T]_{293}^{733} - 16908/2 \times 10^{-4} [T^2]_{293}^{733} - 4 \times 10^{-7} [T^3]_{293}^{733}$$

so :  $\Delta H_{fCH_4(g) 773K} = -452,3 \text{ Kcal/mol}$  .

- Calculate the internal energy  $\Delta U_{fCH_4(g)}$  at 773K :



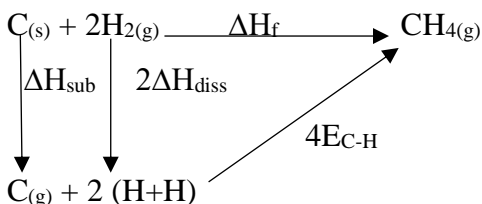
$$\Delta H = \Delta U + \Delta n RT \text{ with } \Delta n = \sum n_{\text{prod}(g)} - \sum n_{\text{react}(g)} \text{ so: } \Delta n = 1 - 2 = -1$$

$$\Delta U = \Delta H - (\Delta n)RT = -452,3 \times 10^3 - (-1) 2 (773)$$

We find that the internal energy is :  $\Delta U_{fCH_4(g) 773K} = -450,7 \times 10^3 \text{ cal}$

### EXERCISE IV.B.5:

- a-** Calculate the bond energy of C-H :

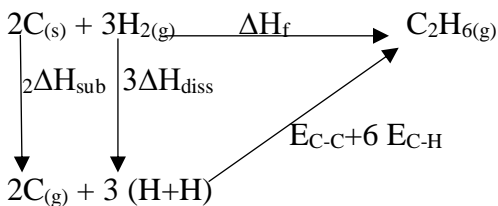


$$\Delta H_{\text{sub}C(s)} + 2\Delta H_{\text{diss}H_2} + 4E_{C-H} - \Delta H_{fCH_4} = 0$$

$$E_{C-H} = (-\Delta H_{\text{sub}C(s)} - 2\Delta H_{\text{diss}H_2} + \Delta H_{fCH_4})/4 = (-715 - 2 \times 436 - 74,85)/4$$

We find:  $E_{C-H} = -415,46 \text{ KJ}$

- b-** Calculate the bond energy of C-C :

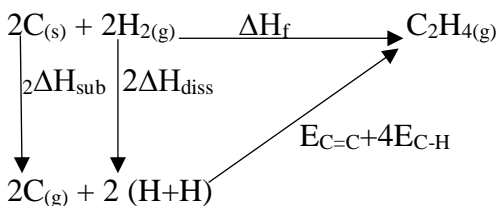


$$2\Delta H_{\text{sub}} + 3\Delta H_{\text{diss}} + E_{C-C} + 6 E_{C-H} - \Delta H_{fC_2H_6} = 0$$

$$E_{C-C} = \Delta H_{fC_2H_6} - 2\Delta H_{\text{sub}} - 3\Delta H_{\text{diss}} - 6 E_{C-H}$$

We find :  $E_{C-C} = -329,91 \text{ KJ}$ .

- c-** Calculate the bond energy of C=C :

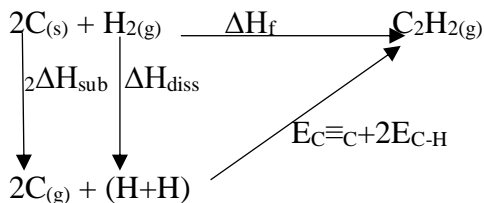


$$2\Delta H_{\text{sub}} + 2\Delta H_{\text{diss}} + E_{C=C} + 4E_{C-H} - \Delta H_{fC_2H_4} = 0$$

$$E_{C=C} = \Delta H_{fC_2H_4} - 2\Delta H_{sub} - 2\Delta H_{diss} - 4 E_{C-H}$$

We find :  $E_{C=C} = -587,28 \text{ Kj}$ .

**d-** Calculate the bond energy of  $C\equiv C$  :



$$2\Delta H_{sub} + \Delta H_{diss} + E_{C\equiv C} + 2E_{C-H} - \Delta H_{fC_2H_2} = 0$$

$$E_{C\equiv C} = \Delta H_{fC_2H_2} - 2\Delta H_{sub} - \Delta H_{diss} - 2E_{C-H}$$

We find :  $E_{C\equiv C} = -808,33 \text{ Kj}$ .

### **EXERCISE IV.B.6:**



$$\Delta H_R = \sum n_i E_{prod} - \sum n_i E_{react}$$

$$\Delta H_R = 2E_{O-H} + E_{C-C} + 4E_{C-H} - (E_{C-C} + E_{C-O} + E_{O-H} + E_{C-H})$$

Finally the bond energy  $E_{(O-H)} = -462,3 \text{ kj}$ .

**CHAPTER V: SECOND PRINCIPLE OF THERMODYNAMICS:****LEARNING OBJECTIVES:**

The learning objectives of fifth chapter “the second principle of thermodynamics” involve understanding:

- Definition of entropy (S).
- Calculation of the change in entropy ( $\Delta S$ ).
- The change in entropy ( $\Delta S$ ) of an Ideal Gas.
- The change in entropy ( $\Delta S$ ) of a mixture of ideal Gas.
- The thermal machines.

**EXERCISES OF CHAPTER V:****ENTROPY AND THERMAL MACHINES:****EXERCISE V.1:**

Consider the gas  $O_{2(g)}$  as an ideal gas, occupying a volume of 8 liters at  $27^{\circ}C$ , under 1 atmosphere.

This gas is compressed isothermally to a volume of 5 liters,

Calculate the change in entropy  $\Delta S$  of this transformation.

**EXERCISE V.2:**

The table represent the series of reversible transformations of an ideal gas,

$C_v = 3,03 \text{ calK.mol}$ :

Calculate the entropy  $\Delta S$  in each case.

Calculate  $\Delta S_{\text{cycl}}$ , what can you conclude?

	P (atm)	V (L)	T (K)
1	10	1	600
2	2	5	600
3	1	5	300
4	10	1,25	750

**EXERCISE V.3:**

I. In a calorimeter, a mixture of:

100 g of water at 10 C° with 200g of wter at 40 C°.

Calculate the change in entropy, knowing that  $C_{\text{water}} = 4,18 \text{ J/g.K}$ .

II. What is the value of entropy  $\Delta S_{\text{mixtu}}$  if:

0,5 moles of  $\text{CCl}_4$  are mixed with 0,5 moles of  $\text{CH}_2\text{Cl}_2$ .

### SOLUTIONS OF EXERCISES OF CHAPTER V:

#### ENTROPY AND THERMAL MACHINES:

##### EXERCISE V.1:

First we calculate the value of amount of substance:

$$PV=nRT ; n=PV/RT = 0,325 \text{ mol.}$$

The transformation is isothermal so:

The change in entropy of this transformation is:

$$\Delta S = n R \ln (V_2/V_1) = 0,325 \times 2 \times \ln (5/8) = - 0,305 \text{ cal.}$$

##### EXERCISE V.2:

First we must calculate the amount of substance n :

$$PV=nRT \text{ so } n=PV/RT \text{ finally } n=0,203 \text{ mol.}$$

The transformation:	The type of transformation:	$\Delta S$ :
1-2	Isothermal transformation	$\Delta S = n R \ln (V_2/V_1)$ $= 0,653 \text{ cal}$
2-3	Isochoric transformation	$\Delta S = n C_v \ln (T_3/T_2)$ $= -0,426 \text{ cal}$
3-4	Adiabatic transformation	$\Delta S = 0$
4-1	Isobaric transformation	$\Delta S = n C_p \ln (T_1/T_4)$ $= -0,228 \text{ cal}$
Cycl	$\Delta S = \sum S_i$	$\Delta S = 0$

$$\Delta S_T = \sum S_i = 0 \text{ cal.}$$

We can conclude that the entropy  $\Delta S$  is a state function.

##### EXERCISE V.3:

I. The mixture 100g  $\text{H}_2\text{O}$  + 200g  $\text{H}_2\text{O}$  :

- Calculate  $\Delta S$ :

$$\Delta S_T = \Delta S_1 + \Delta S_2 = m_1 C_p \ln(T_{\text{eq}}/T_1) + m_2 C_p \ln(T_{\text{eq}}/T_2)$$

We must calculate  $T_{\text{eq}}$  :

In a calorimeter,  $\sum Q_i = 0$

$$\text{so : } m_1 C_1(T_{\text{eq}} - T_1) + m_2 C_2(T_{\text{eq}} - T_2) = 0$$

$$T_{\text{eq}} = (m_1 C_1 T_1 + m_2 C_2 T_2) / (m_1 C_1 + m_2 C_2)$$

With  $C_1 = C_2$  so :  $T_{\text{eq}} = (m_1 T_1 + m_2 T_2) / (m_1 + m_2)$

$$= [100(283) + 200(313)] / (100 + 200) \text{ we find: } T_{\text{eq}} = 303\text{K.}$$

$$\Delta S_T = 100 (4.18) \ln(303/283) + 200 (4.18) \ln(303/313) = 1,4 \text{ J/K.}$$

**II.** The mixture of  $\text{CCl}_4 + \text{CH}_2\text{Cl}_2$  :

$$\Delta S = -R \sum n_i \ln(x_i)$$

with the mol fraction  $x_i = n_i / n_T$

$$x_1 = n_1 / n_T = 0,5 / (0,5 + 0,5) = 0,5$$

$$x_2 = n_2 / n_T = 0,5 / (0,5 + 0,5) = 0,5 \text{ so :}$$

$$\Delta S = - 1,987 (0,5 \ln 0,5 + 0,5 \ln 0,5)$$

$$\Delta S = 1,38 \text{ cal / K.}$$

## CHAPTER VI: THIRD PRINCIPLE OF THERMODYNAMICS AND ABSOLUTE ENTROPY:

### LEARNING OBJECTIVES:

The learning objectives of sixth chapter “the third principle of thermodynamics and absolute entropy” involve understanding:

- Statement of the 3rd Principle, absolute entropy at zero Kelvin ( $^{\circ}\text{K}$ ).
- The standard molar absolute entropy of a pure body .
- Standard molar absolute entropy at T Kelvin ( $T_{\text{K}}$ ) .
- A pure's standard absolute molar entropy  $S_{\text{T}}$  (solid, liquid, gas).
- The entropy change of a chemical reaction  $\Delta S_{\text{R}}$
- The entropy change of a chemical reaction at a temperature T,  $\Delta S_{\text{R}}(T)$ .

### EXERCISES OF CHAPTER VI:

#### **A. ABSOLUTE ENTROPY:**

##### **EXERCISE VI.A.1:**

Calculate the change in entropy due to the transformation of 2 moles of ammonia  $\text{NH}_3$ , at a temperature of ( $-40\text{ C}^{\circ}$ ), into ammonia gas at ( $200\text{ C}^{\circ}$ ) under a pressure ( $P = 1\text{ atm}$ ).

Knowing that:

$$C_{\text{pNH}_3 \text{ liquid}} = 17,9 \text{ cal/mol.K}$$

$$C_{\text{pNH}_3 \text{ gaz}} = 8,04 + 7 \cdot 10^{-4} T + 5,1 \cdot 10^{-5} T^2 \text{ (cal/mol.K)}.$$

$$\Delta H_{\text{vap NH}_3 (243\text{K})} = 5,560 \text{ Kcal/mol}$$

##### **EXERCISE VI.A.2:**

From the following data, calculate the absolute entropy of (Pb) vapor ( $S^{\circ}_{\text{Pb gaz}}$ ) at  $25\text{ C}^{\circ}$  and 1 atm.

$$C_{\text{p Pb solid}} = 6,7 \text{ cal/mol.K.}$$

$$C_{\text{p Pb liquid}} = 6,3 \text{ cal/mol.K.}$$

$$C_{\text{p Pb gaz}} = 4,97 \text{ cal/mol.K.}$$

$$T_{\text{melting Pb}} = 600\text{K.}$$

$$T_{\text{boiling Pb}} = 2023\text{K.}$$

$$\text{entropy of melting Pb} = 1,9 \text{ cal/mol.K.}$$

$$\text{entropy of boiling Pb} = 22,4 \text{ cal/mol.K.}$$

$$\text{entropy of solid Pb at } 25\text{ C}^{\circ} = 15,53 \text{ cal/mol.K.}$$

**B. THE ENTROPY CHANGE OF CHEMICAL REACTION:****EXERCISE VI.B.1:**

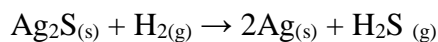
Consider the following reaction:  $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$  at  $T = 298 \text{ K}$ ,  $P = 1 \text{ atm}$ .

Compound:	$S^\circ \text{ (J/K)}$
$\text{N}_2(\text{g})$	191,49
$\text{O}_2(\text{g})$	205,03
$\text{NO}_2(\text{g})$	240,45
$\text{N}_2\text{O}_4(\text{g})$	304,30

- 1- Calculate the standard entropy change of formation of both  $\text{N}_2\text{O}_4(\text{g})$  and  $\text{NO}_2(\text{g})$ .
- 2- Calculate the standard entropy change of reaction.

**EXERCISE VI.B.2:**

We consider the reaction:



- 1- Calculate the standard enthalpy change of reaction.
- 2- Calculate the internal energy change of reaction at 298 K.
- 3- Calculate the enthalpy change of reaction at (1000 K).
- 4- Calculate the standard entropy change of reaction.
- 5- Calculate the entropy change of reaction at (1000 K).

	$\Delta H^\circ_{f 298} \text{ (cal)}$	$S^\circ_{f 298} \text{ (cal/K)}$	$C_p \text{ (cal/mol.K)}$
$\text{Ag}_2\text{S}(\text{s})$	-7600	34.5	10.1
$\text{Ag}(\text{s})$	*	10.2	5.1
$\text{H}_2(\text{g})$	*	31.2	6.5
$\text{H}_2\text{S}(\text{g})$	-4800	49.1	7

**EXERCISE VI.B.3:**

-Calculate the change in entropy of the formation of  $\text{H}_2\text{O}(\text{g})$  at 390 K  $\Delta S^\circ_{f \text{H}_2\text{O}(\text{g})}$ .

Knowing that:

$$\Delta S^\circ_{f 298\text{K} \text{H}_2\text{O}(\text{L})} = -136,62 \text{ kcal/mol.}$$

$$\Delta S^\circ_{\text{vap} \text{H}_2\text{O}(\text{L})} = 9702 \text{ cal/mol.}$$

Compound:	H <sub>2(g)</sub>	O <sub>2(g)</sub>	H <sub>2O(L)</sub>	H <sub>2O(g)</sub>
C <sub>p</sub> (cal/mol.K):	6,86	8,29	18	8

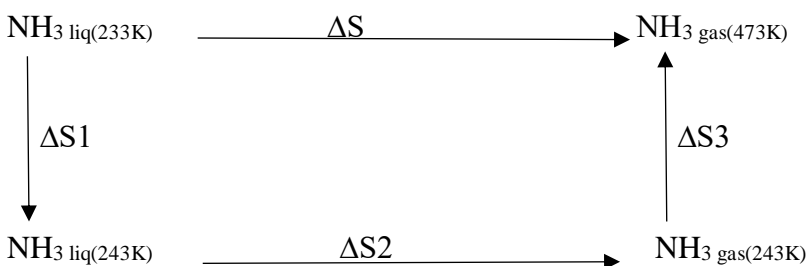
## SOLUTIONS OF EXERCISES OF CHAPTER VI:

### A. ABSOLUTE ENTROPY:

#### EXERCISE VI.A.1

- Calculate the change in entropy due to the transformation of 2 moles of ammonia

NH<sub>3</sub> :



With:

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

$$= n C_{p\text{liq}} \int dT/T + n \times L_{\text{vap}}/T_{\text{vap}} + n \int C_{p\text{gas}} dT/T.$$

$$= n C_{p\text{liq}} \ln T] + n \times L_{\text{vap}}/T_{\text{vap}} + n \int (8,04 (1/T) + 7 \times 10^{-4} + 5,1 \times 10^{-5} T).$$

$$= n C_{p\text{liq}} \ln(T_{\text{vap}}/T_1) + n \times L_{\text{vap}}/T_{\text{vap}} + n (8,04 \ln (T_2/T_{\text{vap}}) + 7 \times 10^{-4} (T_2 - T_{\text{vap}}) + (5,1 \times 10^{-5})/2 (T_2^2 - T_{\text{vap}}^2)).$$

$$= 2(17,9) \ln(243/233) + 2 \times 5,560 \times 10^3/243 + 2 (8,04 \ln (473/243) + 7 \times 10^{-4} (473 - 243) + (5,1 \times 10^{-5})/2 (473^2 - 243^2)).$$

Finally:  $\Delta S = 0,0965 \text{ Kcal/K}$ .

#### EXERCISE VI.A.2:

Calculate the absolute entropy of (Pb) vapor ( $S^\circ_{\text{Pb gaz}}$ ) at 25 C° and 1 atm:

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5.$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5.$$

$$\Delta S_1 = n C_{p(s)} \ln(T_2/T_1) = 1(6,7) \ln (600/298) = 4,68 \text{ cal/K}.$$

$$\Delta S_2 = \Delta S_{\text{melting}} = 1,9 \text{ cal/K}.$$

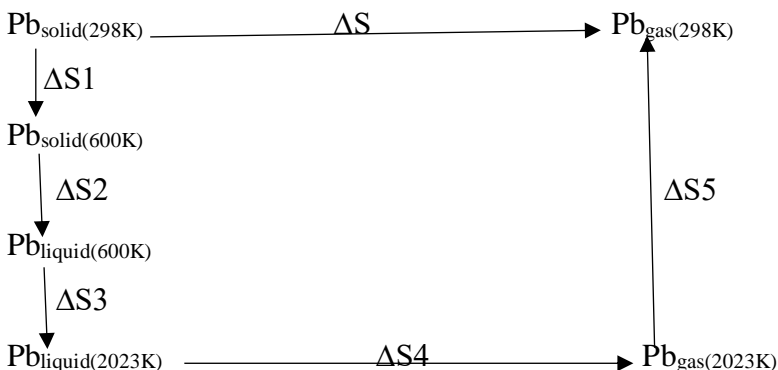
$$\Delta S_3 = n C_{p(L)} \ln(T_3/T_2) = 1(6,3) \ln (2023/600) = 7,65 \text{ cal/K}.$$

$$\Delta S_4 = \Delta S_{\text{boiling}} = 22,4 \text{ cal/K}.$$

$$\Delta S_5 = n C_{p(G)} \ln(T_1/T_3) = 1 (4,97) \ln (298/2023) = -9,5 \text{ cal/K}.$$

So :  $\Delta S_T = 27,13 \text{ cal/K}$ .

$$\Delta S_T = S_{\text{Pb gas}} - S_{\text{Pb solid}} \text{ SO } S_{\text{Pb gas}} = \Delta S_T + S_{\text{Pb solid}} = 27,13 + 15,53 = 42,66 \text{ cal/K.}$$

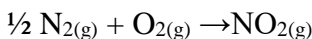


## B. THE ENTROPY CHANGE OF CHEMICAL REACTION:

### EXERCISE VL.B.1:

1- Calculate the standard entropy change of formation of  $\text{NO}_2(\text{g})$  and  $\text{N}_2\text{O}_4(\text{g})$ :

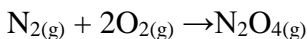
- calculate the standard entropy change of formation of  $\text{NO}_2(\text{g})$ :



$$\Delta S^\circ_{\text{f NO}_2(\text{g})} = S^\circ_{\text{f NO}_2(\text{g})} - S^\circ_{\text{f O}_2(\text{g})} - \frac{1}{2} S^\circ_{\text{f N}_2(\text{g})}$$

$$\Delta S^\circ_{\text{f NO}_2(\text{g})} = -60,32 \text{ j/K.}$$

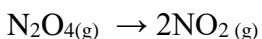
- calculate the standard entropy change of formation of  $\text{N}_2\text{O}_4(\text{g})$  :



$$\Delta S^\circ_{\text{f N}_2\text{O}_4(\text{g})} = S^\circ_{\text{f N}_2\text{O}_4(\text{g})} - 2 S^\circ_{\text{f O}_2(\text{g})} - S^\circ_{\text{f N}_2(\text{g})}$$

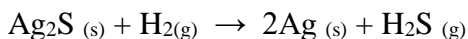
$$\Delta S^\circ_{\text{f N}_2\text{O}_4(\text{g})} = -297,25 \text{ j/K.}$$

2- Calculate the standard entropy change of reaction:



$$\Delta S^\circ_{\text{R}} = 2 \Delta S^\circ_{\text{f NO}_2(\text{g})} - \Delta S^\circ_{\text{f N}_2\text{O}_4(\text{g})} = 176,61 \text{ j/K.}$$

### EXERCISE VL.B.2:



1- Calculate the standard enthalpy change of reaction:

$$\Delta H^\circ_{\text{R}} = \sum \Delta H^\circ_{\text{f prod}} - \sum \Delta H^\circ_{\text{f react}} = \Delta H^\circ_{\text{f H}_2\text{S}(\text{g})} - \Delta H^\circ_{\text{f Ag}_2\text{S}(\text{s})} ; \Delta H^\circ_{\text{R}} = 2800 \text{ j.}$$

2- Calculate the internal energy change of reaction at 298 K:

$$\Delta U^\circ_{\text{R}} = \Delta H^\circ_{\text{R}} - \Delta n(\text{g}) RT \text{ with } \Delta n(\text{g}) = \sum n(\text{g})_{\text{prod}} - \sum n(\text{g})_{\text{react}} = 0 \text{ so } \Delta U^\circ_{\text{R}} = \Delta H^\circ_{\text{R}} = 2800 \text{ j.}$$

3- Calculate the enthalpy change of reaction at (1000 K):

$$\Delta H_{R\ 1000\ K} = \Delta H_{R\ 298\ K} + \int \Delta C_p\ dT \quad \text{Kirchoff law.}$$

$$\text{With: } \Delta C_p = \sum C_{p\ \text{prod}} - \sum C_{p\ \text{react}} = C_{p\ \text{H}_2\text{S}(\text{g})} + 2C_{p\ \text{Ag}(\text{s})} - C_{p\ \text{Ag}_2\text{S}(\text{s})} - C_{p\ \text{H}_2(\text{g})}$$

$$\text{So: } \Delta H_{R\ 1000\ K} = 3221,2\ \text{cal.}$$

4- Calculate the standard entropy change of reaction:

$$\Delta S^\circ_R = \sum \Delta S^\circ_{f\ \text{prod}} - \sum \Delta S^\circ_{f\ \text{react}} = S^\circ_{f\ \text{H}_2\text{S}(\text{g})} + 2S^\circ_{f\ \text{Ag}(\text{s})} - S^\circ_{f\ \text{Ag}_2\text{S}(\text{s})} - S^\circ_{f\ \text{H}_2(\text{g})}$$

$$\Delta S^\circ_R = 3,8\ \text{cal/K.}$$

5- Calculate the entropy change of reaction at (1000 K):

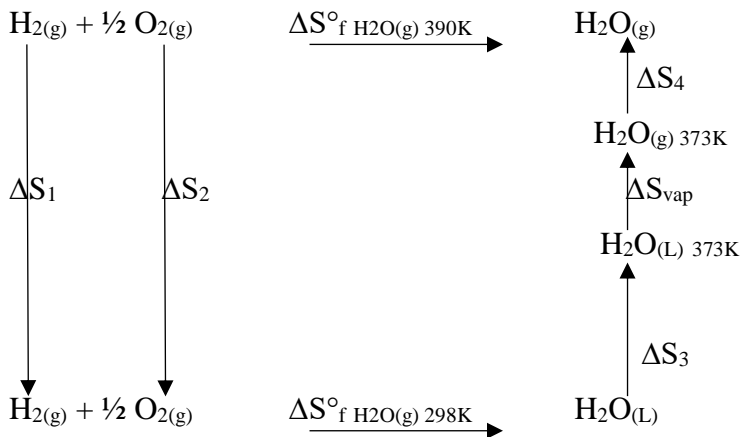
$$\Delta S_{R\ 1000\ K} = \Delta S^\circ_{R\ 298\ K} + \int (\Delta C_p/T)\ dT \quad \text{Kirchoff's law.}$$

$$\text{With: } \Delta C_p = \sum C_{p\ \text{prod}} - \sum C_{p\ \text{react}} = C_{p\ \text{H}_2\text{S}(\text{g})} + 2C_{p\ \text{Ag}(\text{s})} - C_{p\ \text{Ag}_2\text{S}(\text{s})} - C_{p\ \text{H}_2(\text{g})}$$

$$\text{So: } \Delta S_{R\ 1000\ K} = 4,53\ \text{cal/mol.}$$

### EXERCISE VI.B.3:

Calculate the change in entropy of the formation  $\Delta S^\circ_{f\ \text{H}_2\text{O}(\text{g})}$  of  $\text{H}_2\text{O}(\text{g})$  at 390 K.



$$\Delta S^\circ_{f\ \text{H}_2\text{O}(\text{g})\ 390\text{K}} = \sum \Delta S_i$$

$$= \Delta S_1 + \Delta S_2 + \Delta S^\circ_{f\ \text{H}_2\text{O}(\text{g})\ 298\text{K}} + \Delta S_3 + \Delta S_{\text{vap}} + \Delta S_4$$

$$= C_{p\ \text{H}_2(\text{g})} \ln(390/298) + \frac{1}{2} C_{p\ \text{O}_2(\text{g})} \ln(390/298) + \Delta S^\circ_{f\ \text{H}_2\text{O}(\text{g})\ 298\text{K}}$$

$$+ C_{p\ \text{H}_2\text{O}(\text{L})} \ln(373/298) + \Delta S^\circ_{\text{vap}\ \text{H}_2\text{O}(\text{L})} + C_{p\ \text{H}_2\text{O}(\text{g})} \ln(390/373)$$

$$= 1,846 + 1,115 - 136,62 \times 10^3 + 4,041 + 9702 + 0,356 = -126,910\ \text{kcal/mol.}$$

$$\Delta S^\circ_{f\ \text{H}_2\text{O}(\text{g})\ 390\text{K}} = -126,910\ \text{kcal/mol.}$$

**CHAPTER VII: FREE ENERGY AND ENTHALPY CRITERIA FOR THE  
EVOLUTION OF A SYSTEM:**

**LEARNING OBJECTIVES:**

The learning objectives of sixth chapter “the third principle of thermodynamics and absolute entropy” involve understanding:

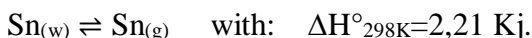
- 6- The concept of free energy and enthalpy.
- 7- Standard free enthalpy of formation
- 8- Free enthalpy of a chemical reaction (Hess's law).
- 9- Law of mass action and equilibrium constants.
- 10- Influence of temperature on equilibrium constants.
- 11- Van't Hoff relation.
- 12- Laws of equilibrium shift (Le Chatelier's principle): Effect of temperature (Van't Hoff law), Effect of the concentration of constituents, Effect of pressure.
- 13- Dissociation coefficient.
- 14- Progress degree of a chemical reaction.
- 15- The yield of a chemical reaction.

**EXERCISES OF CHAPTER VII:**

**A. FREE ENERGY AND ENTHALPY:**

**EXERCISE VII.A.1:**

Tin (Sn) exists in two forms : white Tin and gray Tin.



Which form is more stable at 25°C?

$$S^{\circ}_{\text{Sn}(w)} = 26,33 \text{ j/K.mol}$$

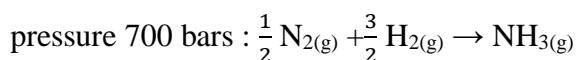
$$S^{\circ}_{\text{Sn}(g)} = 25,75 \text{ j/K.mol}$$

**EXERCISE VII.A.2:**

**I.** Express the free enthalpy  $\Delta G$  of the following reaction as a function of standard free enthalpy  $\Delta G^{\circ}$  and partial pressures:



**II.** At 298 K, 100 moles of  $\text{NH}_3$ , 50 moles of  $\text{N}_2$ , 70 moles of  $\text{H}_2$  are mixed under the total

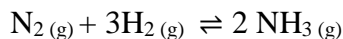


Calculate the free enthalpy  $\Delta G$  of the reaction, what can you conclude?

**B. CHEMICAL EQUILIBRIA AND LAWS OF EQUILIBRIUM SHIFT:**

**EXERCISE VII.B.1:**

$\text{NH}_3$  (g) is prepared in an isobaric reactor at 27 C°:



The total pressure is constant 1 atm, the initial gas mixture is: 3 moles of  $\text{N}_2$ , and 9 moles of  $\text{H}_2$ , 2 moles of  $\text{NH}_3$ :

a- Calculate  $\Delta H^\circ_{\text{R}(298\text{K})}$  and  $\Delta S^\circ_{\text{R}(298\text{K})}$ , is this reaction exothermic or endothermic.

What is the effect of an increase in temperature on the direction of equilibrium .

b- Calculate  $\Delta G^\circ_{(400\text{K})}$ . Deduce the value of the equilibrium constant K at 400K:

( $\Delta C_p = 0$  ).

c- Determine the composition of the mixture at equilibrium if 1,74 mol of  $\text{N}_2$

reacted, calculate the partial pressures of each constituent at equilibrium.

$$\Delta H^\circ_{\text{fNH}_3(\text{g})} = -11040 \text{ cal/mol.K.}$$

$$S^\circ \text{NH}_3(\text{g}) = 46 \text{ cal/mol.K.}$$

$$S^\circ \text{H}_2(\text{g}) = 31,2 \text{ cal/mol.K.}$$

$$S^\circ \text{N}_2(\text{g}) = 45,8 \text{ cal/mol.K.}$$

**EXERCISE VII.B.2:**



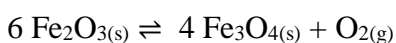
A- Calculate the free enthalpy of reaction if all partial pressures are ( $P_{\text{C}_2\text{H}_5\text{OH}} = 2 \text{ atm}$  and  $P_{\text{C}_2\text{H}_4} = P_{\text{H}_2\text{O}} = 0,25 \text{ atm}$ ).

B- In which direction the reaction will be thermodynamically possible if all partial pressures are each 2 atm .

C- If ( $P_{\text{C}_2\text{H}_5\text{OH}} = 2 \text{ atm}$  and  $P_{\text{C}_2\text{H}_4} = 1 \text{ atm}$ ) what is the value of  $P_{\text{H}_2\text{O}}$  at the state of equilibrium.

D- Explain and discuss the effect of  $P_{\text{H}_2\text{O}}$  on the direction of the reaction.

**EXERCISE VII.B.3:**



1- Discuss the evolution of this system at constants pressure and temperature.

2- Calculate at 298k:

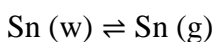
- The standard enthalpy of reaction.
  - The standard entropy of reaction.
- 3- In which direction will be the equilibrium by changing the temperature.
- 4- Give the expression of the temperature T at which  $O_{2(g)}$  begins to form.

	$\Delta H_f^\circ$ Kcal	$S_f^\circ$ cal/K
$Fe_3O_{4(s)}$	-266,9	36,2
$Fe_2O_{3(s)}$	-196,3	20,9
$O_{2(g)}$	-	49,02

### SOLUTIONS OF EXERCISES OF CHAPTER VII:

#### A. FREE ENERGY AND ENTHALPY:

##### EXERCISE VII.A.1:



To know which form is more stable at  $25^\circ C$ , we must calculate the standard free enthalpy

$$\Delta G^\circ_{298K}$$

$$\Delta G^\circ_{298K} = \Delta H^\circ_{298K} - T\Delta S^\circ_{298K}$$

$$\text{with } \Delta S^\circ_{298K} = S^\circ_{Sn(g)} - S^\circ_{Sn(w)} = -0,58 \text{ J/K.mol}$$

$$\Delta G^\circ_{298K} = 2,21 \times 10^3 - 298 (-0,58).$$

$$\Delta G^\circ_{298K} = 2Kj.$$

The value of the standard free enthalpy  $\Delta G^\circ_{298K}$  is positive, so the transformation from  $Sn(w)$  to  $Sn(g)$  is impossible at 298K.

So the form white is the more stable.

##### EXERCISE VII.A.2:

**I-** Expression of the free enthalpy  $\Delta G$  for the reaction:



$$\Delta G = \Delta G^\circ + RT \ln(K_p) \text{ with: } K_p = \frac{P_{NH_3} P_{HCl}}{P_{NH_4Cl}} \text{ and } P_{NH_4Cl(solid)} = 1$$

$$\Delta G^\circ_{298} = \sum \Delta G^\circ_{\text{prod}} - \sum \Delta G^\circ_{\text{react}}$$

$$= \Delta G^\circ_{fNH_3} + \Delta G^\circ_{fHCl} - \Delta G^\circ_{fNH_4Cl}$$

$$\text{Finally: } \Delta G = \Delta G^\circ_{fNH_3} + \Delta G^\circ_{fHCl} - \Delta G^\circ_{fNH_4Cl} + RT \ln P_{NH_3} + RT \ln P_{HCl}.$$

**II-** Calculate  $\Delta G$  of the system :  $1/2 N_2 + 3/2 H_2 \rightarrow NH_3$  :

$$\Delta G = \Delta G^\circ + RT \ln(K_p)$$

- first we must calculate  $\Delta G^\circ$ :

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \text{ with: } \Delta S^\circ = -R \sum n_i \ln(x_i) \text{ and } \Delta H^\circ = 0 \text{ (T is constant)}$$

$$\text{We find : } \Delta G^\circ = RT \sum n_i \ln(x_i)$$

The mole fractions:

$$X_{\text{NH}_3} = n/n_T = 100/(100+50+70) = 0,455.$$

$$X_{\text{N}_2} = n/n_T = 50/(100+50+70) = 0,227.$$

$$X_{\text{H}_2} = n/n_T = 70/(100+50+70) = 0,318.$$

$$\Delta G^\circ = 2 (298) (100 \ln 0,455 + 50 \ln 0,227 + 70 \ln 0,318)$$

$$\Delta G^\circ = -138919 \text{ cal .}$$

- Calculate  $K_p$  :

$$K_p = P_{\text{NH}_3} / ((P_{\text{H}_2})^{3/2} (P_{\text{N}_2})^{1/2}) \text{ with } P_i = X_i \times P_T .$$

$$\text{So: } P_{\text{NH}_3} = X_{\text{NH}_3} \times P_T = 0,455 (700) = 318,50 \text{ bar .}$$

$$P_{\text{N}_2} = X_{\text{N}_2} \times P_T = 0,227 (700) = 158,90 \text{ bar .}$$

$$P_{\text{H}_2} = X_{\text{H}_2} \times P_T = 0,318 (700) = 222,60 \text{ bar .}$$

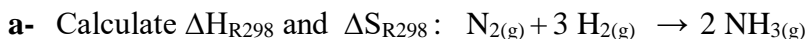
$$K_p = 0,0076$$

$$\Delta G = \Delta G^\circ + RT \ln(K_p) = -138919 + 2 (298) \ln 0,0076 = -141827,25 \text{ cal .}$$

The value of  $\Delta G < 0$  so the reaction occurs in direction  $\rightarrow$  "spontaneously"

## B. CHEMICAL EQUILIBRIA AND LAWS OF EQUILIBRIUM SHIFT:

### EXERCISE VII.B.1:



$$\Delta H_{R298} = \sum n_i \Delta H_{i \text{ prod}} - \sum n_i \Delta H_{i \text{ react}} = 2 \Delta H_{f \text{ NH}_3} - \Delta H_{f \text{ N}_2} - 3 \Delta H_{f \text{ H}_2} = 2 \Delta H_{f \text{ NH}_3} = -22080 \text{ cal/mol .}$$

$$\Delta S_{298} = \sum n_i S_{i \text{ prod}} - \sum n_i S_{i \text{ react}} = 2 S_{\text{NH}_3} - S_{\text{N}_2} - 3 S_{\text{H}_2} = -47,4 \text{ cal/mol.K .}$$

$\Delta H_R < 0$  so this reaction is exothermic.

- The increasing in (T) leads the equilibrium to the direction of formation of  $\text{N}_{2(g)}$ :  
 $\Delta G_{R298} = \Delta H_{R298} - T \Delta S_{298}$  with ( $\Delta H_R < 0$  and  $\Delta S < 0$ ) . In this case the increasing of T leads  $\Delta G_{R298} > 0$  (the direction of formation of  $\text{N}_{2(g)}$  and  $\text{H}_{2(g)}$ )

- b-** Calculate  $\Delta G_{R400}$ :

$$\Delta G_{R400} = \Delta H_{R400} - T \Delta S_{400} \text{ with:}$$

$$\Delta H_{R400} = \Delta H_{R298} + \int \Delta C_p dT \quad \text{and} \quad \Delta C_p = \sum n_i C_{p_i \text{ prod}} - \sum n_i C_{p_i \text{ react}} .$$

In this case :  $\Delta S_{400} = \Delta S_{298}$  and  $(\Delta C_p = 0)$  so:  $\Delta H_{R400} = \Delta H_{R298}$ .

$$\text{Finally: } \Delta G_{R400} = \Delta H_{R298} - 400 \Delta S_{298} = -3120 \text{ cal.}$$

- Deduce  $K_p$ :

$$\Delta G_R = \Delta G_{R298} + RT \ln(K_p) ,$$

in the case of equilibrium  $\Delta G_R = 0$  so:  $\Delta G_{R298} + RT \ln(K_p) = 0$

$$K_p = e^{-(\Delta G_{R298} / RT)} \text{ with:}$$

$$\Delta G_{R298} = \Delta H_{R298} - T \Delta S_{298} = -22080 - 298 (-47,4) = -7954,8 \text{ cal}$$

$$\text{We find: } K_p = e^{-(-7954,8 / 2 \times 400)} = 20,81 \times 10^3$$

- c- The composition of the mixture at equilibrium if 1,74 mol of  $N_2$  reacted:

1,74 mol of  $N_2$  reacted so  $\alpha = 1,74$  mol.

	$N_2$	$H_2$	$NH_3$	Total
$n_i$ :	3	9	2	
$n_f$ :	$3 - \alpha$	$9 - 3\alpha$	$2 + 2\alpha$	$n_T = 14 - 2\alpha$

$$X_{N_2} = n_f / n_T = (3 - \alpha) / 14 - 2\alpha = 1,25 / 10,52 = 0,120$$

- Calculate the partial pressures of each constituent at equilibrium if 1,74 mol of  $N_2$  reacted,  $\alpha = 1,74$  mol:

With  $P_i = X_i \times P_T$  and  $P_T = 1 \text{ atm}$ .

First we must calculate the mol fractions of all constituents:

$$X_i = n_f / n_T$$

$$X_{N_2} = n_f / n_T = (3 - \alpha) / 14 - 2\alpha = 1,25 / 10,52 = 0,120.$$

$$X_{H_2} = n_f / n_T = (9 - 3\alpha) / 14 - 2\alpha = 3,78 / 10,52 = 0,359.$$

$$X_{NH_3} = n_f / n_T = (2 + 2\alpha) / 14 - 2\alpha = 0,521.$$

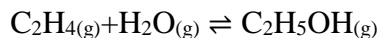
Finally, the partial pressures of each constituent:

$$P_{N_2} = X_{N_2} \times P_T = 0,120 \text{ atm.}$$

$$P_{H_2} = X_{H_2} \times P_T = 0,359 \text{ atm.}$$

$$P_{NH_3} = X_{NH_3} \times P_T = 0,521 \text{ atm.}$$

### **EXERCISE VII.B.2:**



- A- Calculate the free energy of reaction  $\Delta G_R$  :

$$\Delta G_R = \Delta G_{R298} + RT \ln(K_p)$$

$$\text{with } K_p = P_{C_2H_5OH} / (P_{C_2H_4} \times P_{H_2O}) = 2 / (0,25 \times 0,25) = 32$$

$$\Delta G_R = -1,95 \times 10^3 + 2(298) \ln 32 = 115,58 \text{ cal.}$$

$\Delta G_R > 0$  the reaction occurs in the direction 2 .

**B-** The direction of reaction if all  $P_i = 2 \text{ atm}$  :

$$K_p = P_{C_2H_5OH} / (P_{C_2H_4} \times P_{H_2O}) = 2 / (2 \times 2) = 0,5.$$

$$\Delta G_R = -1,95 \times 10^3 + 2(298) \ln 0,5 = -2363,12 \text{ cal.}$$

$\Delta G_R < 0$  the reaction occurs in the direction of formation of  $C_2H_5OH_{(g)}$  (spontaneously) .

**C-** The equilibrium state:

$\Delta G_R = \Delta G_{R298} + RT \ln(K_p)$  , in the case of equilibrium  $\Delta G_R = 0$  so:  $\Delta G_{R298} + RT \ln(K_p) = 0$

$$K_p = e^{-(\Delta G_{R298} / RT)} \text{ with } K_p = P_{C_2H_5OH} / (P_{C_2H_4} \times P_{H_2O}) = 2 / (1 \times P_{H_2O}) = e^{-(\Delta G_{R298} / RT)}$$

$$\text{So: } P_{H_2O} = 2 / e^{-(\Delta G_{R298} / RT)} = 0,076 \text{ atm.}$$

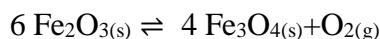
**D-** The effect of  $P_{H_2O}$ :

$P_{H_2O} = 0,076 \text{ atm}$   $\Delta G_R = 0$  equilibrium state .

$P_{H_2O} > 0,076 \text{ atm}$   $\Delta G_R < 0$  the reaction occurs in the direction of formation of  $C_2H_5OH_{(g)}$  (spontaneously).

$P_{H_2O} < 0,076 \text{ atm}$   $\Delta G_R > 0$  the reaction occurs in the direction of formation of  $C_2H_4_{(g)}$

### **EXERCISE VII.B.3:**



**1-** Discuss the evolution of this system at constants pressure and temperature:

$\Delta G = \Delta G^\circ + RT \ln(K_p)$  in this case:  $K_p = P_{O_2(g)}$ , with  $\text{Fe}_3\text{O}_4(s)$  and  $\text{Fe}_2\text{O}_3(s)$  are solid, so:

$$\Delta G = \Delta G^\circ + RT \ln(P_{O_2(g)}).$$

We find that the more oxygen pressure increases, the more the free enthalpy value increases, and thus the equilibrium shifts to the opposite direction.

**2-** Calculate at 298k:

• The standard enthalpy of reaction:

$$\Delta H^\circ_{R298} = \sum n_i \Delta H^\circ_{i \text{ prod}} - \sum n_i \Delta H^\circ_{i \text{ react}}$$

$$= \Delta H^\circ_f O_2(g) + 4 \Delta H^\circ_f Fe_3O_4(s) - 6 \Delta H^\circ_f Fe_2O_3(s) \text{ with } \Delta H^\circ_f O_2(g) = 0$$

$$= 111,4 \text{ K.cal.}$$

• The standard entropy of reaction:

$$\begin{aligned}\Delta S^{\circ}_{R298} &= \sum n_i \Delta S^{\circ}_{i \text{ prod}} - \sum n_i \Delta S^{\circ}_{i \text{ react}} \\ &= \Delta S^{\circ}_{f \text{ O}_2(\text{g})} + 4 \Delta S^{\circ}_{f \text{ Fe}_3\text{O}_4(\text{s})} - 6 \Delta S^{\circ}_{f \text{ Fe}_2\text{O}_3(\text{s})} \\ &= 68,42 \text{ cal/K.}\end{aligned}$$

- 3-** In which direction will be the equilibrium by changing the temperature, Assuming that the values of standard enthalpy and standard entropy remain constant when the temperature changes:

$$\Delta G^{\circ}_{R298} = \Delta H^{\circ}_{R298} - T \Delta S^{\circ}_{R298}$$

- The values of enthalpy of reaction  $\Delta H^{\circ}_{R298}$  and entropy of reaction  $\Delta S^{\circ}_{R298}$  are positives so the increasing in temperature T, leads the equilibrium to the direction of formation of  $\text{O}_{2(\text{g})}$  “spontaneously”.

Also the decreasing in temperature T, leads the equilibrium to the direction of formation of  $\text{Fe}_2\text{O}_{3(\text{s})}$ .

- 4-** Give the expression of the temperature T at which  $\text{O}_{2(\text{g})}$  begins to form:

$\text{O}_{2(\text{g})}$  begins to form in the case of  $\Delta G_R < 0$

$$\Delta H - T \Delta S < 0 \text{ so } \Delta H / \Delta S < T$$

We find that the temperature T at which  $\text{O}_{2(\text{g})}$  begins to form is  $T = 1630 \text{ K}$ .

At temperatures higher than the mentioned value  $T = 1630 \text{ K}$ , the equilibrium is shifted towards the formation of oxygen.

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