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 PROBLEMS IN CHEMICAL THERMODYNAMICS.

1st 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 (ΔU), the change in enthalpy (ΔH), the heat capacity and standard molar enthalpy of formation $\Delta H°_f$, the standard enthalpy of a reaction $\Delta H°_R$, Hess's law, Kirchhoff's law, bond energy, cycle method.

TABLE OF CONTENTS

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- 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^3 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) :

- N2 = 75,52 %
- O2 = 23,15 %
- Ar = 1,28 %
- Co2 = 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 :

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

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

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- $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)$ with PV=nRT 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 10^{-3} 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 10^{-3} 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 bar^{-1} .

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

$\alpha = P\ (1/T)\ (1/P) = 1/T$ 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. - planet earth. - a care engine. - a student in lecture hall.	- Air fryer. - a pressure cooker. - air inside a car tire. - Refrigerator. - a bottle of orange juice. - perfume bottle.	- solution of NaCl in a thermos flask. - a calorimeter containing a mixture of water and ice.

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

- swing without air resistance	

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 $T_c=1064$ °C:

$T_K= 1064 + 273,15 = 1337,15$ K.

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

2- Boiling point of nitrogen $T_c= -195,8$°C:

$T_K= -195,8 + 273,15 = 77,35$ K.

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

3- Freezing point and evaporation point of pure water:

- Freezing point $T_c=0$°C:

$T_K= 0+273,15= 273,15$K.

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

- Evaporation point $T_c=100$°C:

$T_K= 100+273,15= 373,15$K.

$T_F= 1,8\ (100) +32 = 212$ 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 °C.

C- Calculate the pressure:

"1 atm=1,013 10^5 Pa = 1,013 bar =760 mmHg =760 torr"

P =10 bar = 10/1,013 = 9,87 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) = 1atm (22,4L)/1mol(273,15K) = 0,082 l.atm /K.mol.

R= 1×1,01310^5 Pa (22,4 10^{-3} m^3) / 1mol (273,15K) = 8,314 j/K.mol.

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

1 cal=4,186j we find R=1,98 cal/ K.mol.

EXERCISE I.C.2:

A- Calculate the pressure P_2 :

Data: m_1=3,062g m_2=0,435g

V_1=1,224L → V_2=0,3L

T_1= 283,15K T_2=298,15K

P_1= 2 atm P_2= …?

For ideal gas : PV=nRT

$P_1V_1=nRT_1$ → $P_1V_1=(m_1/M)RT_1$ (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 atm .

B- Calculate the number of balloons:

V_1= 4,6 L V_2= ?

T_1= 23 C° → T_2=23 C°

P_1= 150 atm P_2=1,2 atm

The temperature is constant so $P_1V_1=P_2V_2$ *Boyl-Mariotte* law

$V_2=(P_1 V_1)/P_2 = (150\times4,6)/1,2 = 575L$

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

C- Calculate the new pressure P_2:

V_1=0,6 m^3 V_1=0,6 m^3

T_1= 333,15K → T_2=273,15K

P_1= 1,2 atm P_2= …?

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

$P_2 = (P_1T_2)/T_1 = (1,2\times273,15)/333,15 = 0,984$ atm

EXERCISE I.C.3:

Calculate the partial pressure of each constituent:

- First we must calculate the amount of substance :

n = m/M

$n_{N2} = m_{N2}/M_{N2} = 75,52/28 = 2,7$ mol.

$n_{02} = m_{O2}/M_{O2} = 23,15/32 = 0,723$ mol.

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

$n_{C02} = m_{CO2}/M_{CO2} = 0,046/44 = 0,001$ mol.

- Calculate the mol fractions :

$X_i = n_i/n_t$ with $n_t=\sum n_i = 3,456$ mol.

$X_{N2} = n_{N2}/n_t = 2,7/3,456 = 0,782.$

$X_{O2} = n_{O2}/n_t = 0,723/3,456 = 0,209.$

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

$X_{CO2} = n_{CO2}/n_t = 0,001/3,456 = 0,0003.$

- Partial pressure P_i :

$P_i=X_i\times P_T$ with P_T=1 atm.

$P_{N2} = X_{N2}/P_T = 0,782/1 = 0,782$ atm.

$P_{O2} = X_{O2}/P_T = 0,209/1 = 0,209$ atm.

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

$P_{CO2} = X_{CO2}/P_T = 0,0003/1 = 0,0003$ 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, Cv and specific heat at constant pressure, Cp.
- 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:

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

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

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

The molar enthalpies of changing state (latent heats):

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

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

EXERCISE II.A.2:

A mole of N2 (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: $C_{p\,(N2,\,g)}$ = 29,08 J. mol^{-1} .K^{-1} and R = 8,31 J. mol^{-1} .K^{-1}

B. THE CALORIMETRY :

EXERCISE II.B.1:

In an experiment, a student introduced a quantity of hot water "T_2 = 90°C" to a calorimeter that contained cold water "T_1 = 10°C".

As a result, the temperature and the mass of this mixture were: m=90g water and T_f = 50°C.

Deduce the mass of both hot and cold water.

Data : $Cp_{(H2O,L)}$ = 75 J/K.mol. C_{cal} = 338 j/K.

EXERCISE II.B.2:

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

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

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

Data: $Cp_{(H_2O,l)}$ = 4190 J/K.Kg ; and L_{fusion}= 3,35×10^5 J/Kg.

C. THE WORK :

EXERCISE II.C.1:

A mole of an ideal gas is irreversibly compressed, at a constant temperature of 25 °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} m^3 , R= 8.31 J/K.mol , Cp= 29,08 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 V1, this gas is :

a- expanded isothermally to twice its original volume,

b- cooled isobarically to V1.

c- heated at constant volume back to T1.

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:

$(I_2,s)_{300K} \xrightarrow{Q1} (I_2,s)_{387K} \xrightarrow{Q2} (I_2,L)_{387K} \xrightarrow{Q3} (I_2,L)_{457K} \xrightarrow{Q4} (I_2,g)_{457K} \xrightarrow{Q5} (I_2,g)_{500K}$

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

$Q1 = nCp_s(\Delta T) = 1\times5,4\ (387-300) = 0,469$ K cal.

$Q2 = nL_f = 1\times3,74 = 3,74$ K cal.

$Q3 = nCp_L(\Delta T) = 1\times19,5\ (457-387) = 1,365$ K cal.

$Q4 = nL_v = 1\times6,10 = 6,10$ K cal.

$Q5 = nCp_g(\Delta T) = 1\times5,4\ (387-300) = 0,469$ K cal.

$Q_T = \sum Q_i = 12,062$ 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 $Q = Q_v = nC_v\ \Delta T$

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

So $Q_v = 1\times20,77\ (100-20) = 1661,6$ j = ΔU " the internal energy" .

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

$Q_p = 1\times29,08\ (100-20) = 2326,4$ j = ΔH " enthalpy".

B. THE CALORIMETRY :

EXERCISE II.B.1:

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

$Q_1+Q_2+Q_{cal}=0$ so : $n_1C_{pH2O(L)}(T_f-T_1)+ n_2C_{pH2O(L)}(T_f-T_2)+ C_{cal}(T_f-T_1)= 0$

With the amount of substance is:

$n_T = m_T/M_{H2O} = 90/18 = 5$ mol. $n_1+n_2= 5$ mol.

From the previous equation:

$n_1C_{pH2O(L)}(T_f-T_1)+ (5-n_1) C_{pH2O(L)}(T_f-T_2)+C_{cal}(T_f-T_1)= 0$

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

After solving the previous equation:

$n_1=0,25$ mol and $n_2= 5-n_1 = 4,75$ mol .

The mass of cold water:

$m_1= n_1\times M_{H2O} = 0,25\times18 = 4,5$ g

The mass of hot water:

$m_2= n_2\times M_{H2O} = 4,75\times18 = 85,5$ 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:

$m_1 C_{pH2O(L)}(T_f-T_1)+ C_{cal}(T_f-T_1)+ m_2 C_{pH2O(L)}(T_f-T_2)+ m_2 \times L_{fusion}=0$

$C_{cal} = -[m_1 C_{pH2O(L)}(T_f-T_1)+ m_2 C_{pH2O(L)}(T_f-T_2)+ m_2 \times L_{fusion}] / (T_f-T_1)$

$= [m_1 C_{pH2O(L)}(T_f-T_1)+ m_2 C_{pH2O(L)}(T_f-T_2)+ m_2 \times L_{fusion}] / (T_1-T_f)$

$= [0,35 \times 4190\,(-8)+ 0,045 \times 4190\,(15)+ 0,045\,(3,35\times10^5)] / (8)$

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

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

$C_{cal} = M_{cal} \times C_{pH2O(L)}$ so: $M_{cal}= C_{cal} / C_{pH2O(L)}$

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

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

C. THE WORK :

EXERCISE II.C.1:

P1=1 atm → P2=10 atm

T1= 25C° → T2=25C°

V1= … ? V2=… ?

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

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

2- Calculate the work (W_{rev}) wich for the inverse transformation:

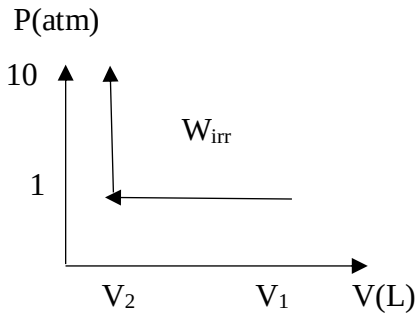
W_{rev} =$\int$-P_{ext} dV =$\int$(-nRT/V) dV = -nRT ln (V_1/V_2)

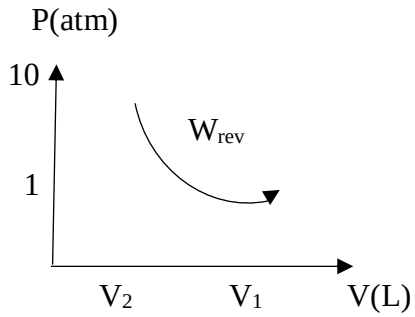
= -nRT ln (P_2/P_1) so W_{rev} = -5705 J W_{rev}<0

The negative value of W_{rev} wich 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= - 600j and Q =1350j , V_i=10^{-3} m^3 and V_f 4V_i .

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

the final pressure

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

P_fV_f =nRT_f (1)

P_iV_i =nRT_i (2)

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

P_fV_f – P_iV_i = nR (T_f-T_i)

Pi = (4P_fV_i – nR (T_f-T_i)]/V_i with:

n (T_f-T_i) = Q/C_p

P_i = 4P_f –(RQ)/(C_pV_i) = 4×2×10^5 - 8,31×1350/(29,08×10^{-3})

= 4,1×10^5 Pa =4 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:

$P_iV_i=nRT$ so $Vi= nRT/P = 1,2(8,31)\ (298)/0,2\times10^6 = 0,0148\ m^3$.

A- Isothermally expand:

$W_1= -\int PdV = -nRT\ ln(V_2/V_1) = -1,2(8,314)(298)\ ln2 =-2060j.$

B- Isobarically cool down to V_1:

$W_2= -\int PdV = -P_2(V_1-V_2) = -0,1\times10^6\ (-14,865\times10^{-3}) =1487j.$

P2 is calculated from first process "isothermally expand"

$P_1V_1=P_2V_2$ so: $P_2=(P_1\times V_1)/V_2 = (P_1\times V_1)/\ 2V_1 = P_1/2 = (0,2\ Mpa)\ /2 = 0,1\ Mpa.$

C- heated at constant volume back to T_1:

$W_3= -\int PdV = 0.$

We have returned the system to its original state :

$W_T = \sum W_i = W_1+W_2+W_3 = -573j.$

- 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 ΔU.
- 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°C under 1 atmosphere.

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

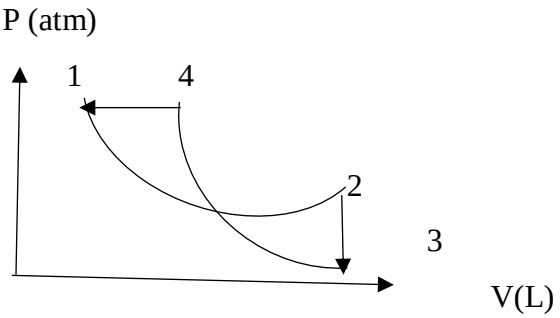
- The pressure P2.
- The amount of heat Q.
- The work W.
- The internal energy ΔU.

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

- The pressure P2.
- The temperature T_2.
- The amount of heat Q.
- The work W.
- The internal energy ΔU.

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: *Cv=3,03 cal/K.mol.*

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

	W (cal)	Q(cal)	ΔU(cal)
1→2	….	….	…..
2→3	….	….	….
3→4	….	….	….
4→1	….	….	….

B. THE CONCEPT OF ENTHALPY :

EXERCISE III.B.1:

Consider $Cl_{2(g)}$ as an ideal with: V=10L and T=25°C and P=1 atmosphere.

This gas is transformed isobarically to a volume V= 4L deduce:

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

- The work W.
- The internal energy ΔU.
- The change in enthalpy ΔH.

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 ΔU, the enthalpy ΔH.

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

EXERCISE III.B.3:

An ideal gas initially in state A (TA=293K, PA=1 atm, VA=12 L) with Cv=3R, undergoes the following transformations:

a- reversible adiabatic compression up to TB = 400 K (state B)

b- reversible isothermal compression up to VC = 1 L (state C)

c- reversible adiabatic expansion up to TD = TA (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) :	ΔU (J):	ΔH (J):
A→B					
B→C					
C→D					
D→A					
Cycle					

EXERCISE III.B.4 :

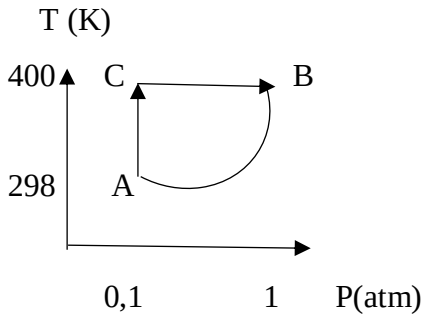
The transformation of 1 mole of ideal gas from an initial (state A) to final (state B) takes place along two paths in the diagram:

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

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

Calculate for each path the work W, the amount of heat Q and the internal energy ΔU, and conclude.

Cp=37,69j/mol.K γ= 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 so n=PV/RT so: n=0,325 mol.

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

P_1=1atm, V_1=8L, T_1= 27°C=300K, and V_2=5L, isothermally so T_2= 27°C=300K.

- The pressure P_2:

$P_2 = (nRT_2/V_2)$ = 1,6 atm.

- The amount of heat and the work and the internal energy ΔU:

This gas is compressed isothermally so

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

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

And $Q = -W = 381$ j .

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

- Calculate the pressure P_2 :

$P_1V_1^{\gamma}=P_2V_2^{\gamma}$ with $\gamma=(Cp/Cv)$, this gas is a diatomic gas so

$Cp = (7/2)R$ and $Cv=(5/2)R$ finally: $\gamma=(Cp/Cv) =1,4$ so $P_2 = 1,93$atm.

- The temperature T_2 :

$T_2 = (P_2V_2)/(nR) = 362$ K.

- The amount of heat Q:

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

- The work W and the internal energy ΔU:

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

EXERCISE III.A.2:

- Calculate the amount of substance n:

$PV = nRT$ so $n=P_1V_1/RT_1 = 0,203$ mol.

- Identify the type of transformation in each case.
- Complete the table:

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

Also $\gamma=C_p/C_v = 1,66$

		W (cal)	Q(cal)	ΔU(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	$=(P_4V_4- P_3V_3)/(\gamma-1)$ = 272,73 cal	= 0	$= nC_v (T_4-T_3)$ = W=272,73cal
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= -92,61cal

A. THE CONCEPT OF ENTHALPY :

EXERCISE III.B.1:

Consider $Cl_{2(g)}$ as an ideal with: V=10L and T=25°C and P=1 atmosphere.

This gas is transformed isobarically to a volume V= 4L:

First we must calculate the amount of substance:

PV=nRT so n=(PV)/(RT) n=0,409 mol .

- The temperatue T_2:

$P_2V_2=(nRT_2)$ and $T_2= P_2V_2/nR=119,267K$.

- The amount of heat Q:

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

- The work W:

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

- The internal energy ΔU:

ΔU=Q+W= -1517,5 j.

- The change in enthalpy ΔH:

This gas is transformed isobarically so:

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

EXERCISE III.B.2:

1- Calculate for each process, the work W, and the amount of heat Q, the internal energy ΔU, the enthalpy ΔH:

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

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

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

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

$\Delta H_{A-B} = \Delta U_{A-B} +\Delta(PV) = \Delta U_{A-B} +V(P2-P1) = \Delta U_{A-B} +V(nRT_B/V-nRT_A/V)$

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

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

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

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

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

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

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

- Process C-A: isobaric compression:

ΔU and ΔH are state functions so:

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

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

the second method:

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

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

the second method:

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

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

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

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

Process:	Q (j)	W (j)	ΔU (j)	ΔH (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 eversible way and compare it with that W_{B-C} in the table $W_{B-C} = -730$ j .

$W_{B-C\ reversible} = -nRT_B \ln (V_C/V_B) = nRT_B \ln (V_B/V_C)$, 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 : $W_{B-C\ reversible}$

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

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

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:

P_A=1atm V_A=12L T_A=293K — dQ=0 → — P_B=3,48atm V_B=4,72L T_B=400K

dT=0 ↑ dT=0 ↓

P_D=4,72atm V_D=2,54L T_D=293K — dQ=0 ← — P_C=16,4atm V_C=1L T_C=400K

The amount of substance: $P_AV_A=nRT_A$ so $n= P_AV_A/RT_A$ = 0,5 mol.

Calculate the variables in each case:

$T_AV_A{}^{\gamma-1}=T_BV_B{}^{\gamma-1}$ so V_B = 4,72L.

P_BV_B = n RT_B so P_B = 3,48 atm.

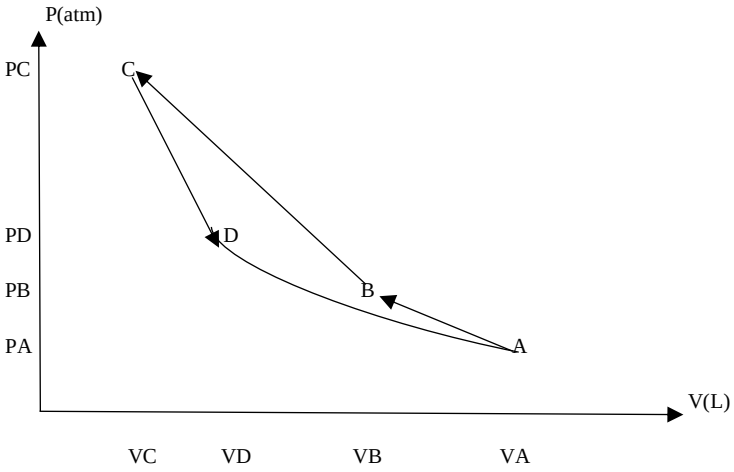
$P_CV_C=P_BV_B$ so P_C=16,4 atm.

P_CV_C = n RT_C so T_C = 400K.

$T_CV_C{}^{\gamma-1}=T_DV_D{}^{\gamma-1}$ so V_D = 2,54L.

P_DV_D = n RT_D so P_D = 4,72 atm.

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



3- Complete the table below:

Process A-B: adiabatic so Q=0j 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=0j 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) :	ΔU (J):	ΔH (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: ΔU and ΔH are state functions.
- $Q_{cycl.}\neq 0$ and $W_{cycl.}\neq 0$ so: ΔU and ΔH are path functions.

EXERCISE III.B.4 :

Calculate for each path:

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

P1=0.1 atm → (isobar) P2=0.1atm → (isotherm) P3=1atm

T1= 298K → T2=400K → T3=400K

V1= 244.36L → V2= 328L → V3=32.8L

$W_{1-2} = -P(V2-V1) = -0.1\times 1.013\times10^5 (328-244.36) \times10^{-3} = -848$ J.

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

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

$W_{2-3} = -nRT\ln V_3/V_2 = -8,314\times400 \ln (32,8/328) = 7657,48$ J.

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

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

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

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

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

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

P1=0.1 atm — adiabatic → P2=1atm — isobar → P3=1atm

T1= 298K — adiabatic → T2=495,28K — isobar → T3=400K

V1= 244.38L — adiabatic → V2= 40,61L — isobar → V3=32.8L

$P_1V_1^{\gamma} = P_2V_2^{\gamma}$ so $V_2 = (P_1/P_2)\, V_1^{1/\gamma} = 244,38,38(0,1)^{1/1,283} = 40,61L$.

$P_2V_2 = nRT2$ so $T2 = P_2V_2/nR = 495,28K$.

$Q_{1-2}=0$

$\Delta U_{1-2} = Q_{1-2}+W_{1-2} = W_{1-2} = nCv\,(T2-T1) = 5795,44$ J. with $Cv=Cp/\gamma = 29,37$ j/K.mol.

$W_{2-3} = -P3(V_3-V_{2)} = 791,86$ J.

$Q_{2-3} = Qp = nCp(T3-T2) = -3591,1$ J.

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

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

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

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

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

ΔU_T has the same value according to the two paths 1 or 2, so ΔU 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:

$2\ NH3\ (g) + 5/2\ O2\ (g) \rightarrow 2\ NO\ (g) + 3H2O\ (g)$ $\quad \Delta H°_{R\ 298\ K} = -\ 109$ kcal

Calculate the standard enthalpy of formation of $NH_{3(g)}$.

$\Delta H_{f\ 298K\ NO(g)} = 21,5$ kcal ; $\Delta H_{f\ 298K\ H2O(g)} = -58,0$ kcal.

EXERCISE IV.A.2:

Knowing that the combustion of 1,2 g of acetic acid $C_2H_4O_2$ under constant pressure 10^5 Pa in a calorimetric bomb immersed in a container containing 20 kg of water at Ti= 298K, after reaction the temperature of water in this container increased by 0,209 K.

- Calculate the enthalpy of formation of acetic acid

$\Delta H_{f\ CO2\ (g)} = -393,5$ Kj/mol ; $\Delta H_{f\ H2O\ (l)} = -285,8$ Kj/mol ; $C_{H2O\ (l)} = 1$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:

a- At temperature of 0 C°: $CH_{4\ (L)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$

b- At temperature of 25 C°: $CH4_{(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(L)}$

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:

$C_{(s)} + 1/2\ O_{2(g)} \rightarrow CO_{(g)}$

If you know:

$C_{(s)} + O_{2(g)} \rightarrow CO_{2\,(g)}$ $\Delta H_1 = -94$ kcal/mol

$CO_{(g)} + 1/2\ O_{2(g)} \rightarrow CO_{2\,(g)}$ $\Delta H_2 = -67,,6$ kcal/mol

EXERCISE IV.B.2:

Calculate the enthalpy of reaction ΔH_R:

$2CH_{4\ (g)} \rightarrow C_2H_{6\ (g)} + H_{2\ (g)}$

Knowing that: $\Delta H_{f\,H2O(g)} = -285,84$ kj/mol ; $\Delta H_{f\,CO2(g)} = -393,51$ kj/mol

$\Delta H_{com\,CH4\,(g)} = -890,35$ kj/mol ; $\Delta H_{com\,C2H6\,(g)} = -1559,88$ kj/ mol

EXERCISE IV.B.3:

The mixture $H_{2\,(g)} + Br_{2\,(g)}$ is reacted at constant pressure 1 atm and 63°C.

Calculate under these conditions, the enthalpy of the reaction :

$H_{2\,(G)} + Br_{2\,(G)} \rightarrow 2\ HBr_{\,(G).}$

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

$\Delta H_{vap\,Br2} = 29,3$ kj/ mol (at 336 K)

Compound :	$HBr_{\,(g)}$	$H_{2(g)}$	$Br_{2\,(l)}$
Cp: J /mol .K	27,8	28,5	71,6

EXERCISE IV.B.4:

Determine at 25°C and 500°C the heat of formation of methane CH_4 .

Deduce the internal energy of formation of methane $\Delta U_{f\,CH4(g)}$ at 500°C .

Knowing that:

$C(s) + O2(g) \rightarrow CO2(g)$ $\Delta H_{298\,K} = -94,2$ Kcal/ mol

$H2(g) + ½\ O2(g) \rightarrow H2O(l)$ $\Delta H_{298\,K} = -68,35$ Kcal/ mol

$CH4(g) + 2O2(g) \rightarrow CO2(g) + 2H2O(l)$ $\Delta H_{298\,K} = -212,98$ Kcal/ mol

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

$Cp_{\,H2(g)} = 6,5 + 9 \times 10^{-1}\ T$ cal/mol. K

$Cp_{CH4(g)} = 5{,}34 + 1140 \times 10^{-4}\ T$ 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:

CH_4 = -74,85 Kj/mol C_2H_6 = -84, 67 Kj/mol

C_2H_4 = 52,88 Kj/mol C_2H_2= 226,75 Kj/mol

$\Delta H_{diss\ H2\ (g)}$ = 436 Kj/mol $\Delta H_{sub\ C}$ = 715 Kj/mol

EXERCISE IV.B.6:

Consider the following reaction:

$C_2H_6O \rightarrow H_2O + C_2H_4$

The value of enthalpy of reaction is ΔH_R = 40,5 KJ

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

$E_{(C=C)}$ = - 605,2 KJ/mol $E_{(C-O)}$ = - 351 KJ/mol

$E_{(C-H)}$ = - 410 KJ/mol $E_{(C-C)}$ = - 347 KJ/mol

SOLUTIONS OF EXERCISES OF CHAPTER IV:

A. STANDARD ENTHALPY OF FORMATION:

EXERCISE IV.A.1:

2 NH3 (g) + 5/2 O2 (g) → 2 NO (g) + 3H2O (g)

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

$\Delta H_R = \sum \Delta H_{f\ prod} - \sum \Delta H_{f\ react} = 2\Delta H_{f\ NO\ (g)} + 3\Delta H_{f\ H2O(g)} - 2\Delta H_{f\ NH3(g)} - 5/2\Delta H_{f\ O2(g)}$

with: $\Delta H_{f\ O2(g)} = 0$

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

$\Delta H_{f\ O2(g)} = 0$

$\Delta H_{f\ NH3(g)} = (2\Delta H_{f\ NO\ (g)} + 3\Delta H_{f\ H2O(g)} - 5/2\Delta H_{f\ O2(g)} - \Delta H_R) / 2$

$\Delta H_{f\ NH3(g)} = ((2\times 21{,}5) + (3\times (-58)) + 109) / 2$

$\Delta H_{f\ NH3(g)}$ = - 11 Kcal

We find that the standard enthalpy of formation of NH3 (g) is: - 11 Kcal

EXERCISE IV.A.2:

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

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

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

So ΔH_{comb} = - 17,5 kj for 1,2 g of acetic acid, with an amount of substance of n=m/M = (1,2)/60 = 0,02mol.

So the heat of one mol of acetic acid $C_2H_4O_2$ is :

$\Delta H_{comb\ CH3COOH\ (1mol)}$ = -17,5 kj/0,02mol

= -873,5kj/mol for 1mol of acetic acid.

With: $CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O$

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

$\Delta H_{comb\ CH3COOH\ (1mol)} = 2\Delta H_{f\ CO2\ (g)} + 2\Delta H_{f\ H2O(g)} - 2\Delta H_{f\ O2(g)} - \Delta H_{fCH3COOH(g)}$

with: $\Delta H_{f\ O2(g)} = 0$ and $\Delta H_{f\ CO2\ (g)}$ =-393,5 Kj/mol and $\Delta H_{f\ H2O\ (l)}$ =-285,8 Kj/mol

We find: $\Delta H_{f\ CH3COOH\ (g)}$ = - 485,1 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:

a- At temperature of 0 C°: $CH_{4\ (L)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$

The difference between the heat of reaction at constant volume and the heat of reaction at constant pressure is: $\Delta U_R - \Delta H_R$

$\Delta U_R = \Delta H_R - P\Delta V = \Delta H_R - \Delta n_{(g)}RT$ so $\Delta U_R - \Delta H_R = -\Delta n_{(g)}RT$

$\Delta n(g) = \sum n_{i(g)}$ prod - $\sum n_{i(g)}$ prod.

In this case: $\Delta n(g) = (1+2) - 2 = 1$ mol.

$\Delta U_R - \Delta H_R = -(1) \times 8,31 \times 273 = -2268,63$ j.

b- At temperature of 25 C°: $CH4_{(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(L)}$

$\Delta U_R = \Delta H_R - P\Delta V = \Delta H_R - \Delta n_{(g)}RT$ so $\Delta U_R - \Delta H_R = -\Delta n_{(g)}RT$

In this case: $\Delta n(g) = 1 - (1+2) = -2$ mol.

$\Delta U_R - \Delta H_R = -(-2) \times 8,31 \times 298 = 4952,76$ 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 j.

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

EXERCISE IV.B.1:

$C_{(s)} + 1/2\ O_{2(g)} \rightarrow CO_{(g)}$

$\Delta H_R = \sum \Delta H_{f\ prod} - \sum \Delta H_{f\ react} = \Delta H_{f\ CO\ (g)} - ½\ \Delta H_{f\ O2(g)} - \Delta H_{f\ C\ (s)}$ with: $\Delta H_{f\ C(s)} = \Delta H_{f\ O2(g)} =$ 0 "elements" so : $\Delta H_R = \Delta H_{f\ CO\ (g)}$ (1)

With: $\Delta H_2 = \Delta H_{f\ CO2\ (g)} - \Delta H_{f\ CO\ (g)}$ (2)

$\Delta H_1 = \Delta H_{f\ CO2\ (g)}$ (3)

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

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

- Second method:

$C_{(s)} + O_{2(g)} \rightarrow CO_{2\ (g)}$ $\Delta H_1 = -94$ kcal/mol

$CO_{(g)} + 1/2\ O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H_2 = -67,,6$ kcal/mol

$C_{(s)} + 1/2\ O_{2(g)} \rightarrow CO_{(g)}$ $\Delta H_R = ?$

Finally:

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

EXERCISE IV.B.2:

Calculate the enthalpy of reaction ΔH_R:_ $2CH_{4\ (g)} \rightarrow C_2H_{6\ (g)} + H_{2\ (g)}$

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

$\Delta H_R = \Delta H_{f\ C2H6\ (g)} + \Delta H_{f\ H2\ (g)} - 2\Delta H_{f\ CH4\ (g)}$ with: $\Delta H_{f\ H2(g)} = 0$ "element"

First we must calculate $\Delta H_{f\ CH4\ (g)}$ and $\Delta H_{f\ C2H6\ (g)}$:

- The reaction of combustion of CH_4 is : $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$

$\Delta H_{com\ CH4\ (g)} = \Delta H_{f\ CO2} + 2\Delta H_{f\ H2O} - \Delta H_{f\ CH4} - 2\Delta H_{f\ O2}$

So $\Delta H_{f\ CH4} = 2\Delta H_{f\ H2O} + \Delta H_{f\ CO2} - \Delta H_{com\ CH4\ (g)} = 2(-285,84) + (-393,51) - (-890,35)$

we find: $\Delta H_{f\ CH4} = -74,84$ kj/mol.

- The reaction of combustion of C_2H_6 is : $C_2H_{6(g)} + 7/2\ O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$

$\Delta H_{com\ C2H6\ (g)} = 2\Delta H_{f\ CO2} + 3\Delta H_{f\ H2O} - \Delta H_{f\ C2H6} - 7/2\Delta H_{f\ O2}$

So $\Delta H_{f\ C2H6} = 2\Delta H_{f\ CO2} + 3\Delta H_{f\ H2O} - \Delta H_{f\ C2H6} = 2(-393,51) + 3(-285,84) - (-1559,88)$

we find: $\Delta H_{f\ C2H6} = -84,66$ kj/mol.

- Finally : $\Delta H_R = \Delta H_{f\ C2H6\ (g)} - 2\Delta H_{f\ CH4\ (g)} = -84,66 - 2(-74,84)$

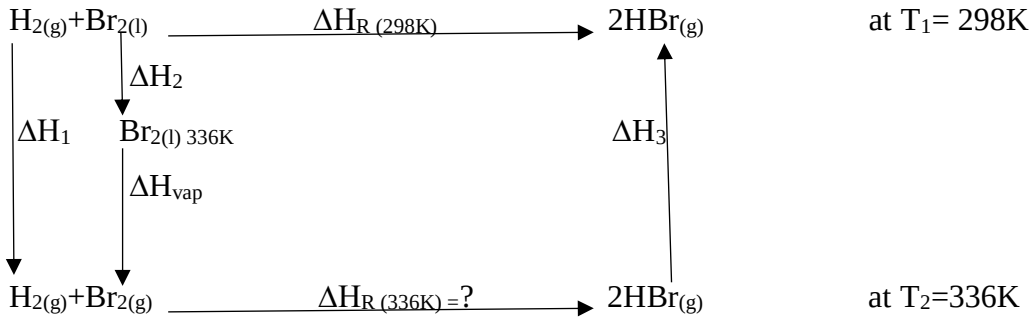
we find: $\Delta H_R = 65,02$kj for 2 mol of CH_4.

The positive value of enthalpy ΔH_R indicates that this reaction is "endothermic".

EXERCISE IV.B.3:

Calculate the enthalpy of the reaction :

$H_{2\,(G)} + Br_{2\,(G)} \rightarrow 2\,HBr_{\,(G)}$ at 63°C=336K



With:

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

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

$\Delta H_3 = nCp_{HBr}\,(T1-T2) = 2(27,8)\,(25-63) = -2112,8$ J.

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

$\Delta H_2 = nCp_{Br2}\,(T2-T1) = 1(71,6)\,(63-25) = 2720,8$J.

$\Delta H_1 = nCp_{H2}\,(T2-T1) = 1(28,5)\,(63-25) = 1083$J.

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

EXERCISE IV.B.4:

- Calculate $\Delta H_{f\,CH4(g)}$ at 293 K:

$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}\ \Delta H_{comb}$

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

$\Delta H_{comb} = \Delta H_{f\,CO2}(g) + 2\Delta H_{f\,H2O(l)} - 2\Delta H_{f\,O2(g)} - \Delta H_{f\,CH4(g)}$ with $\Delta H_{f\,O2(g)} = 0$

$\Delta H_{f\,CH4(g)} = \Delta H_{f\,CO2}(g) + 2\Delta H_{f\,H2O(l)} - \Delta H_{comb}$

$= -94,2 + 2\,(-68,35) - (-212,98)$ so: $\Delta H_{f\,CH4(g)} = -17,92$ kcal/mol at 293 K

- Calculate $\Delta H_{f\,CH4(g)}$ at 773 K:

$\Delta H_{f\,CH4(g)\,773K} = \Delta H_{f\,CH4(g)\,293K} + \int \Delta C_p\, dT$ Kirchoff law.

The reaction of formation of CH4 is:

$C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$

$\Delta Cp = \sum Cp_{\,prod} - \sum Cp_{\,react} = Cp_{CH4(g)} - Cp_{C(s)} - 2Cp_{H2(g)}$

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

$\Delta H_{f\,CH4(g)\,773K} = -17,92 \times 10^3 - 8,76[T]_{293}^{733} - 16908/2 \times 10^{-4}[T^2]_{293}^{733} - 4 \times 10^{-7}[T^3]_{293}^{733}$

so : $\Delta H_{f\,CH4(g)\,773K} = -452,3$ Kcal/mol .

- Calculate the internal energy $\Delta U_{fCH4(g)}$ at 773K :

$C_{(s)}+2H_{2(g)} \rightarrow CH_{4(g)}$; $\Delta U_{fCH4(g)}$ at 773K

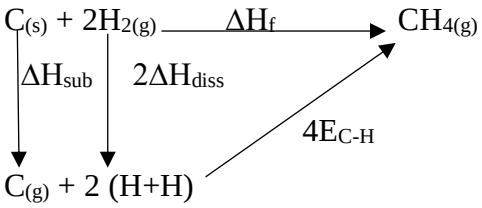
$\Delta H=\Delta U+\Delta n\,RT$ with $\Delta n=\sum n_{prod\,(g)} - \sum n_{react\,(g)}$ so: $\Delta n = 1-2 = -1$

$\Delta U=\Delta H-(\Delta n)RT = -452,3\times10^3 -(-1)\,2\,(773)$

We find that the internal energy is : $\Delta U_{fCH4(g)773K} = -450,7\times10^3$ cal

EXERCISE IV.B.5:

a- Calculate the bond energy of C-H :

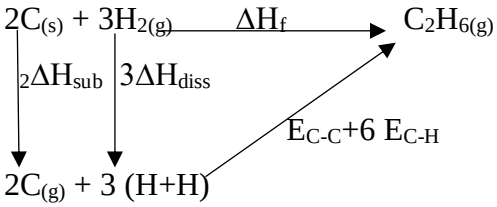


$\Delta H_{subC(s)} + 2\Delta H_{dissH2}+4E_{C-H} -\Delta H_{fCH4} =0$

$E_{C-H} = (-\Delta H_{subC(s)} -2\Delta H_{diss\,H2}+\Delta H_{fCH4})/4 = (-715-2\times436-74,85)/4$

We find: $E_{C-H} = -415,46$Kj

b- Calculate the bond energy of C-C :

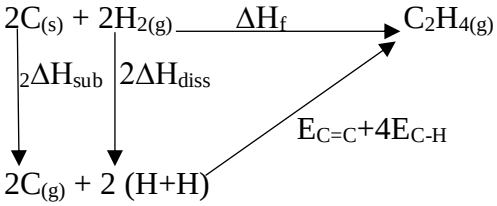


$2\Delta H_{sub}+3\Delta H_{diss} + E_{C-C} +6\,E_{C-H} - \Delta H_{fC2H6} = 0$

$E_{C-C} = \Delta H_{fC2H6} - 2\Delta H_{sub} - 3\Delta H_{diss} - 6\,E_{C-H}$

We find : $E_{C-C} = -329,91$ Kj.

c- Calculate the bond energy of C=C :

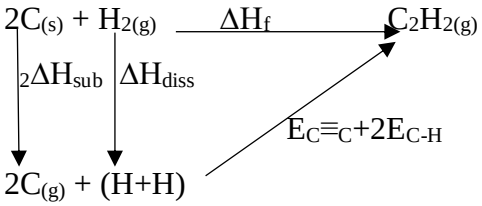


$2\Delta H_{sub}+2\Delta H_{diss} + E_{C=C} +4E_{C-H} - \Delta H_{fC2H4} = 0$

$E_{C=C} = \Delta H_{fC2H4} - 2\Delta H_{sub} - 2\Delta H_{diss} - 4\,E_{C-H}$

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

d- Calculate the bond energy of C≡C :



$2\Delta H_{sub} + \Delta H_{diss} + E_{C\equiv C} + 2E_{C-H} - \Delta H_{fC2H2} = 0$

$E_{C\equiv C} = \Delta H_{fC2H2} - 2\Delta H_{sub} - \Delta H_{diss} - 2E_{C-H}$

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

EXERCISE IV.B.6:

$C_2H_6O \rightarrow H_2O + C_2H_4$ with: $\Delta H_R = 40{,}5$ KJ

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

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

Finally the bond energy $E_{(O-H)} = -462{,}3$ 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 (ΔS).
- The change in entropy (ΔS) of an Ideal Gas.
- The change in entropy (ΔS) 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°C, under 1 atmosphere.

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

Calculate the change in entropy ΔS of this transformation.

EXERCISE V.2:

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

C_v= 3,03 calK.mol:

Calculate the entropy ΔS in each case.

Calculate ΔS_{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_{water} = 4,18 J/g.K.

II. What is the value of entropy ΔS_{mixtu} if:

0,5 moles of CCl_4 are mixed with 0,5 moles of CH_2Cl_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 mol.

The transformation is isothermal so:

The change in entropy of this transformation is:

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

EXERCISE V.2:

First we must calculate the amount of substance n :

PV=nRT so n=PV/RT finally n=0,203mol.

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

$\Delta S_T = \sum S_i = 0$ cal.

We can conclude that the entropy ΔS is a state function.

EXERCISE V.3:

I. The mixture 100g H2O + 200g H2O :

- Calculate ΔS:

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

We must calculate T_{eq} :

In a calorimeter, $\sum Qi = 0$

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

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

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

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

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

II. The mixture of $CCl_4 + CH_2Cl_2$:

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

with the mol fraction $x_i = n_i/n_T$

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

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

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

$\Delta S = 1{,}38$ 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 (°K).
- The standard molar absolute entropy of a pure body .
- Standard molar absolute entropy at T Kelvin (T_K) .
- A pure's standard absolute molar entropy S_T (solid, liquid, gas).
- The entropy change of a chemical reaction ΔS_R
- The entropy change of a chemical reaction at a temperature T, $\Delta S_{R\,(T)}$.

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 NH_3 , at a temperature of (-40 C°), into ammonia gas at (200 C°) under a pressure (P =1 atm).

Knowing that:

$Cp_{NH3\ liquid}$ =17,9 cal/mol.K

$Cp_{NH3\ gaz} = 8{,}04+7.10^{-4}\ T +5{,}1.10^{-5}\ T^2$ (cal/mol.K).

$\Delta H_{vap\ NH3\ (243K)} = 5{,}560$ Kcal/mol

EXERCISE VIA.2:

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

Cp Pb solid = 6,7 cal/mol.K.

Cp Pb liquid = 6,3 cal/mol.K.

Cp Pb gaz = 4,97 cal/mol.K.

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

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

entropy of melting Pb = 1,9 cal/mol.K.

entropy of boiling Pb = 22,4 cal/mol.K.

entropy of solid Pb at 25 C° = 15,53 cal/mol.K.

B. THE ENTROPY CHANGE OF CHEMICAL REACTION:

EXERCISE VI.B.1:

Consider the following reaction: $N_2O_{4(g)} \rightarrow 2NO_{2\,(g)}$ at T = 298 K, P =1 atm.

Compound:	S° (J/K)
$N_{2\,(g)}$	191,49
$O_{2(g)}$	205,03
$NO_{2\,(g)}$	240,45
$N_2O_{4(g)}$	304,30

1- Calculate the standard entropy change of formation of both $N_2O_{4(g)}$ and $NO_{2(g)}$.

2- Calculate the standard entropy change of reaction.

EXERCISE VI.B.2:

We consider the reaction:

$Ag_2S_{(s)} + H_{2(g)} \rightarrow 2Ag_{(s)} + H_2S_{\,(g)}$

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).

	$\Delta H°_{f\,298}$ (cal)	$S°_{f\,298}$ (cal/K)	Cp (cal/mol.K)
Ag2S(s)	-7600	34.5	10.1
Ag(s)	*	10.2	5.1
H2(g)	*	31.2	6.5
H2S(g)	-4800	49.1	7

EXERCISE VI.B.3:

-Calculate the change in entropy of the formation of $H_2O_{(g)}$ at 390 K $\Delta S°_{f\,H2O(g)}$.

Knowing that:

$\Delta S°_{f\,298K\,H2O(L)}$= -136,62 kcal/mol.

$\Delta S°$ vap $_{H2O(L)}$= 9702 cal/mol.

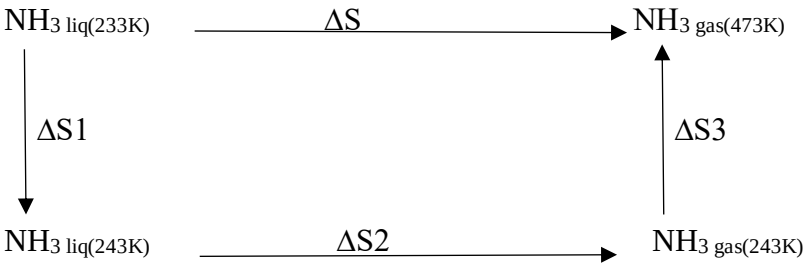
Compound:	$H_{2(g)}$	$O_{2(g)}$	$H_2O_{(L)}$	$H_2O_{(g)}$
Cp (cal/mol.K):	6,86	8,29	18	8

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_3 :



With:

$\Delta S = \Delta S1+\Delta S2+\Delta S3$.

$= nC_{pliq} \int dT/T + n\times L_{vap}/T_{vap} + n\int C_{pgas}\, dT/T$.

$= nC_{pliq}\, lnT] + n\times L_{vap}/T_{vap} + n \int (8{,}04\,(1/T) + 7\times10^{-4} + 5{,}1\times10^{-5}\,T)$.

$= nC_{pliq}\, \ln(T_{vap}/T_1) + n\times L_{vap}/T_{vap} + n\,(8{,}04 \ln(T_2/T_{vap}) + 7\times10^{-4}\,(T_2-T_{vap}) + (5{,}1\times10^{-5})/2\,(T_2^2-T_{vap}^2))$.

$= 2(17{,}9) \ln(243/233) + 2\times5{,}560\times10^3/243 + 2\,(8{,}04 \ln(473/243) + 7\times10^{-4}\,(473-243) + (5{,}1\times10^{-5})/2\,(473^2-243^2))$.

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

EXERCISE VI.A.2:

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

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

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

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

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

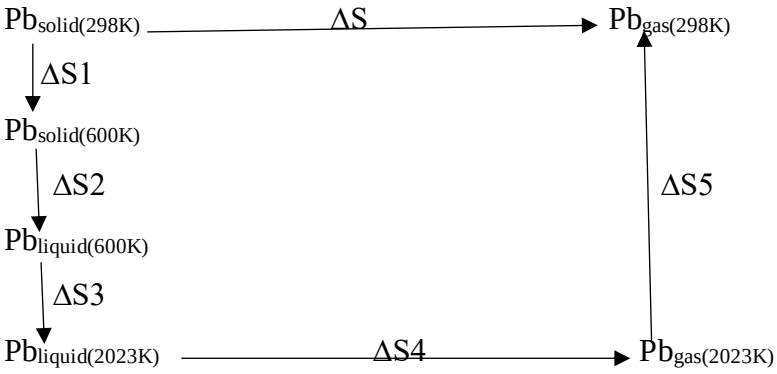
$\Delta S_3 = n\, C_{p(L)} \ln(T_3/T_2) = 1(6{,}3) \ln(2023/600) = 7{,}65$ cal/K.

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

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

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

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



B. THE ENTROPY CHANGE OF CHEMICAL REACTION:

EXERCISE VI.B.1:

1- Calculate the standard entropy change of formation of $NO_{2(g)}$) and $N_2O_{4(g)}$:

- calculate the standard entropy change of formation of $NO_{2(g)}$):

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

$\Delta S°_{f\ NO2(g)} = S°_{f\ NO2(g)} - S°_{f\ O2(g)} - \frac{1}{2}\ S°_{f\ N2(g)}$

$\Delta S°_{f\ NO2(g)} = -60,32$ j/K.

- calculate the standard entropy change of formation of $N_2O_{4(g)}$:

$N_{2(g)} + 2O_{2(g)} \rightarrow N_2O_{4(g)}$

$\Delta S°_{f\ N2O4(g)} = S°_{f\ N2O4(g)} - 2\ S°_{f\ O2(g)} - S°_{f\ N2(g)}$

$\Delta S°_{f\ N2O4(g)} = -297,25$ j/K.

2- Calculate the standard entropy change of reaction:

$N_2O_{4(g)} \rightarrow 2NO_{2\ (g)}$

$\Delta S°_R = 2\ \Delta S°_{f\ NO2(g)} - \Delta S°_{f\ N2O4(g)} = 176,61$ j/K.

EXERCISE VI.B.2:

$Ag_2S_{\ (s)} + H_{2(g)} \rightarrow 2Ag_{\ (s)} + H_2S_{\ (g)}$

1- Calculate the standard enthalpy change of reaction:

$\Delta H°_R = \sum \Delta H°_{f\ prod} - \sum \Delta H°_{f\ react} = \Delta H°_{f\ H2S(g)} - \Delta H°_{f\ Ag2S(s)}$; $\Delta H°_R = 2800$j.

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

$\Delta U°_R = \Delta H°_R - \Delta n_{(g)}\ RT$ with $\Delta n_{(g)} = \sum n(g)_{prod} - \sum n(g)_{react} = 0$ so $\Delta U°_R = \Delta H°_R = 2800$j.

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

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

With: $\Delta Cp = \sum Cp_{prod} - \sum Cp_{react} = Cp_{H2S(g)} + 2Cp_{Ag(s)} - Cp_{Ag2S(s)} - Cp_{H2(g)}$

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

4- Calculate the standard entropy change of reaction:

$\Delta S°_{R} = \sum \Delta S°_{f\ prod} - \sum \Delta S°_{f\ react} = S°_{f\ H2S(g)} + 2S°_{f\ Ag(s)} - S°_{f\ Ag2S(s)} - S°_{f\ H2(g)}$

$\Delta S°_{R} = 3{,}8$ cal/K.

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

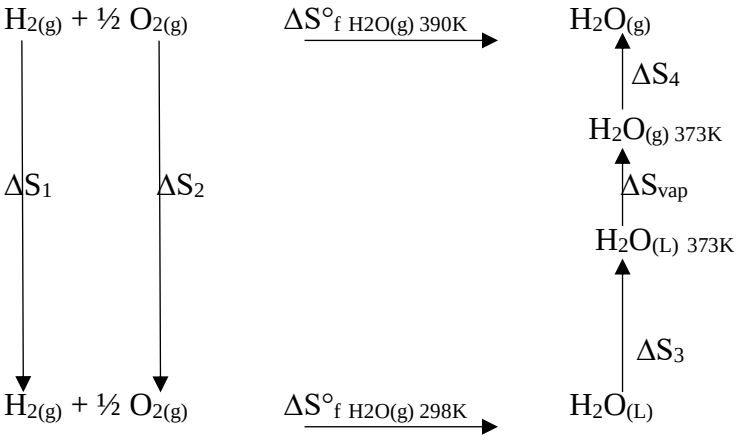
$\Delta S_{R\ 1000\ K} = \Delta S°_{R\ 298\ K} + \int (\Delta C_p/T)\ dT$ Kirchoff's law.

With: $\Delta Cp = \sum Cp_{prod} - \sum Cp_{react} = Cp_{H2S(g)} + 2Cp_{Ag(s)} - Cp_{Ag2S(s)} - Cp_{H2(g)}$

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

EXERCISE VI.B.3:

Calculate the change in entropy of the formation $\Delta S°_{f\ H2O(g)}$ of $H_2O_{(g)}$ at 390 K.



$\Delta S°_{f\ H2O(g)\ 390K} = \sum \Delta S_i$

$= \Delta S_1 + \Delta S_2 + \Delta S°_{f\ H2O(g)\ 298K} + \Delta S_3 + \Delta S_{vap} + \Delta S_4$

$= Cp_{H2(g)} \ln(390/298) + ½\ Cp_{O2(g)} \ln(390/298) + \Delta S°_{f\ H2O(g)\ 298K}$

$+ Cp_{H2O(L)} \ln(373/298) + \Delta S°_{vap\ H2O(L)} + Cp_{H2O(g)} \ln(390/373)$

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

$\Delta S°_{f\ H2O(g)\ 390K} = -126{,}910$ 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.

$Sn_{(w)} \rightleftharpoons Sn_{(g)}$ with: $\Delta H°_{298K}$=2,21 Kj.

Which form is more stable at 25°C?

$S°_{Sn(w)}$ = 26,33 j/K.mol

$S°_{Sn(g)}$ = 25,75 j/K.mol

EXERCISE VII.A.2:

I. Express the free enthalpy ΔG of the following reaction as a function of standard free enthalpy ΔG° and partial pressures:

$NH_4Cl_{(s)} \rightarrow NH_{3(g)} + HCl_{(g)}$

II. At 298 K, 100 moles of NH3, 50 moles of N2, 70 moles of H2 are mixed under the total pressure 700 bars : $\frac{1}{2} N_{2(g)} + \frac{3}{2} H_{2(g)} \rightarrow NH_{3(g)}$

Calculate the free enthalpy ΔG of the reaction, what can you conclude?

B. CHEMICAL EQUILIBRIA AND LAWS OF EQUILIBRIUM SHIFT:

EXERCISE VII.B.1:

NH_3 (g) is prepared in an isobaric reactor at 27 C°:

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2\,NH_{3\,(g)}$$

The total pressure is constant 1 atm, the initial gas mixture is: 3 moles of N_2, and 9 moles of H_2, 2 moles of NH_3:

a- Calculate $\Delta H°_{R(298K)}$ and $\Delta S°_{R(298K)}$, is this reaction exothermic or endothermic. What is the effect of an increase in temperature on the direction of equilibrium .

b- Calculate $\Delta G°_{(400K)}$. 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 N_2 reacted, alculate the partial pressures of each constituent at equilibrium.

$\Delta H°_{f\,NH3(g)}$ = -11040 cal/mol.K.

S° NH3(g) = 46 cal/mol.K.

S° H2(g) = 31,2 cal/mol.K.

S° $N_{2(g)}$ = 45,8 cal/mol.K.

EXERCISE VII.B.2:

$$C_2H_{4(g)} + H_2O_{(g)} \rightleftharpoons C_2H_5OH_{(g)} \text{ with } \Delta G°_R = -1{,}95 \text{ Kcal.}$$

A- Calculate the free enthalpy of reaction if all partial pressures are (P_{C2H5OH} =2 atm and $P_{C2H4} = P_{H2O}$ =0,25 atm).

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

C- If (P_{C2H5OH} =2 atm and P_{C2H4} = 1 atm) what is the value of P_{H2O} at the state of equilibrium.

D- Explain and discuss the effect of P_{H2O} on the direction of the reaction.

EXERCISE VII.B.3:

$$6\,Fe_2O_{3(s)} \rightleftharpoons 4\,Fe_3O_{4(s)} + O_{2(g)}$$

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 wich $O_{2(g)}$ begins to form.

	$\Delta H°_f$ Kcal	$S°_f$ 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:

Sn (w) ⇌ Sn (g)

To know which form is more stable at 25°C, we must calculate the standard free enthalpy $\Delta G°_{298K}$:

$\Delta G°_{298K} = \Delta H°_{298K} - T\Delta S°_{298K}$

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

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

$\Delta G°_{298K} = 2$Kj.

The value of the standard free enthalpy $\Delta G°_{298K}$ 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 ΔG for the reaction:

$NH_4Cl_{(s)} \rightarrow NH3_{(g)} + HCl_{(g)}$

$\Delta G = \Delta G° + RT \ln(K_p)$ with: $Kp = P_{NH3}\, P_{HCl} / P_{NH4Cl}$ and $P_{NH4Cl\ (solid)} = 1$

$\Delta G°_{298} = \sum \Delta G°_{prod} - \sum \Delta G°_{react}$

$= \Delta G°_{f\ NH3} + \Delta G°_{f\ HCl} - \Delta G°_{f\ NH4Cl}$

Finally : $\Delta G = \Delta G°_{f\ NH3} + \Delta G°_{f\ HCl} - \Delta G°_{f\ NH4Cl} + RT\ln P_{NH3} + RT\ln P_{HCl}$.

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

$\Delta G=\Delta G° + RT \ln(K_p)$

- first we must calculate $\Delta G°$:

$\Delta G°= \Delta H°-T\Delta S°$ with: $\Delta S°= -R \sum n_i \ln(x_i)$ and $\Delta H° =0$ (T is constant)

We find : $\Delta G° = RT \sum n_i \ln(x_i)$

The mole fractions:

$X_{NH3}= n/n_T = 100/(100+50+70) = 0,455.$

$X_{N2}= n/n_T = 50/(100+50+70) = 0,227.$

$X_{H2}= n/n_T = 70/(100+50+70) = 0,318.$

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

$\Delta G°= -138919$ cal .

- Calculate Kp :

$Kp= P_{NH3} / ((P_{H2})^{3/2} (P_{N2})^{1/2})$ with $P_i=X_i \times P_T$.

So: $P_{NH3}= X_{NH3} \times P_T = 0,455\ (700) = 318,50$ bar .

$P_{N2}= X_{N2} \times P_T = 0,227\ (700) = 158,90$ bar .

$P_{H2}= X_{H2} \times P_T = 0,318\ (700) = 222,60$ bar .

$Kp= 0,0076$

$\Delta G=\Delta G° + RT \ln(K_p) = -138919 + 2\ (298) \ln 0,0076 = -141827,25$ cal .

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

B. CHEMICAL EQUILIBRIA AND LAWS OF EQUILIBRIUM SHIFT:

EXERCISE VII.B.1:

a- Calculate ΔH_{R298} and ΔS_{R298} : $N_{2(g)} + 3\ H_{2(g)} \rightarrow 2\ NH_{3(g)}$

$\Delta H_{R298} = \sum ni\ \Delta H_{i\ prod} - \sum ni\ \Delta H_{i\ react} = 2\ \Delta H_{fNH3} - \Delta H_{f\ N2} - 3\Delta H_{f\ H2} = 2\ \Delta H_{fNH3} = -22080$ cal/mol .

$\Delta S_{298} = \sum ni\ S_{i\ prod} - \sum ni\ S_{i\ react} = 2\ S_{NH3} - S_{N2} - 3\ S_{H2} = -47,4$ 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 $N_{2(g)}$: $\Delta G_{R298} = \Delta H_{R298} - T\ \Delta S_{298}$ 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 $N_{2(g)}$ and $H_{2(g)}$)

b- Calculate ΔG_{R400}:

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

$\Delta H_{R400} = \Delta H_{R298} + \int \Delta Cp\ dT$ and $\Delta Cp = \sum ni\ Cp_{i\ prod} - \sum ni\ Cp_{i\ react}$.

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

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

- Deduce Kp:

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

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

$K_p = e^{-(\Delta GR298 / RT)}$ with:

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

We find: $K_p = e^{-(-7954,8 / 2\times400)} = 20,81\times10^3$

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

1,74 mol of N_2 reacted so α=1,74 mol.

	N_2	H_2	NH_3	Total
n_i:	3	9	2	
n_f:	3- α	9-3 α	2+2 α	n_T= 14-2α

$X_{N2} = nf / nT = (3-\alpha) / 14-2\alpha = 1,25/10,52 = 0,120$

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

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

  First we must calculate the mol fractions of all constituents:

  $X_i = nf / nT$

  $X_{N2} = nf / nT = (3-\alpha) / 14-2\alpha = 1,25/10,52 = 0,120$.

  $X_{H2} = nf / nT = (9-3\alpha) / 14-2\alpha = 3,78/10,52 = 0,359$.

  $X_{NH3} = nf / nT = (2+2\alpha) / 14-2\alpha = 0,521$.

  Finally, the partial pressures of each constituent:

  $P_{N2} = X_{N2} \times P_T = 0,120$ atm.

  $P_{H2} = X_{H2} \times P_T = 0,359$ atm.

  $P_{NH3} = X_{NH3} \times P_T = 0,521$ atm.

EXERCISE VII.B.2:

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

A- Calculate the free energy of reaction ΔG_R :

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

with $Kp = P_{C2H5OH} / (P_{C2H4} \times P_{H2O}) = 2/(0,25 \times 0,25) = 32$

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

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

B- The direction of reaction if all Pi=2 atm :

$Kp = P_{C2H5OH} / (P_{C2H4} \times P_{H2O}) = 2/(2 \times 2) = 0,5$.

$\Delta G_R = -1,95 \times 10^3 + 2(298) \ln 0,5 = -2363,12$ 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: $\Delta G_{R298} + RT \ln(Kp) = 0$

$K_p = e^{-(\Delta GR298 / RT)}$ with $Kp = P_{C2H5OH} / (P_{C2H4} \times P_{H2O}) = 2/(1 \times P_{H2O}) = e^{-(\Delta GR298 / RT)}$

So: $P_{H2O} = 2 / e^{-(\Delta GR298 / RT)} = 0,076$ atm.

D- The effect of P_{H2O}:

$P_{H2O} = 0,076$ atm $\Delta G_R = 0$ equilibrium state .

$P_{H2O} > 0,076$ atm $\Delta G_R < 0$ the reaction occurs in the direction of formation of $C_2H_5OH_{(g)}$ (spontaneously).

$P_{H2O} < 0,076$ atm $\Delta G_R > 0$ the reaction occurs in the direction of formation of $C_2H_{4(g)}$

EXERCISE VII.B.3:

$$6\ Fe_2O_{3(s)} \rightleftharpoons 4\ Fe_3O_{4(s)} + O_{2(g)}$$

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

$\Delta G = \Delta G° + RT \ln(K_p)$ in this case: $K_p = P_{O2(g)}$, with $Fe_3O_{4(s)}$ and $Fe_2O_{3(s)}$ are solid, so:

$\Delta G = \Delta G° + RT \ln(P_{O2(g)})$.

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:

$\Delta H°_{R298} = \sum ni\ \Delta H°_{i\ prod} - \sum ni\ \Delta H°_{i\ react}$

$= \Delta H°_{f\ O2(g)} + 4\ \Delta H°_{f\ Fe3O4(s)} - 6\ \Delta H°_{f\ Fe2O3(s)}$ with $\Delta H°_{f\ O2(g)} = 0$

$= 111,4$ K.cal.

- The standard entropy of reaction:

$\Delta S°_{R298} = \sum ni\ \Delta S°_{i\ prod} - \sum ni\ \Delta S°_{i\ react}$

$= \Delta S°_{f\ O2(g)} + 4\ \Delta S°_{f\ Fe3O4(s)} - 6\ \Delta S°_{f\ Fe2O3(s)}$

= 68,42 cal/K.

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:

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

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

Also the decreasing in temperature T, leads the equilibrium to the direction of formation of $Fe_2O_{3(s)}$.

4- Give the expression of the temperature T at wich $O_{2(g)}$ begins to form:

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

$\Delta H - T\Delta S < 0$ so $\Delta H / \Delta S < T$

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

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

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