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Thermodynamic Fundamentals & Exercises (Chemistry II)

First cycle (1st Year)
bachelor's, and engineering programs

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Preface

This Chemistry II (Thermodynamics) course booklet is intended primarily for first-year undergraduate students enrolled in the Common Core Licenses (L1) and first-year engineering students (IG1) in Science and Technology (ST) programs. The content focuses mainly on the three laws of thermodynamics and their applications, including a section dedicated to Gibbs free energy.

The primary purpose of this booklet is to serve as an educational support tool, enabling students to quickly review the fundamental concepts of Thermodynamics (Chemistry II). Its secondary function is to provide a collection of solved exercises through which students can practice applying thermodynamic formulas and principles.

This document presents both lecture notes and guided exercises in Thermodynamics, covering key topics such as general concepts, mathematical preliminaries, temperature, heat, work, calorimetry, the first law of thermodynamics and its applications in thermochemistry, the second law of thermodynamics, the third law and entropy, as well as energy and free enthalpy, among others. Each section is supplemented with typical exercises and solutions to help students better assimilate new concepts and successfully prepare for examinations.

This course booklet is the result of over ten years of teaching experience in the Department of Science and Technology (ST) at Ibn Khaldoun University of Tiaret.

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Abbreviations and Nomenclature

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c	Speed of sound, m/s
c	Specific heat, kJ/kg·K
c_p	Constant-pressure specific heat, kJ/kg·K
c_v	Constant-volume specific heat, kJ/kg·K
C	Heat capacity
C_P	Heat capacity at constant pressure
C_V	Heat capacity at constant volume
d	Total derivative
e	Coefficient of performance
f	Function
f'	Derivative function
F	Force, N
g	Gravitational acceleration, m/s2
G	Total Gibbs function, H – TS, kJ
H	Total enthalpy, U + PV , kJ_
J	Joule
K	Kelvin
K_P	Equilibrium constant
kg	Kilogram
L	Latent heat
l	Liter
m	Mass, kg
M	Molar mass, kg/kmol
m_f	Mass fraction
n	Number of moles, mol
p	Power
P	Pressure, kPa
Pa	Pascal
P_i	Partial pressure, kPa
P_T	Total pressure, kPa
P0	Surroundings pressure, kPa
q	Heat transfer per unit mass, kJ/kg
Q	Total heat transfer, kJ
R	Universal gas constant, J/k.mol.
s	Specific entropy, kJ/kg·K
S	Total entropy, kJ/K
STP	Standard Temperature and Pressure
t	Time, s
T	Temperature, °C or K

μ	Specific internal energy, kJ/kg
U	Total internal energy, kJ
v	Specific volume, m^3/kg
V	Total volume, m^3
w	Work per unit mass, kJ/kg
W	Total work, kJ
W_{rev}	Reversible work, kJ
W_{irrev}	Irreversible work, kJ
X_i	Mole fraction

Subscripts

∂	Partial derivative
Δ	Difference or change
γ	Adiabatic index
α	Isobaric thermal expansion coefficient
β	Isochoric pressure coefficient
χ	Isothermal compressibility coefficient
ρ	Density, kg/m
0	Initial state
E	Equilibrium
ext	External
f	Final state
F	Fusion (melting)
g	Ice
i	Initial state
rever	Reversible
irrev	Irreversible
int	Internal
surr	Surroundings
sys	System
v	Water vapor
1	Initial or inlet state
2	Final or exit state

Chapter I

Basic Concepts in Thermodynamics

Chapter I: Basic Concepts in Thermodynamics

Thermodynamics as a Science emerged at the beginning of the 18th century, coinciding with the advent of steam engines an innovation that marked the Industrial Revolution. This branch of science is devoted to the study of energy transformations, as well as the energetic characteristics associated with physical and chemical transformations of matter.

Thermodynamics is broadly categorized into several branches:

Classical Thermodynamics: This branch focuses on the macroscopic behavior of systems, utilizing measurable quantities such as pressure (P), temperature (T), and volume (V).

Chemical Thermodynamics: This area of study investigates the heat changes associated with chemical reactions and the thermodynamic properties of chemical equilibria.

Statistical Thermodynamics: This branch examines systems from a microscopic perspective, grounding its principles in statistical mechanics to explain macroscopic properties.

Technical Thermodynamics: This applied field of thermodynamics is concerned with the analysis of thermal machines (e.g., engines), refrigeration systems, and other similar engineering applications.

I.1 Concept of System and State Functions

I.1.1 States of Matter

There are three states of matter: solid, liquid, and gas. It is possible to transition from one state to another (Figure I.1).

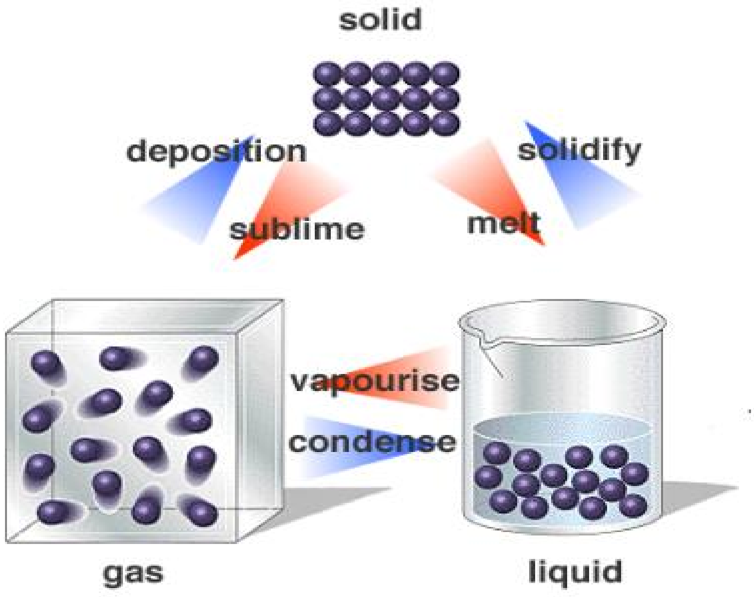
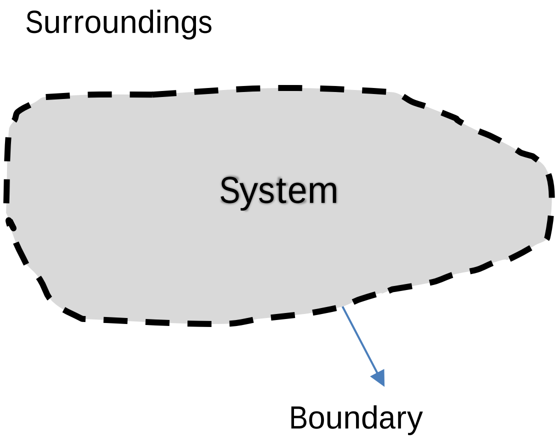


Figure I.1. The solid, liquid and gas phases of matter.

I.1.2 The Thermodynamic System

A thermodynamic system refers to a defined portion of the universe that contains matter or represents the object of study. It is separated from the rest of the universe by a real or hypothetical boundary. Everything outside this boundary constitutes the surroundings, or the external environment of the system (i.e., the rest of the universe).

Universe = system + external environment (surrondings)+boundary.



Thermodynamic systems are classified based on their ability to exchange energy and/or matter with their surroundings, as summarized in Table I-1 and Figure I-2.

- **Open:** Mass and Energy can transfer between the System and the Surroundings
- **Closed:** Energy can transfer between the System and the Surroundings, but NOT mass
- **Isolated:** Neither Mass nor Energy can transfer between the System and the Surroundings

Table I.1**:** Types of Thermodynamic Systems, Energy and Matter Exchange, with Examples

System	Energy Exchange	Matter Exchange	Exemple
Open	Yes	Yes	Living organism
Closed	Yes	No	Sealed flask
Isolated	No	No	The Universe

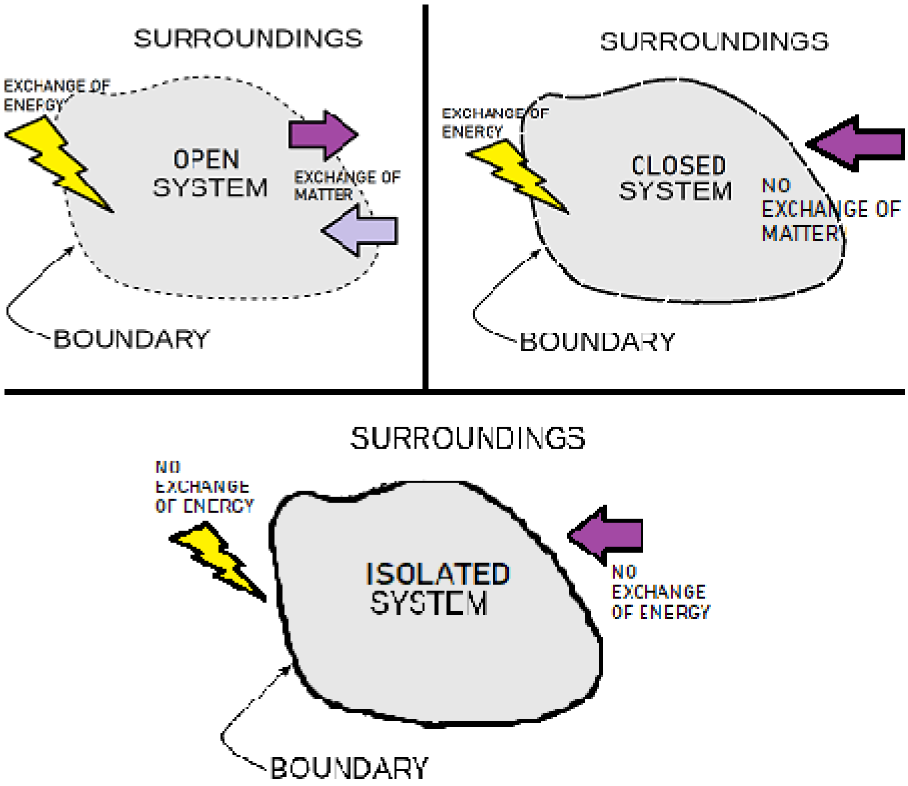


Figure I.2 : Energy and matter exchanges for open, closed, and isolated Systems

I.1.3 State of a System

The state of a system at a given moment is described by a set of macroscopic variables known as state variables.

Describing thermodynamic systems effectively requires considering several key aspects:

- **Macroscopic Properties:** Defining a few macroscopic variables, such as pressure (P), temperature (T), volume (V), number of moles (n), and mass (m).
- **Homogeneity or Heterogeneity:** Determining whether the system consists of a single phase (homogeneous) or multiple phases (heterogeneous).
- **Equilibrium State:** Ascertaining if the system is in an equilibrium state, where its macroscopic properties are constant over time.
- **Number of Components:** Identifying the number of independent chemical species present in the system.

a) State Variables

State variables, whether extensive or intensive, characterize the condition of the system. Extensive variables are proportional to the quantity of matter (e.g., volume), while intensive variables are independent of the system's size or the amount of matter (e.g., pressure and temperature). Unlike extensive variables, intensive variables are not additive.

Extensive Variable: A property that is directly proportional to the amount of matter in a system and is additive. Examples include mass, volume, and the quantity of substance (number of moles n, m, V, ….).

Intensive Variable: A property that is independent of the amount of matter in a system. Examples include temperature(T), concentration, and density.

I.1.4 State Function

A state function is a physical quantity that depends solely on the initial and final states of the system and is independent of the path taken during the transformation.
A state function can defines the state of a system, such as pressure, temperature, volume, and the number of moles.

I.1.5 Differential of a State Function and Condition of Exact Differential (D.T.E)

For a function $f(x,y)$ of two variables x and y, the differential $df\ (x,y)$ is defined as follows:

$$df(x,y) = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \qquad (I.1)$$

, This expression represents the differential of the function $f(x,y)$

$\left(\frac{\partial f}{\partial x}\right)_y$: the partial derivative of f with respect to x, keeping y constant.

$\left(\frac{\partial f}{\partial y}\right)_x$: the partial derivative of f with respect to y, keeping x constant.

For a mathematical function to be considered a **state function**, its differential must be an **exact total differential (ETD)**. To verify this condition, the **cross partial derivatives must be equal**:

$$\left(\frac{\partial\left(\frac{\partial f}{\partial x}\right)_y}{\partial y}\right)_x = \left(\frac{\partial\left(\frac{\partial f}{\partial y}\right)_x}{\partial x}\right)_y \qquad (I.2)$$

This condition ensures that the differential is path-independent and that the function depends only on the state of the system.

I.1.5 Exercises and Solutions

Exercise 1

Calculate the second-order partial derivatives of the following functions:

(a) $f(x,y) = x^2y + y^3$;

(b) $f(x,y) = x^2 + 3xy^2 + y^5$;

(c) $f(x,y) = \frac{x^2}{y} + \frac{y^2}{x}$;

(d) $f(x,y) = x\cos y - y\cos x$.

Solution 1

$$a\begin{cases} f'_x = 2\,xy \\ f'_y = x^2 + 3xy^2 \end{cases} \Rightarrow \begin{cases} f''_{x^2} = 2\,y \\ f''_{y^2} = 6y \end{cases} \Rightarrow \begin{cases} (f'_x)'_y = 2x \\ \left(f'_y\right)'_x = 2x \end{cases}$$

$$b\begin{cases} f'_x = 2x + 3y^2 \\ f'_y = 6xy + 5y^4 \end{cases} \Rightarrow \begin{cases} f''_{x^2} = 2 \\ f''_{y^2} = 6x + 20y \end{cases} \Rightarrow \begin{cases} (f'_x)'_y = 6y \\ \left(f'_y\right)'_x = 6y \end{cases}$$

$$c\begin{cases} f'_x = \frac{2x}{y} + \frac{y^2}{x^2} \\ f'_y = -\frac{x^2}{y^2} + \frac{2y}{x} \end{cases} \Rightarrow \begin{cases} f''_{x^2} = \frac{2}{y} + \frac{2y^2}{x^3} \\ f''_{y^2} = \frac{2x^2}{y^3} + \frac{2}{x} \end{cases} \Rightarrow \begin{cases} (f'_x)'_y = -\frac{2x}{y^2} - \frac{2y}{x^2} \\ \left(f'_y\right)'_x = -\frac{2x}{y^2} - \frac{2y}{x^2} \end{cases}$$

$$d\begin{cases} f'_x = \cos y + y\sin x \\ f'_y = -x\sin y - \cos x \end{cases} \Rightarrow \begin{cases} f''_{x^2} = y\cos x \\ f''_{y^2} = -x\cos y \end{cases} \Rightarrow \begin{cases} (f'_x)'_y = -\sin y + \sin x \\ \left(f'_y\right)'_x = -\sin y + \sin x \end{cases}$$

Exercise 2

Let $f(x,y)$ be a function: $f(x,y) = x^2y^2 + 3x + y^3$

a- Calculate the partial derivatives: $\frac{\partial f}{\partial x}$ and $\frac{\partial f}{\partial y}$, and deduce the differential (df).

b- Calculate $\frac{\partial^2 f}{\partial x\partial y}$ and $\frac{\partial^2 f}{\partial y\partial x}$, and conclude.

Solution 2

a- $\begin{cases} A = f'_x = 2xy^2 + 3 \\ B = f'_y = 2yx^2 + 3y \end{cases} \Rightarrow df = (2xy^2 + 3)\,dx + (2yx^2 + 3y)dy$

b- $\begin{cases} \frac{\partial^2 f}{\partial x\partial y} = 4xy \\ \frac{\partial^2 f}{\partial y\partial x} = 4xy \end{cases}$ => Therefore, the function $f(x,y)$ is an exact total differential.

Exercise 3

Are $\delta z = (4xy + 3y^2 - x)dx + (x^2 + 2xy)\,dy$ and $\delta z = 2xydx + (x^2 + \cos y)dy$ exact total differentials (ETD) ?

Solution 3

- **$\delta z = (4xy + 3y^2 - x)dx + (x^2 + 2xy)\,dy$**

Here , $\begin{cases} A = \frac{\partial z}{\partial x} = z'_x = 4xy + 3y^2 - x \\ B = \frac{\partial z}{\partial y} = z'_y = x^2 + 2xy \end{cases} \Rightarrow \begin{cases} \frac{\partial^2 z}{\partial x \partial y} = 4x + 6y \\ \frac{\partial^2 z}{\partial y \partial x} = 2x + 2 \end{cases}$ from the calculate mixed partial derivatives , we see that these are not equal. Therefore, this differential is not an exact total differential (DTE).

- **$\delta z = 2xydx + (x^2 + \cos y)dy$**

$\begin{cases} A = \frac{\partial z}{\partial x} = z'_x = 2xy \\ B = \frac{\partial z}{\partial y} = z'_y = (x^2 + \cos y) \end{cases} \Rightarrow \begin{cases} \frac{\partial^2 z}{\partial x \partial y} = 2x \\ \frac{\partial^2 z}{\partial y \partial x} = 2x \end{cases}$, we see that these partial derivatives are equal, so this differential is an exact total differential (DTE).

Exercise 4

Let $\delta W = \frac{nRT}{P}\,dP - n.R.dT$ and $\delta Q = n.C_p.dT - \frac{nRT}{P}\,dP$. Show that W and Q are not state functions.

Solution 4

- $\delta W = \frac{nRT}{P}\,dP - n.R.dT$

$\begin{cases} A = \frac{nRT}{P} \\ B = -nR \end{cases} \Rightarrow \begin{cases} A'_T = \frac{nR}{P} \\ B'_p = 0 \end{cases} \Rightarrow A'_T \neq B'_p \Rightarrow$ Therefore, it is not an exact differential (i.e., not an exact total differential), which implies that $W$is not a state function.

- $\delta Q = n.C_p.dT - \frac{nRT}{P}\,dP$

$\begin{cases} A = \text{n.Cp} \\ B = -\frac{nRT}{P} \end{cases}$ => $\begin{cases} A'_T = 0 \\ B'_p = -\frac{nR}{P} \end{cases}$ =>$A'_T \neq B'_p \Rightarrow$ Therefore, it is not a total differential ⇒

W is not a state function..

Exercise 5

The equation of state of a gas is given by the relation:

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

a- Determine the equation for the following partial derivatives:

$\left(\frac{\partial P}{\partial T}\right)_v$ and $\left(\frac{\partial P}{\partial V}\right)_T$

b- Show that dP is an exact total differential (ETD).

Solution 5

a- The partial derivatives $\left(\frac{\partial P}{\partial T}\right)_v$ and $\left(\frac{\partial P}{\partial V}\right)_T$ **:**

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{RT}{(v-b)^2}$$

b- Exact Differential ETD

$$dP = \left(\frac{\partial P}{\partial T}\right)_v dT + \left(\frac{\partial P}{\partial V}\right)_T dV => dP = \frac{R}{v-b}\, dT + \frac{RT}{(v-b)^2}\, dV$$

$$\frac{d}{dV}\left(\frac{\partial P}{\partial T}\right) = -\frac{R}{(v-b)^2}$$

$$\frac{d}{dT}\left(\frac{\partial P}{\partial V}\right) = -\frac{R}{(v-b)^2}$$

⇨ Since the mixed partials are equal,$d$is an exact differential.

I.2 Fundamental Laws of Ideal Gases

I.2.1 Ideal Gas

The ideal gas is an ideal thermodynamic system where the interactions between particles are neglected. For a classical ideal gas (where quantum effects are neglected), the equation of state (ideal gas law) is

$$PV = nRT \qquad (I.3)$$

Where :

- P is the pressure.
- V is the volume.
- n is the number of moles.
- R is the ideal gas constant.
- T is the absolute temperature (in kelvin).
- R = 831 J / K.mol is the ideal gas constant.

I.2.2 Boyle–Mariotte's Law

This law describes the relationship between pressure *(P)* and volume *(V)* under the condition that temperature and the amount of substance (in moles) remain constant. According to it, the volume of a gas varies inversely with the pressure exerted on it.

Mathematically, this is expressed as:

$$P_1V_1 = P_2V_2 = P_3V_3 = C^{te} \qquad (I.4)$$

I.2.3 Gay-Lussac's Law

The volume of a gas varies directly with its temperature when the pressure and the amount of substance (in moles) are held constant (i.e.,P= constant).

This relationship is represented as:

$$\frac{V1}{V2} = \frac{T1}{T2} \qquad (I.5)$$

I.2.4 Charles's Law

The pressure of a gas varies directly with its temperature when the volume and the amount of substance (in moles) are kept constant (i.e.,V= constant).

This relationship is expressed as:

$$P_1/P_2 = T_1/T_2 \qquad (I.6)$$

I.2.5 Mole fraction

The mole fraction of a component 'i' (X_i) is the ratio of the number of moles of that component (n_i) to the total number of moles in the mixture ($\sum ni$).

$$X_i = \sum n_i$$

Mole fraction is a **dimensionless quantity** because it's a ratio of two quantities with the same unit (moles).

Calculating Moles (ni): we can determine the number of moles of a gas (ni) in two ways:

- Using mass and molar mass:

$$ni = \frac{\text{given mass}}{\text{molar mass}}$$

- Using volume and molar volume (for gases at STP):

$$ni = \frac{\text{given volume}}{\text{molar volume } (22.4\ \text{L/mol})}$$

- **Sum of Mole Fractions:** The sum of the mole fractions of all components in a mixture is always equal to one.

$$\sum X_i = 1$$

I.2.6 Pressure

Pressure is defined as a normal force exerted by a fluid per unit area, it has unit of (N/m^2), which is called a pascal (Pa). That is, $1\ Pa = 1\ N/m^2$.

Also pressure have other unit as bar , atm,psi and kgf/cm^2 :

1 bar = 10^5 Pa = 0.1 MPa = 100 kPa

1 atm=101,325 Pa = 101.325 kPa = 1.01325 bars

1 atm = 14.696 psi.

1 kgf/cm^2 =9.807 N/cm^2 = 9.807 × 104N/m^2 = 9.807 × 104 Pa= 0.9807 bar =0.9679 atm

Atmospheric pressure is measured by a device called a **barometer**; thus, the atmospheric pressure is often referred to as the barometric pressure. Which give by :

$$P_{atm} = \rho g h$$

where ρ is the density of mercury, g is the local gravitational acceleration, and h is the height of the mercury column above the free surface.

I.2.7 Dalton's Law of Partial Pressures:

The pressure of a gas results from the numerous collisions of its atoms or molecules against the walls of the container. If a gas mixture is present, the total pressure (P_t) of the mixture is equal to the sum of the partial pressures (P_i) of its individual components.

$$P_t = \sum P_i \qquad (I.7)$$

$$P_{tot} = P_1 + P_2 + P_3 + \ldots = \sum P_i$$

I.3 Thermometry

Thermometry is the science of measuring temperature, and a thermometer is the instrument used for that purpose (Figure I.3). When a thermometer is in thermal equilibrium with an object, meaning there's no net heat transfer between them, the temperature indicated by the thermometer is indeed the temperature of the object. This is a direct consequence of the zeroth law of thermodynamics.

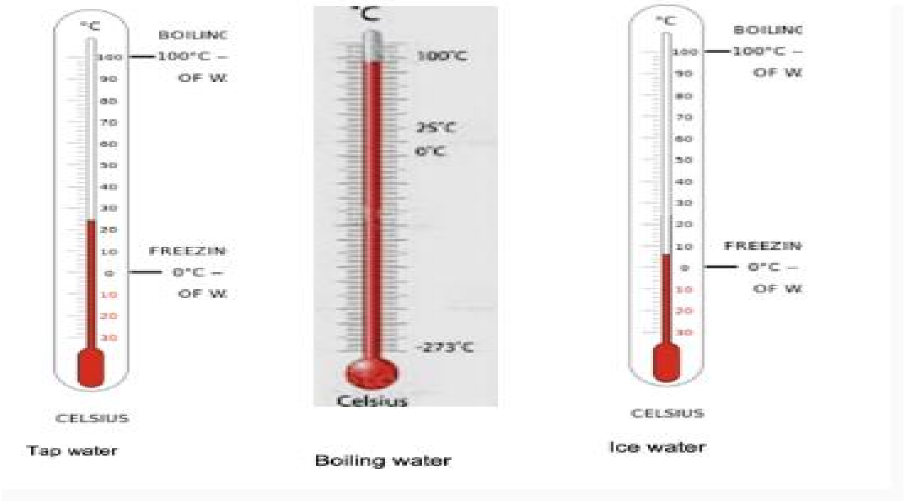


Figure I.3. Thermometer

I.4 Temperature

Temperature Concept: Temperature (T) measures a body's hotness or coldness.

1.9.2. Temperature Scales:

Common scales include **Celsius**, **Fahrenheit**, **Kelvin**, and **Rankine**.

- **Celsius (°C):** Water freezes at 0°C, boils at 100°C.
- **Fahrenheit (°F):** Water freezes at 32°F, boils at 212°F. T(°F) = 1.8 × T(°C) + 32
- **Kelvin (K):** The absolute **SI unit** of temperature. T(K) = T(°C) + 273.15
- **Rankine (R):** An absolute scale used in Anglo-Saxon countries. T(R) = T(°F) + 459.67

I.5 Zeroth Law of Thermodynamics

The Zeroth Law states that if two bodies (**A** and **B**) are each in thermal equilibrium with a third body (C), then they are also in thermal equilibrium with each other. If $A \rightleftarrows C$ and $B \rightleftarrows C$, then $A \rightleftarrows B$ (Transitivity of Equilibrium) .

$$T\ (\text{in K}) = T\ (\text{in °C}) + 273.15 \qquad (I.8)$$

I.6 Transformations of the State of a System (Thermodynamic Processes)

A system undergoes a **thermodynamic process** when there is an energetic change within the system, associated with alterations in properties such as pressure, volume, internal energy, temperature, or any form of heat transfer.

Exemple : The PV diagram of a compression process

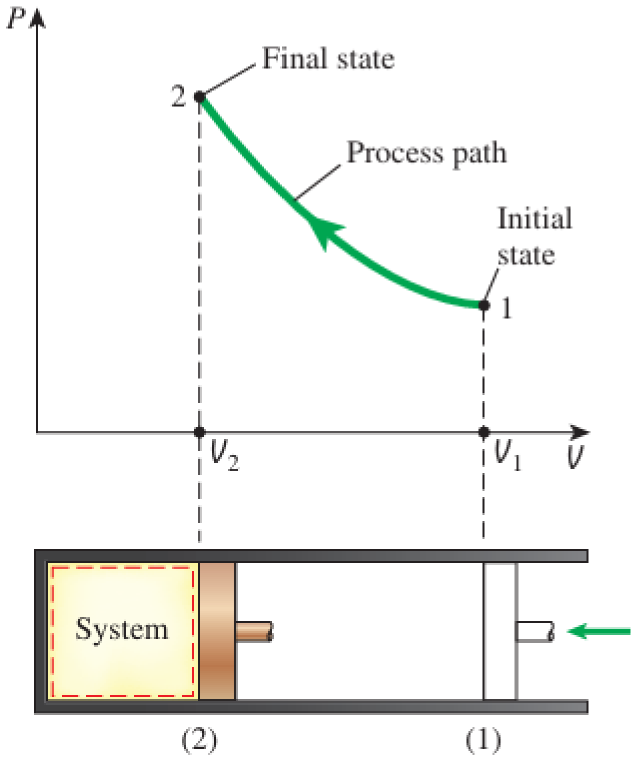


Figure 3.I : P-V diagram of a compression process

There are various types of thermodynamic processes, each possessing unique characteristics; such a :

Adiabatic Process: A process during which no heat is transferred into or out of the system (Q=0).

Isochoric Process: A process where the volume remains constant (dV=0), implying that the system performs no work.

Isobaric Process: A process in which the pressure remains constant (dP=0).

Isothermal Process: A process in which the temperature remains constant (dT=0).

Cyclic Process: A series of processes where, after certain interchanges of heat and work, the system returns to its initial state.

Reversible Process: A reversible process is one whose direction can be reversed by an infinitesimal change in some property of the system.

Irreversible Process: An irreversible process is one whose direction cannot be reversed by an infinitesimal change in some property of the system.

I.7. Clapeyron Diagram

A Clapeyron diagram, also known as a pressure-volume (P-V) diagram, is a thermodynamic diagram that plots the pressure of a system against its volume (P = f(V)). It visually represents the relationship between these two variables during a thermodynamic process (isochoric, isobaric, isothermal, and adiabatic) (Figure I.4). This diagram is particularly useful for analyzing processes involving phase changes or work done by a system.

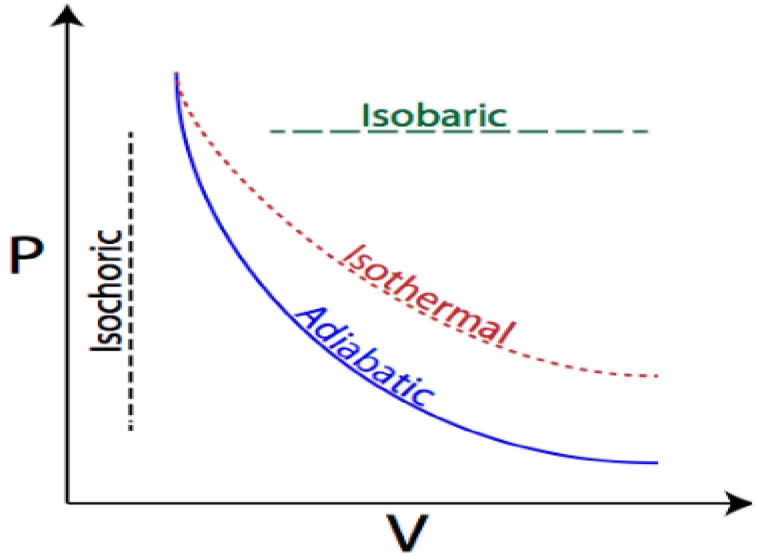


Figure I .4 : P-V diagram of a compression process

I.8. Thermodynamic Equilibrium:

A system is considered to be in **equilibrium** when its properties do not change appreciably over the interval of interest (i.e., within the observation time).

A thermodynamic system is in **thermodynamic equilibrium** if it simultaneously achieves chemical, mechanical, and thermal equilibrium, and all relevant parameters cease to vary with time.

- **Thermal equilibrium** is achieved when the temperature is uniform throughout the entire system.

- **Mechanical equilibrium** is achieved when there is no net change in pressure at any point within the system.
- **Chemical equilibrium** is achieved when the chemical composition of a system remains constant over time.

Exercises and Solutions

Exercise 1

1) List the different units of pressure and provide the relationships between these units.

2) Convert 350 mmHg to bar, Pa, and atm.

3) State the different temperature scales and provide the relationships between these scales.

4) Convert: 25 °C and -100°C to °F, 0°F to °C and K, 0 K to °C and °F.

5) Calculate the value of the ideal gas constant R in L.atm./mol.K,, J/mol.K,, and cal/mol.K,,
knowing that one mole of an ideal gas occupies a volume of 22.4 L at a pressure of 1 atm and a temperature of 0 °C.

Solution 1

1) Pressure is defined as force per unit area. Common units of pressure include:

Pascal (Pa): The SI unit of pressure (1 Pa = 1 N/m^2), Atmosphere (atm): A historical unit, approximately the average atmospheric pressure at sea level, Bar (bar): A unit very close to 1 atm, often used in meteorology and chemistry,and Millimeters of Mercury (mmHg) or Torr: Used in manometry, based on the height of a mercury column.
Relationships between these units: 1atm=101325Pa , 1atm=1.01325bar , 1atm=760mmHg, 1atm=760Torr, 1bar=105Pa, 1bar=100kPa, 1Torr=1mmHg

2) Convert 350 mmHg to bar, Pa, and atm:

Given pressure P=350mmHg.

- **To atm:** Patm=350mmHg×760mmHg1atm≈0.4605atm
- **To Pa:** Using the conversion from atm to Pa: PPa=0.4605atm×1atm101325Pa ≈46660Pa (or 4.666×104Pa)
- **To bar:** Using the conversion from atm to bar: Pbar=0.4605atm×1atm1.01325bar ≈0.4666bar

3) Relationships between these scales:

- Celsius to Kelvin: T_K=T °C +273.15
- Celsius to Fahrenheit: $T_{°F}$= (T°C×9/5) + 32
- Fahrenheit to Celsius: $T_{°C}$= (T°F−32)×5/9

- Fahrenheit to Kelvin: T_K= (T°F−32)×5/9+273.15

4) Convert Temperatures:

- **25 °C to °F :** T°F = (25×9/5)+32=45+32 = **77°F**
- **-100 °C to °F:** T°F = (−100×9/5)+32 =−180+32 = **−148°F**
- **0 °F to °C:** T°C=(0−32)×5/9 = −32×95 = **−17.78°C**
- **0 °F to K:** TK = (−17.78)+273.15 = **255.37K**
- **0 K to °C:** T°C = 0−273.15 = **−273.15°C**
- **0 K to °F:** T°F = (−273.15×9/5)+32 =−491.67+32 = **−459.67°F**

5) Calculate the value of the ideal gas constant R:

Given: n=1mol ; V=22.4L ;P=1atm ; T=0°C=273.15K

The ideal gas law is PV=nRT. Rearranging for R:

R=PV/nT

- **In L·atm/(mol·K):** R=(1atm)×(22.4L)/(1mol)×(273.15K) =**0.082057** $L\cdot atm\cdot mol^{-1}\cdot K^{-1}$
- **In J/(mol·K):** First, convert L·atm to Joules. 1L·atm=101.325J (since 1atm=101325Pa and $1L=10^{-3}m^3$) $1L\cdot atm=(10^{-3}m^3)\times(101325Pa)=101.325J$

  $R=0.082057L\cdot atm\cdot mol^{-1}\cdot K^{-1}\times 101.325J\cdot(L\cdot atm)^{-1}$

  R=**8.314 J·** $mol^{-1}\cdot K^{-1}$

- **In cal/(mol·K):** Using the conversion 1cal=4.184J: $R=8.314J\ mol^{-1}\cdot K^{-1}\times 4.184J1cal$ R=**1.987** $cal\cdot mol^{-1}\cdot K^{-1}$

Exercise 2

An aerosol can contains 50 mL of gas (considered ideal) at a pressure of 1.0×10^7 Pa and a temperature of 20 °C.

1) Calculate the amount of substance (in moles) of this gas.
2) Deduce its molar volume under these conditions.
3) Using Boyle's Law (Mariotte's Law), calculate the volume of gas the can could release into the air at 20 °C and atmospheric pressure.

Solution 2

1. Calculating the amount of substance (in moles) of the gas in the can before use

We use the ideal gas law:

$$PV = nRT \Rightarrow n = PV/(RT)$$

Where: - $V = 50\ 10\text{-}6\ m^3$

- $T = 273+20 = 293$ K

$$n = 1\ 10^7 * 5\ 10^{-5} / (8{,}31*293) = 0{,}205 \text{ mol.}$$

2. Calculating the molar volume under these conditions

$$-V_m = RT/P \Rightarrow V_m = 8{,}31*293/107 = 2{,}43\ 10^{-4}\ m^3/mol = 0{,}243\ L/mol$$

3. Calculating the volume of gas released into the air at 20°C and atmospheric pressure

Using Boyle's Law (Mariotte's Law):

$$PV = P'V'$$

Where :

$P = 10^7$ Pa ;

$V = 5\ 10^{-5}\ m^3$;

$P' = 105$ Pa

The expanded volume V' is :

$V' = PV/P' = 107 * 5\ 10^{-5} / 10^{5} = 5\ 10^{-3}\ m^{3} = 5\ L.$

The actual released gas volume is : $V_{released} = 5 - 0{,}05 = 4{,}95$ L.

Exercise 3

Problem 1

A balloon contains 18.2 g of nitrogen gas (N_2) at 20 °C, occupying a volume of 16 L under a pressure of 99.3 kPa. What will the pressure become if :

- The temperature is increased to 50 °C,
- The volume is reduced to 5 L, and
- 12.8 g of oxygen gas (O_2) is added?

Problem 2

A balloon contains a mixture of 36 g of carbon dioxide (CO_2) and 6.0 moles of nitrogen (N_2). The total pressure of the system is 253 kPa. What is the partial pressure of each gas?

Solution 3

Problem 1

Data given:

- Mass of N_2, $mN_2 = 18.2$g
- Moles of N_2, $n_1 = 18.2/28 = 0.65$mol
- Initial temperature, $T_1 = 20°C + 273 = 293$K
- Initial volume, $V_1 = 16.0$L
- Initial pressure, $P_1 = 99.3$kPa
- Final temperature, $T_2 = 50°C + 273 = 323$K
- Final volume, $V_2 = 16 - 5 = 11$L
- Moles after adding O_2, $n_2 = 0.65 + 3212.8 = 1.05$mol

Using the combined gas law:

$P_1V_1/n_1T_1 = P_2V_2/n_2T_2$

=> P_2= 99,3x16x1,05x323/0,65x293x11

=> P_2=257,20 kPa

Final pressure: P_2=257.20 kPa.

Problem 2

Data given:

- Moles of CO_2, $n_1 = 36/44 = 0.82$mol
- Moles of N_2, $n_2 = 6.0$mol
- Total moles, $n_{tota\ l}$= 0.82+6.0 = 6.82mol
- Total pressure, $P_{tota\ l}$= 253kPa

Using Dalton's Law of Partial Pressures:

For CO_2 :

n_1 = 0.82 mol of CO_2. (n_1 = 0.82mol), and n_2 = 6.0 mol of N_2.

n_{totale} = (0.82 + 6.0) = 6.82 mol of gas.

P_{totale} = 253 KPa

$n_1 /n_{totale} = P_1/ P_{totale}$

0.82/ 6.82= P_1/ 253 ➔ P_1 = 30.4KPa.

For N_2 :

$PN2=P_{total} - P_{CO2=}253-30.4=222.6$kPa

Exercise 4

How many grams of CO_2 are contained in a 3.5 L vessel at a pressure of 101.6 kPa and a temperature of 26.3°C?

Solution 4

Mass of CO_2 m_{CO2}= ? ;

Data given:

- Volume, V = 3.5 L= 3.5×10^{-3} m^3
- Pressure, P = 101.6 kPa = 101600 Pa
- Temperature, $T = 26.3°C$ = 299.45 K
- Molar mass of $\mathbf{CO_2}$, M = 44 g/mol
- Universal gas constant R=8,32 J/mol.K,

n =m/M et PV=nRT =>

m_{CO_2}=n× M=(PV/RT)×M ;

AN :

$m_{CO_2}=(101{,}6\times 10^{3}\ \times 3{,}5\times 10^{-3}/8{,}32\times 299{,}45)\times 44$

Mass of CO_2 : m_{CO_2}=6,29g

Exercise 5

The analysis of a 100g sample of air collected at sea level yields the following results: N_2: 75.52%, O_2: 23.15%, Ar: 1.28%, CO_2: 0.046%.

1) Calculate the number of moles of each gas present in this sample.

2) Calculate the mole fraction as well as the partial pressure of each gas.

Given Data: Pt = 1 atm. N(14), O(16), Ar(40), C(12).

Solution 5

1) Calculate the number of moles of each gas present in this sample.

Calculate the mass of each gas in the 100g sample.

- Mass of N_2 =100g×0.7552 = 75.52g
- Mass of O_2 =100g×0.2315 = 23.15g
- Mass of Ar =100g×0.0128 = 1.28g
- Mass of CO_2 =100g×0.00046 = 0.046g

Calculate the molar mass of each gas**.**

- Molar mass of N_2 = 2×14= 28g/mol
- Molar mass of O_2 = 2×16= 32g/mol
- Molar mass of Ar = 40g/mol
- Molar mass of CO = 12+(2×16) = 12+32 = 44g/mol

The number of moles (n) is calculated as molar massmass.

- nN_2 = 28g/mol75.52g = 2.697mol
- nO_2 = 32g/mol23.15g = 0.723mol

- nAr = 40g/mol1.28g = 0.032mol
- nCO_2 = 44g/mol0.046g = 0.00105mol

Calculate the total number of moles (ntotal):

ntotal=nN_2+nO_2+nAr+nCO_2 ntotal=2.697+0.723+0.032+0.00105 = 3.45305mol

2) Calculate the mole fraction as well as the partial pressure of each gas.

Mole fraction (Xi): Xi= ni / n_{total}

- X of N_2 = 2.697mol / 3.45305mol = 0.7811
- X of O_2 = 0.723mol / 3.45305mol = 0.2094
- X of Ar = 0.032mol / 3.45305mol = 0.0093
- X of CO_2 = 0.00105mol / 3.45305mol = 0.0003

(Note: The sum of mole fractions should be approximately 1.0. 0.7811+0.2094+0.0093+0.0003=1.0001. The slight deviation is due to rounding.)

Partial pressure (Pi): According to Dalton's Law of Partial Pressures, Pi=Xi×Pt. Given Pt =1atm.

- P of N_2 =0.7811×1atm = 0.7811atm
- P of O_2 =0.2094×1atm = 0.2094atm
- P of Ar =0.0093×1atm = 0.0093atm
- P of CO_2 =0.0003×1atm = 0.0003atm

Chapter II

Heat Q, Work W, and Internal Energy U

Chapter II: Heat Q, Work W, and Internal Energy U

II.1. Calorimetry

Calorimetry is the measurement of heat transfers. It's carried out in specialized containers called calorimeters.

A calorimeter is an isolated system, or a thermally insulated enclosure (like a thermos bottle or a calorimetric vessel), that is carefully designed to prevent heat exchange with the external environment. It's also sealed with a stopper to prevent any exchange of matter (Figure II.1).

Calorimeters are used to measure the thermal properties of substances, particularly their heat capacities or the energy of reactions. This is done by measuring the temperature changes that occur within the calorimetric vessel, with heat transfers taking place under atmospheric pressure.

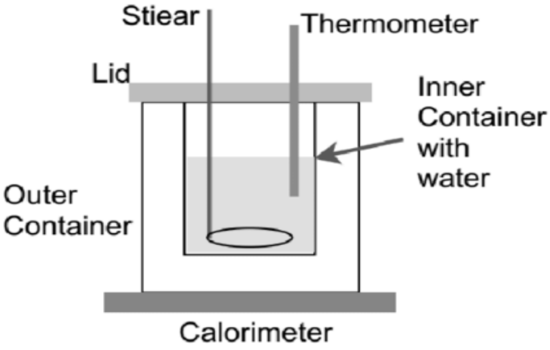
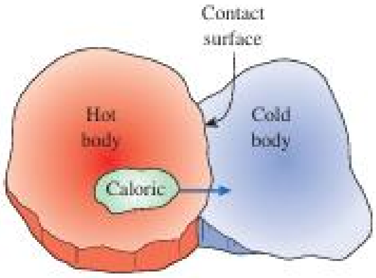


Figure II.1: Calorimeter

II.2. Heat Q :

Heat, denoted by Q, is a measure of the amount of energy transferred from a hot source (Hot body) to a colder system (Cold body) in such a way that the temperature of the system increases. Heat represents the quantity of energy exchanged in a disordered manner between systems or bodies.



The amount of heat is expressed in joules (J) or kilocalories (kcal), and is given by the equation:

$$Q = m.c.(T_2-T_1) \qquad (II.1)$$

Where:

- *m* is the mass of the body (in kilograms, kg),
- *c* is the specific heat capacity of the substance (in J/kg·K or cal/kg·K),
- T_2 is the final temperature (state *2*),
- T_1 is the initial temperature (state *1*).

Units of heat : [Q] = Joule (J) ; [Q] = calorie (cal)

a- Specific Heat at Constant Pressure

The heat transferred at constant pressure (Qp) is given by the equation:

$$Q_p = m.Cp.\Delta T \qquad (II.2)$$

Cp is the specific heat capacity at constant pressure, expressed in Joules per gram per Kelvin ($J.g^{-1}.K^{-1}$).

m is the mass of the substance in grams (g).

Qp is the quantity of heat exchanged during the process at constant pressure, expressed in Joules (J).

b- Specific Heat at Constant Volume

The heat transferred at constant volume (Qv) is given by the equation:

$$Q_v = m.Cv.\Delta T \qquad (II.3)$$

Where:

C_v is the specific heat capacity at constant volume, expressed in Joules per gram per Kelvin ($J.g^{-1}.K^{-1}$).

m is the mass of the substance in grams (g).

Q_v is the quantity of heat exchanged during the processat constant volume, expressed in Joules (J).

II.2.1 Latent Heat

This is the heat (L) required for 1 kilogram of a pure substance to undergo a change of state at a constant temperature. It is defined by:

$$Q = m.L_m \qquad (II.4)$$

Where:

m is the mass of the substance considered.

L_m is the specific latent heat associated with a change of state.

II.2.2 Specific Heat Capacity (c)

Specific heat capacity is the heat needed to raise the temperature of one unit mass (1g) or one mole (1mol) of a substance by 1 °C (or 1 K).

- **c_V' (c_V)**: At constant volume.
- **c_P' (c_P)**: At constant pressure.

Example: Liquid water: $c = 1 cal\cdot g^{-1}\cdot°C^{-1}$

II.2.3 Heat Capacity (C)

Heat capacity is the product of a substance's specific heat capacity (molar) and its mass (or moles). It's measured in cal/K or J/K.

$C=m\cdot c'=n\cdot c$ Thus: $Q=C\cdot\Delta T$

- **C_V**: At constant volume.
- **C_P**: At constant pressure.

For pure solids/liquids: $c_P \approx c_V$ and $C_P \approx C_V$. For pure gases: $c_P \neq c_V$ and $C_P \neq C_V$

II.2.4 Heat Capacity for Ideal Gases

- **Monoatomic ideal gases (e.g., He, Ar):** $c_V=3R/2$; $c_P=5R/2$
- **Diatomic ideal gases (e.g.,** O2, N2**):** $c_V=5R/2$; $c_P=7R/2$
- **Relationship between** cP **and** cV **(Mayer's Relation):** $c_P - c_V = R$; Also: $\gamma = c_P / c_V$ (adiabatic index)

From these, we find: $c_V = R/\gamma^{-1}$ and $c_P= \gamma R/\gamma^{-1}$

II.2.6 Temperature

Temperature is a fundamental physical quantity (measured in units denoted by *T*) that describes the macroscopic thermal state of a system or body. It represents a global, statistical property related to the average kinetic energy of particles within the system.

- Thermal Response: Heating a body increases its temperature, reflecting enhanced molecular motion.
- Measurement: Quantified using thermometers calibrated to standardized scales:
  - Celsius (°C): Relative scale (0°C = water freezing point, 100°C = boiling point at 1 atm).
  - Kelvin (K): Absolute scale (0 K = absolute zero; T(K) = T(°C) + 273.15).
  - Fahrenheit (°F): Empirical scale (32°F = water freezing point, 212°F = boiling point at 1 atm).

II.2.7 Relation between the Heat and Temperature

When a system absorbs energy as heat ($q > 0$), it may undergo a temperature change (ΔT). The quantitative relationship between the heat transferred (Q) and the resulting temperature variation is given by:

$$Q = mC\Delta T \text{ ; where } \Delta T = T_f - T_i \qquad (II.5)$$

Where :

- Q: Heat energy exchanged (in Joules, J). $Q > 0$: System gains heat (endothermic). $Q < 0$: System loses heat (exothermic).
- m: Mass of the substance (in grams, g).

- C: Specific heat capacity (in $J\cdot g^{-1}\cdot K^{-1}$), the energy required to raise the temperature of 1 gram of a substance by 1 Kelvin.
- ΔT: Temperature change (T_f = final, T_i = initial).

II.3 Water Equivalent of the Calorimeter (μ)

The water equivalent (fictitious mass of water, **μ**) is a mass of water considered equivalent to the internal components of the calorimeter itself (such as its walls, thermometer, and stirrer) in terms of heat absorption. It refers to the amount of heat absorbed by these components, as they warm up alongside the substances being studied inside the calorimeter. This water equivalent effectively has the same heat capacity as the substances introduced into the calorimeter.

II.4 Work

This is the mechanical energy that occurs during a volume expansion. Work is the scalar product of the force and the displacement. The work done per unit time is called power and is denoted W. The unit of power is kJ/s, or kW.

$$\partial W = F_{ext}\, dl \qquad (II.6)$$

$$\partial W = -P_{ext}\, dv \Rightarrow {}_1\underline{W}_2 = -\int P_{ext}.dv \qquad (II.7)$$

Units of work :

$[W] = Pa.m^3$ = Joules

[W] = l. atm 1 l.atm = 101.325 J

[W] = Cal 1 Cal = 4.185 J

$${}_1\underline{W}_2 = -\int P_{ext}.dv$$

- If $V_2<V_1$ (compression), $\Delta V<0$ and $W>0$, indicating that the system receives work from the external surroundings.
- If $V_2>V_1$ (expansion), $\Delta V>0$ and $W<0$, indicating that the system provides work to the external surroundings.

Work (w) is not a function of state.

a) Work for irreversible process W_{irr}

Irreversible work corresponds to a system undergoing an irreversible process from an initial state (1) to a final state (2). Such transformations are characterized by:

- Rapid execution (non-quasi-static process),
- Spontaneity (driven by finite imbalances, e.g., pressure gradients),
- Natural behavior: Once initiated, the process cannot be halted or reversed.

For an irreversible expansion or compression against a constant external pressure (*P*) (e.g., free expansion or sudden piston movement), the work done is:

$$W_{irr} = -\int p.dv = -p \int dv = -p[\, v_f - v_i] \qquad (II.8)$$

where:

P = constant external pressure,
Vi and Vf = initial and final volumes.

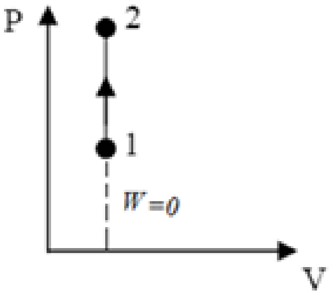


Figure I.4. Work of an Isochoric Heating irreversible

b) Work for reversible process W_{rev}

Reversible work corresponds to a system undergoing a reversible process from state (1) to state (2). Such transformations are characterized by:

- Quasi-static execution: The process occurs infinitely slowly, ensuring the system remains in near-equilibrium at all stages.
- Invertibility: The process can be reversed by an infinitesimal change in a state variable (e.g., pressure or temperature).
- Non-equilibrium constraint: The system pressure (P_{sys}) and external pressure (P_{ext}) are never equal (but differ infinitesimally).

For an ideal gas undergoing reversible expansion/compression, the work done is:

$$W_{rev} = -\int P_{ext}.dv = W_{irr} = -\int (nRT/V).dv = -\,nRT \ln (V_2/V_1) \qquad (II.9)$$

where:

- P = pressure of the system (ideal gas law: $P = nRT/V$),
- n = number of moles, R = gas constant, T = temperature (constant for isothermal processes),
- V_1, V_2 = initial and final volumes.

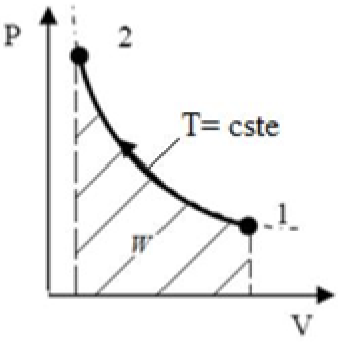


Figure I. 5. Work of an isothermal compression reversible

II.5 Internal Energy U

This is the capacity of a system to perform work or produce heat. Microscopic forms of energy, such as the interaction energy between molecules, are referred to as internal energy **U**. also, Internal energy, U is the total energy of a system. It includes the kinetic energy, potential energy, chemical energy, Electrostatic energy etc. of the system.

$$\Delta U = Q + W \qquad (II.10)$$

Internal energy is a state function that depends only on the initial and final states of the thermodynamic system, and $\Delta U=0$ for a cycle of transformations.

Exercises and Solutions

Exercise 1

We want to obtain a lukewarm water bath at a temperature T=37 °C with a total volume V=250L, by mixing a volume V_1 of hot water at an initial temperature T_f = 70 °C and a volume V_2 of cold water at an initial temperature T_2=15∘C.

Determine V_1 and V_2, assuming that all heat losses during mixing are negligible.

Data given:

Specific heat capacity of water cp=4185J·kg^{-1}·K^{-1} and density ρ=1000kg·m^{-3}.

Solution 1

∑ Qi=0 For an isolated system,

$Q_{\text{released by the hot water}} + Q_{\text{absorbed by the cold water}} = 0$

⇨ $m_2\, c_p\, (T_{eq} - T_2) + m_2\, c_p\, (T_{eq} - T_1) = 0$

Since density is $\rho = \frac{m}{v}$ =>, we have : $\cancel{\rho} v_2 \cancel{c_p} (T_{eq} - T_2) + \cancel{\rho} v_1 \cancel{c_p} (T_{eq} - T_1) = 0$

Which simplifies to : $v_2(T_{eq} - T_2) + v_1(T_{eq} - T_1) = 0$ => $\frac{v2}{v2} = \frac{-(Teq - T1)}{(Teq - T2)}$ =>

Numerical Application : $\begin{cases} v1 + v2 = 250\ l \\ \frac{v2}{v2} = 1{,}5 \end{cases}$ $=> v1 + 1.5v2 = 250\ l$ $=> \begin{cases} v1 = 100\ l \\ v2 = 150\ l \end{cases}$

Exercise 2

In a calorimeter with a heat capacity C = 209 J·K^{-1} containing a mass of water m_1 = 350g at an initial temperature T_1 = 16 °C, a lead block with a mass m_2 = 280 g at a temperature T_2= 98 °C is immersed. The measured equilibrium temperature is T_e=17.7∘C. Determine the specific heat capacity of lead.

Data given: Specific heat capacity of water cp = 4185 J·kg^{-1}·K^{-1} and density of water ρ = 1 kg·L^{-1}.

Solution 2

$\sum Q_i=0$ For an isolated system,

$Q_{\text{released by the hot water}} + Q_{\text{absorbed by the cold water}} = 0$

$Q_{\text{water}}+Q_{\text{calorimeter}}+Q_{\text{lead}}=0$

$\Rightarrow m_1 c_p (T_{eq} - T_1)+C(T_{eq} - T_1)+ c_{pb}\, m_2 (T_{eq} - T_2) =0$

$(T_{eq} - T_1) (m_1 c_p - C) = - c_{pb}\, m_2 (T_{eq} - T_2)$

Solving for the specific heat capacity of lead (c_{pb})

$$c_{pb} = \frac{-(T_{eq} - T_1)\,(m_1 c_p - C)}{m_2\,(T_{eq} - T_2)} = 126{,}5\ \text{J.Kg}^{-1}.\text{K}^{-1}$$

Substituting the numerical values:

$c_{pb}= -(0.280\text{kg})\ (17.7{\circ}\text{C}-98°\text{C})(17.7°\text{C}-16°\text{C})((0.350\text{kg})(4185\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1})+209\text{J}\cdot\text{K}^{-1})$

$c_{pb}=-(0.280\text{kg})(-80.3\text{K})(1.7\text{K})(1464.75\text{J}\cdot\text{K}^{-1}+209\text{J}\cdot\text{K}^{-1})$

$c_{pb}=--22.484\text{kg}\cdot\text{K}(1.7\text{K})(1673.75\text{J}\cdot\text{K}^{-1})$

$c_{pb}\approx126.5\text{J}\cdot\cdot\text{kg}^{-1}\cdot\text{K}^{-}$

Exercise 3

Calculate the quantity of heat required to transform an ice cube weighing 235 g from −18 °C to +115 °C.Given:

Specific heat capacity of ice (H_2O,s) = 0.516 $\text{cal}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$

Specific heat capacity of liquid water (H2O,l) = 1.032 $\text{cal}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$

Specific heat capacity of water vapor (H2O,g) = 0.493 $\text{cal}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$

Latent heat of fusion of water = 80.15 $\text{cal}\cdot\text{g}^{-1}$

Latent heat of vaporization of water = 539.5 $\text{cal}\cdot\text{g}^{-1}$

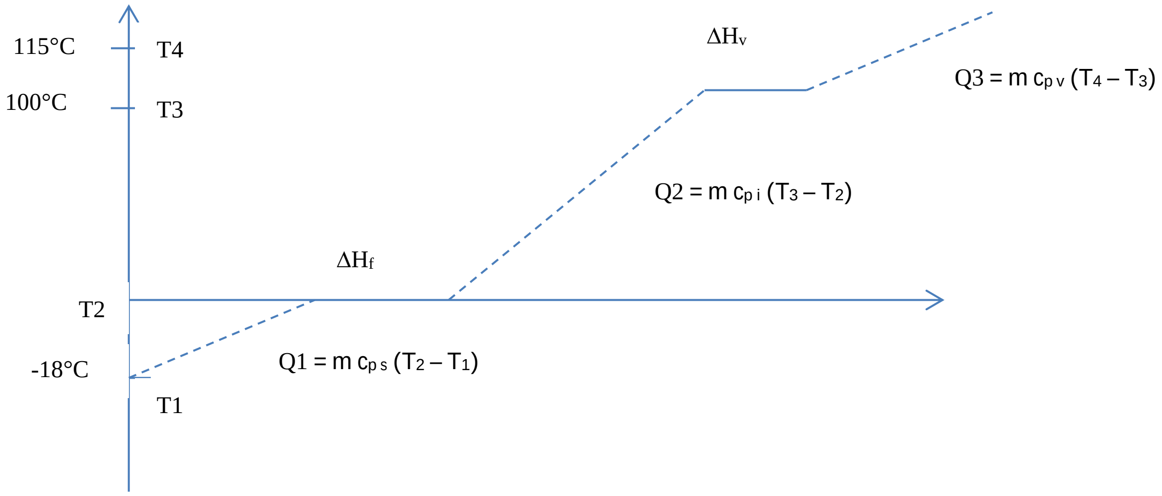
Melting point of water = 0 °C

Boiling point of water = 100 °C

,

Solution 3

The total heat required (Q) is the sum of the heat needed for each step of the transformation: heating the ice to its melting point (Q_1), melting the ice (ΔH_f), heating the liquid water to its boiling point (Q_2), vaporizing the liquid water (ΔH_v), and heating the water vapor to the final temperature (Q_3)



Therefore:

$$Q = Q_1 + \Delta H_f + Q_2 + \Delta H_v + Q_3 \Rightarrow$$

$$Q = m\, c_{p\,s}\,(T_2 - T_1) + \Delta H_f + Q2 = m\, c_{p\,i}\,(T_3 - T_2) + \Delta H_v + m\, c_{p\,v}\,(T_4 - T_3)$$

Q=2176.08 cal +18835.25 cal + 24252 cal + 126782.5 cal + 1733.875 cal

Q=173780.705 cal

Therefore, the quantity of heat required is approximately 173780.7calories.

Exercise 4:

I. Calculate the quantity of heat required to raise the temperature of the air in a room from 0°C to 1°C.

Data: Density of air (ρair) = 1.30 g/L

Dimensions of the room: 5 m x 4 m x 2.5 m

Specific heat capacity of air (cair) = 820 J/(kg·K)

II. Calculate the internal energy change (ΔU) for each of the following systems:

1-A system absorbs Q=2kJ while providing external work W=500J.

2-gas maintained at constant volume releases Q=5kJ.

3-Adiabatic compression of a gas is accomplished with work W=80J.

Solution 4

I)-

Calculate the volume of the room. Vroom= 5m×4m×2.5m = 50m^3

Calculate the mass of air in the room. mair=ρair×Vroom mair=1.30kg/m3×50m3=65kg

Calculate the quantity of heat (**Q**). The heat required to raise the temperature of a substance is given by

Q=m·c·ΔT. Q=65kg×820J/(kg·K)×1K Q=53300J

Therefore, the quantity of heat required is 53.3kJ.

II)-

1. A system absorbs Q=2kJ while providing external work W = 500J.

- Q= +2 kJ = +2000 J (absorbed by the system)
- Work provided *by* the system (external work) means W is negative: W = −500J

ΔU = Q+W ➔ ΔU= 2000J + (−500J) ➔ ΔU = 1500 J or 1.5kJ

2. A gas maintained at constant volume releases Q = 5kJ.

- Since the volume is constant, dV = 0. For a pressure-volume work, W = −∫PdV=0.

- $Q = -5kJ = -5000J$ (released by the system)

$\Delta U = Q+W \Rightarrow \Delta U = -5000J+0J \Rightarrow \Delta U = -5000J$ or $-5kJ$

3. Adiabatic compression of a gas is accomplished with work W=80J.

- **Adiabatic process** means no heat exchange, so $Q=0$.
- Work is accomplished *with* work $W = 80J$ during compression. This implies work is done *on* the system, so $W = +80J$.

$\Delta U = Q+W \Rightarrow \Delta U = 0J+80J \Rightarrow \Delta U=80J$

Exercice 5

A calorimeter with a heat capacity $C=150J\cdot K^{-1}$ contains a mass $m_1=200g$ of water at an initial temperature $T_1=50$ °C. An ice cube with a mass $m_2=160$ g is placed in the calorimeter, taken from a freezer at a temperature $T_2=-23$ °C. Determine the final equilibrium state of the system (final temperature, mass of the different substances present in the calorimeter).

Data given:

- Specific heat capacity of ice: $c_{p,ice} = 2100\ J\cdot kg^{-1}\cdot K^{-1}$ (or $2.1\ J\cdot g^{-1}\cdot K^{-1}$)

- Specific heat capacity of liquid water: $c_{p,water} = 4186\ J\cdot kg^{-1}\cdot K^{-1}$ (or $4.18\ J\cdot g^{-1}\cdot K^{-1}$)

- Latent heat of fusion of ice: $L_f = 334\ J\cdot g^{-1}$

Solution 5

We need to consider the heat exchange between the hot water, the calorimeter, and the ice. We'll assume an isolated system where the total heat exchange is zero. Let the final equilibrium temperature be T_f.

Step 1: Calculate the heat required to raise the ice to its melting point (0 °C).

$Q_{ice\_heating} = m_2 \cdot c_{p,ice} \cdot (0°C - T_2)$

$Q_{ice\_heating} = 160 \cdot 2.1 \cdot (0-(-23))$

$Q_{ice\_heating} = 7728\ J$

Step 2: Calculate the heat required to melt all the ice at 0 °C.

$Q_{melting} = m_2 \cdot L_f$

$Q_{melting} = 160 \cdot 334 = 53440$ J

Step 3: Calculate the heat released by the water cooling down to 0 °C.

$Q_{water\_cooling} = m_1 \cdot c_{p,water} \cdot (0^\circ C - T_1)$

$Q_{water_cooling} = 200 \cdot 4.186 \cdot (0 - 50) = -41860$J (negative sign indicates heat released)

Step 4: Calculate the heat released by the calorimeter cooling down to 0 °C.

$Q_{calorimeter\_cooling} = C \cdot (0 - T_1) = 150 \cdot (0 - 50) = -7500$ J (negative sign indicates heat released)

Step 5: Compare the heat absorbed by the ice to the heat released by the water and calorimeter cooling to 0 °C.

Total heat absorbed by the ice to reach 0 °C and melt = $Q_{ice\_heating} + Q_{melting} = 7728$ J$+53440$ J $=61168$ J

Total heat released by the water and calorimeter cooling to 0 °C = $|Q_{water\_cooling}| + |Q_{calorimeter\_cooling}| = 41860$ J + 7500 J = 49360 J

Since the total heat absorbed by the ice to melt completely (61168 J) is greater than the total heat released by the water and calorimeter cooling to 0 °C (49360 J), not all the ice will melt, and the final temperature of the system will be 0 °C.

Step 6: Determine the mass of ice that melts.

The amount of heat available to melt the ice is 49360 J. We can calculate the mass of ice that melts using the latent heat of fusion:

$m_{ice\_melted} = Q_{available} / L_f = 49360 / 334 = 147.78$ g

Step 7: Determine the final state of the system.

- Final Temperature: 0 °C (since not all the ice melted)

- Mass of liquid water: Initial mass of water + mass of ice melted : $m_{water\_final} = m_1 + m_{ice\_melted} = 200\ g + 147.78\ g = 347.78\ g$
- Mass of ice remaining: Initial mass of ice - mass of ice melted: $m_{ice\_final} = m_2 - m_{ice\_melted} = 160\ g - 147.78\ g = 12.22\ g$

Final Equilibrium State: The system will be at a final temperature of 0 $^\circ$C, consisting of approximately 347.78 g of liquid water and 12.22 g of ice in thermal equilibrium with the calorimeter.

Exercise 6

Calculate the work exchanged with the surroundings during the isothermal compression of 56 g of nitrogen from a pressure P_1=1 atm to P_2=20 atm at a temperature of 25°C in the following cases:

-a)- Reversible compression.

-b)- Irreversible compression.

- Compare the results obtained.

Data given : Atomic mass of nitrogen ($M_{(N2)}$ = 28 g/mol). Assume nitrogen behaves as an ideal gas.

Solution 6

-a-) Reversible Transformation:

In a reversible transformation, the system pressure is equal to the external pressure ($P_{system} = P_{external}$). The work done on the gas during an isothermal reversible compression of an ideal gas is given by:

n = m/M = l56/28 = 2 mol

$$W = -\int_{v_1}^{v2} P_{\text{ext}}\, dV = -\int_{v_1}^{v2} \frac{nRT}{V}\, dV = -nRT.\ln\frac{V_2}{V_1} = -nRT.\ln\frac{P_1}{P_2}$$

$$W = 14838\, J = 14{,}84\ kJ$$

-b) Irreversible Transformation: P = C^{te}

In an irreversible process against a constant external pressure equal to the final pressure, $P_{ext} = P_2$, the work done on the gas is:

$$W = -\int_{v_1}^{v2} P_{\text{ext}}\, dV = -P_{\text{ext}} \int_{v_1}^{v2} dV = -P_{\text{ext}}.(V_2 - V_1)$$

As : $P_{\text{ext}} = P_2$ Donc $W = -2RT\left(1 - \frac{P_1}{P_2}\right) = -2.8{,}32.298\left(1 - \frac{20}{1}\right) = 94{,}21\, KJ$

Comparison of Results: The work done during the irreversible compression (94190J) is significantly greater than the work done during the reversible compression (14852J), $W_{irr} > W_{rev}$. This illustrates the general principle that for a given compression, irreversible processes require more work input than reversible ones. The greater the irreversibility (here, a large difference between system and external pressure), the more energy is "lost" to the surroundings.

Exercise 7: Consider one mole of a gas undergoing a quasi-static and isothermal compression from (P_0 , T_0) to ($2P_0$, T_0). Give the expression for the work done *on* the gas in the following cases:

1) An ideal gas (express W as a function of T_0).

2) A Van der Waals gas: $(P + a / V^2) (V - b) = R T$ (express W as a function of V_i and V_f , the initial and final volumes, respectively).

Solution 7

1) Ideal gas :

$$W = -RT \int_{v_1}^{v2} \frac{1}{V}\, dV = -nRT.\ln\frac{V_f}{V_i} = -nRT.\ln\frac{P_i}{P_f} = -nRT.\ln\frac{1}{2} = -nRT.\ln 2$$

$W = RT_0 \operatorname{Ln} 2$

2) Van der Waals Gas:

$$W = -\int_{v_i}^{vf} \left(\frac{RT}{V-b} - \frac{a}{V_2}\right) dV = -\Big(RT\ln(v-b) + \frac{a}{V_f} - RT\ln(v-b) + \frac{a}{V_i}\Big)$$

$$= RT\ln\frac{V_i - b}{V_f - b}(v-b) + a\left(\frac{1}{V_f} + \frac{1}{V_i}\right)$$

$W = -RT_0 \operatorname{Ln}\frac{Vf-b}{Vi-b} + \left(\frac{1}{vi} - \frac{1}{Vf}\right)$

Chapter III

The First Law of Thermodynamics

Chapter III: The First Law of Thermodynamics

After the Zeroth Law of Thermodynamics states that if two systems are each in thermal equilibrium with a third system, they are in thermal equilibrium with each other. Therefore, this law helps to define the concept of temperature.

The First Law of Thermodynamics, also known as the Law of Conservation of Energy, states that the energy of a system remains constant during transformations within the system. This aligns with Lavoisier's principle: "nothing is lost, nothing is created, everything is transformed."The first law of thermodynamics states that the energy can neither be created nor destroyed but can be converted from one to another. Therefore, every bit of energy should be accounted for during a process.

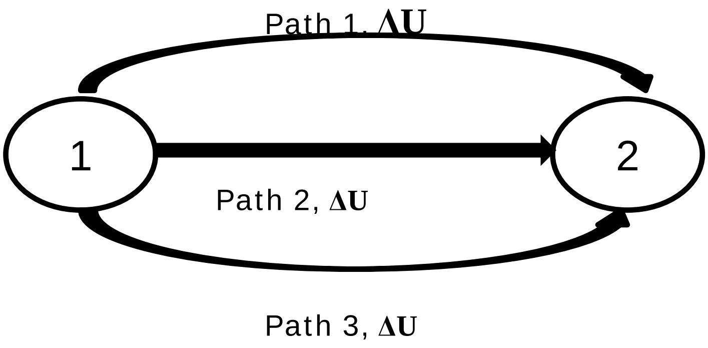
III.1 The First Law of Thermodynamics and Different Transformations:

III.1.1 Statement of the First Law of Thermodynamics

In thermodynamics, the total energy of a system is called the internal energy U. Experimentally, it has been shown that the internal energy U of a system can be changed either by energy supplied to the system in the form of work or by energy transferred to the system in the form of heat.

It is impossible to calculate the internal energy (U) of a system. Instead, the change in the U of a system, ΔU, must be measured.

Let U_1 be the energy of a system in state (1) and U_2 in state (2). The system changes from state (1) to state (2) by following path 1, path 2 and path 3. Since, U is the state function, so ΔU depends only on initial and final state of the system i.e.



$$\Delta U = U_2 - U_1$$

The change in ΔU of a system is affected by two distinct variables. These two variables are designated at heat (Q), and work (w). Suppose the system while undergoing change absorbs heat q from the surroundings and also perform some work equal to w. Hence the change of internal energy ΔU in the above process will given by :

$$\Delta U = W + Q \qquad (III.1)$$

This Equation is the mathematical statement of the first law of thermodynamics, where:

W : energy transferred to the system as work

Q : energy transferred to the system as heat

ΔU is expressed in kJ, and ΔU_m (molar) en $kJ.mol^{-1}$

The expression for ΔU in specific system cases:

- Isolated system: $\Delta U = 0$
- Closed system and cyclic transformation: $\Delta U = 0$
- Closed system and process from state (1) to (2): $\Delta U = Q_1 + W_1 = Q_2 + W_2$
- Isochoric (constant volume) transformation: $\Delta U = Q$
- Adiabatic transformation: $\Delta U = W$

III.2 Joule's Laws

In his experiment (Figure II.15), Joule considered two reservoirs (submerged in a water bath at T_0) connected by a closed valve. In reservoir (A), he placed a quantity of compressed air at P_0 (an ideal gas), while reservoir (B) was evacuated (P=0 bar). When he opened the valve, the air flowed into (B) and expanded: the air pressure decreased ($P_1 < P_0$) and the volume it occupied increased ($V_1 > V_0$).

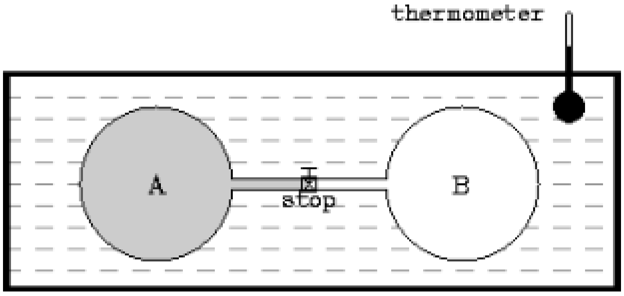


Figure II.5. The Joule experiment

Joule observed that the bath's temperature (T_0) remained constant throughout the experiment. This indicated no heat exchange between the air and the water ($\delta Q=0$). Furthermore, no work was involved, as nothing was moved, lifted, or driven, meaning $\delta W=0$ as well.

Applying the First Law of Thermodynamics, we can write:

$$dU=\delta W+\delta Q=0$$

From this, Joule concluded that the internal energy (U) of an ideal gas remains constant at a constant temperature, even if the pressure (P) and volume (V) change. This is known as Joule's First Law.

III.3 Process in Thermodynamics:

A system is said to undergo a process or evolution in thermodynamics when its energetic state changes from state (1) to state (2) through interaction with the surroundings due to changes in variables.

a) **Reversible Process**

This is a process that proceeds slowly and through a series of infinitesimally close equilibrium states. Such a process is called a reversible transformation.

b) **Irreversible Process**

This is a process that does not satisfy the conditions for equilibrium (reversibility) and is characterized by its rapid progression. It is called an irreversible transformation.

III.3.1 Types of Process (Transformations)

The various transformations possible in thermodynamics include:

a) Isothermal Process: Occurring at a constant temperature (T=constant).

b) Isobaric Process: Occurring at a constant pressure (P=constant).

c) Isochoric Process Occurring at a constant volume (V=constant).

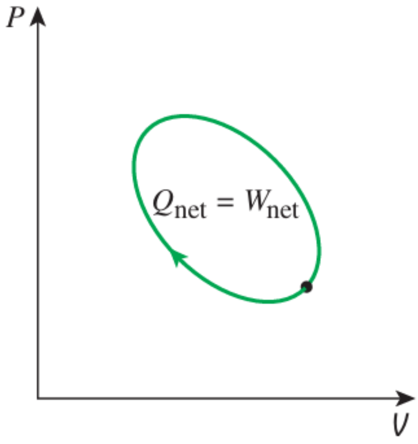
d) Adiabatic Process: A process during which the system does not exchange heat with the surroundings (Q=0).

III.3.2 Cycle Process (Cycle of transformations):

For a closed system undergoing a cycle, the initial and final states are identical, and thus $\Delta U_{system} = U_2 - U_1 = 0$. Then the energy balance for a cycle simplifies to $U_{in} - U_{out} = 0$ or $U_{in} = U_{out}$. Noting that a closed system does not involve any mass flow across its boundaries, the energy balance for a cycle can be expressed in terms of heat and work interactions as

$$W_{net,out} = Q_{net,in} \quad \text{or} \quad W_{net,out} = Q_{net,in} \quad (\text{ for a cycle }) \qquad (III.2)$$

That is, the net work output during a cycle is equal to net heat input .



For a cycle ΔU= 0, thus Q=W

III.4 Heat of Transformations and the First Law:

III.4.1 Heat of an Isochoric Process (Q_v):

From the first Law: $\Delta U = W + Q$

For an isochoric transformation, the volume of the system is constant ($v_1 = v_2$), therefore the work done by or on the system is zero (W = 0).

Thus, $\Delta U = Q_v$ *(III.3)*

III.4.2 Heat of an Isobaric Process (Q_p) – Concept of Enthalpy

From the First Law: $\Delta U = W + Q$

For an isobaric transformation, the pressure of the system is constant ($P_1=P_2$). The work done is $W = -P_{ext}(V_f - V_i)$. Substituting this into the First Law:

=> $\Delta U = W + Q_p$ and $W = -P_{ext}(V_f - V_i)$

=> $\Delta U = -P_{ext}(V_f - V_i) + Q_p = U_f - U_i$

Rearranging the terms:

=> $Q_p = (U_f + P_{ext} V_f) - (U_i + P_{ext} V_i)$ *(III.4)*

Since U, P, and V are state functions, any combination of these functions will also yield a state function. The state function defined by H=U+PV is called enthalpy (H). It is equal to the internal energy of the system plus the product of pressure and volume.

Therefore:

$$H = U + PV$$

and the equation (II.3) can be writer as :

$$H_2 - H_1 = \Delta H = Q_p \qquad (III.5)$$

Which mean that Enthalpy is equivalent to the total heat content of a system at constant pressure.

If $\Delta H<0$ => exothermic transformation.

If $\Delta H>0$ => endothermic transformation.

$\Delta H = \Delta U + P\Delta V$ (Where ΔV is the increase in volume undergone by the system) For infinitesimal change the above expression can be written as: $dH = dU + PdV$

III.5 Relationship between Cp and Cv

We have the definition of enthalpy (H):

$$H=U+PV \qquad (III.6)$$

Differentiating with respect to temperature T:

dH/dT = dU/dT + nR dT/dT

For an ideal gas, PV=nRT, ➔ $C_p=C_v+nR$ (*)

Since $C_p = (\partial H/\partial T)_P$ and $C_v = (\partial U/\partial T)_V$, we get:

$Cp=Cv+nR$ (I)

This is known as Mayer's relation.

The ratio of the specific heat capacities is defined as the adiabatic index, γ:

$$Cp/Cv = \gamma \qquad (**)$$

Combining equations (*) and (**), we can express Cv and Cp in terms of n, R, and γ:

$$Cv= nR/(\gamma -1) \text{ and } Cp= nR\gamma/(\gamma -1) \qquad (III.7)$$

Relation de Mayer $Cp/Cv = \gamma$ (**)

(*) And (**) ➔ $Cv= nR/(\gamma -1)$ et $Cp= nR\gamma/(\gamma -1)$ *(III.8)*

Exercises and Solutions

Exercice 1

Consider an ideal gas in state A characterized by the following state variables: TA = 293K ; VA = 12 L; and PA = 1 atm.

It undergoes a reversible adiabatic compression to state B defined by TB = 400 K.

a) Calculate the number of moles of gas used.

b) Calculate the following state variables: PB and VB .

c) Calculate for this gas and during this transformation: heat, work, and the changes in internal energy and enthalpy.

Data given : $c_p = 7$ cal.K^{-1}.mol^{-1} ; R = 2 cal.K^{-1}.mol^{-1} = 0.082 l.atm.K^{-1}.mol^{-1}

Solution 1

a) Number of moles of gas:

Using the ideal gas law for state A:

PA VA = nRTA => $n = \frac{\text{PA VA}}{\text{RTA}} = 0.5\, mol$

b) State variables P_B and V_B:

$\text{TA VA}^{\gamma-1} = \text{TB VB}^{\gamma-1} \Rightarrow \frac{\text{TA}}{\text{TB}} = \left(\frac{\text{VB}}{\text{VA}}\right)^{\gamma-1}$ => $V_B = VA \,.\left(\frac{TA}{TB}\right)^{1/(\gamma-1)}$

Using : $\begin{cases} \gamma = \frac{Cp}{Cv} \\ Cp - Cv = R \end{cases}$ => γ=1,4 ; Then : $V_B = 12 \,.\left(\frac{293}{400}\right)^{1/(1,4-1)} = 6{,}3\, l$

Also, using the ideal gas law for state B: PB VB = nRTB

=> $PB = \frac{\text{nRTB}}{\text{VB}} = 2.6\, atm$

c) Calculation of W, Q, ΔU, ΔH

- Heat (Q): For an adiabatic transformation, by definition : Q = 0
- Change in Internal Energy (ΔU): $\Delta U = n\, c_v\, (T_B - T_A) = 267{,}5$ cal
- Change in Enthalpy (ΔH): $\Delta H = n\, c_p\, (T_B - T_A) = 374{,}5$ cal
- Work (W): From the First Law of Thermodynamics (ΔU=W+Q), since Q=0 for an adiabatic process :

=> W=ΔU= 267,5 cal

Exercise 2

The initial state of one mole of an ideal gas is characterized by $P_0 = 2.10^5$ Pa and $V_0 = 14$ L. The gas undergoes the following reversible transformations successively:

- An isobaric expansion that doubles its volume.
- An isothermal compression that returns it to its initial volume.
- An isochoric cooling that returns it to the initial state.

1) At what temperature does the isothermal compression occur? Deduce the maximum pressure reached.

2) Represent the cycle of transformations in a (P,V) diagram.

3) Calculate the work and heat transfers exchanged by the system during each step of the cycle (W_1 , W_2 , W_3 , Q_1 , Q_2, Q_3) as a function of P_0 , V_0 and $\gamma = \frac{Cp}{Cv}$= 1,4 (assumed constant in the studied temperature range).

4) Verify that ΔU=0 for the cycle.

Solution 2

1) Isothermal Compression at Temperature 2 T_0

The maximum pressure reached is 2 P_0 .

3) Work and Heat Exchanges:

Isobaric Expansion (W1,Q1):

$W_1 = - P_0 V_0 = - 2,8.10^3$ J ;

$Q_1 = \frac{\gamma}{\gamma-1} . P_0 V_0 = 9,8.10^3$ J ;

Isothermal Compression (W2,Q2):

$W_2= 2 P_0V_0 \ln 2 = 3,9.103$ J ;

$Q_2 = - 2 P_0V_0 \ln 2 = - 3,9.103$ J ;

Isochoric Cooling (W3,Q3):

$W_3 = 0$ and $Q_3 = - \frac{1}{\gamma-1} . P_0 V_0 = - 7 . 10^3$ J

4) Change in Internal Energy: The change in internal energy over the cycle is $\Delta U_{\text{cycle}} = 0$; Energy is conserved over the cycle.

Exercise 3

Consider the polytropic expansion of an ideal gas with a constant index q (a process for which the volume V and pressure P satisfy P $V^q = C^{st}$ =Constant, where q is a positive constant), leading it from a state (P_1 , V_1 , T_1) to a state (P_2 , V_2 , T_2) with $V_2 > V_1$. Let $\gamma = \frac{Cp}{Cv}$ (assumed constant).

For what values of the coefficient q does the expansion of the gas involve:

1. Absorption of heat and heating of the gas?
2. Absorption of heat and cooling of the gas?

On considère la détente polytropique d'indice q constant (process pour laquelle le volume V et la pression P vérifient P $V^q = C^{te}$, avec q constante positive, d'un gaz parfait le menant d'un état (P_1 , V_1 , T_1) à un état (P_2 , V_2 , T_2) avec $V_2 > V_1$. On pose $\gamma = \frac{Cp}{Cv}$ (supposé constant).

Pour quelles valeurs du coefficient q , la détente du gaz s'accompagne-t-elle :

1. d'absorption de chaleur et d'échauffement du gaz ?
2. d'absorption de chaleur et de refroidissement du gaz ?

Solution 3

The heat transfer Q for a polytropic process of an ideal gas is given by:

$$Q = \frac{nR(T2-T1)}{(1-q)} + W1$$

The work done by the gas during the expansion is:

$$W = \frac{P2V2-P1V1}{(1-\gamma)} = \frac{nR(T2-T1)}{(1-q)}$$

Therefore, the heat transfer simplifies to:

$$Q = \frac{nR(T2-T1)}{(1-q)} + \frac{nR(T2-T1)}{(1-\gamma)} = \text{n R } (T_2 - T_1) \frac{q-\gamma}{(\gamma-1)(q-1)}$$

Since $V_2>V_1$ and PV_q=constant, we have $P_2<P_1$ and $T_2<T_1$ if q>0. Thus, $(T_2 – T_1)<0$. Also, for an ideal gas, $\gamma>1$, so $(1–\gamma) < 0$.

1) If q > g or q < 1

2) If 1 < q < g

Exercise 4

An ideal gas transitions from a state (P_1 , V_1 , T_1) to a state (P_2 , V_2 , T_2) following an adiabatic transformation. Let $\gamma = \frac{Cp}{Cv}$ (assumed constant).

1) Show that if there exists a continuous sequence of internal thermodynamic equilibrium states during the transformation, the pressure P and volume V of the gas are related by: $P V^{\gamma}$ = constant.

2) The gas is compressed and goes from pressure P_1 to pressure $P_2 = 2 P_1$. Calculate the work exchanged by the gas and the surroundings as a function of P_1 , V_1 , and γ.

Data given: P_1 = 1 bar , V_1 = 1 dm^3, and γ=1.4.

Solution 4

2) $W = \frac{1}{\gamma-1} . P_1 V_1 (2^{(\gamma-1)/\gamma} – 1) = 54{,}75\, J$

III.6 Thermochemical, Application of the First Law to Chemical Reactions

III.6.1 Thermochemistry

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

III.6.2 Chemical Reaction

During a chemical reaction, matter evolves from an initial to a final state. This evolution is characterized by changes in temperature, pressure, volume, or the amount of substance.

III.6.3 Application to Heats of Reaction

According to the First Law of Thermodynamics, we have:

$$dU = dQ + dW \qquad (III.9)$$

Isochoric Transformation (V=constant): In an isochoric process (constant volume), no work is done by or on the system due to volume change ($dW=0$ if only P-V work is considered). Therefore, the change in internal energy equals the heat exchanged: $\Delta U=Qv$ (where Qv denotes heat at constant volume)

For the enthalpy change, recall that $H=U+PV$.

So, $dH=dU+d(PV)= dU+PdV+VdP$.

Since dV=0 for an isochoric process, $dH=dU+VdP$. Integrating this gives:

$$\Delta H=\Delta U+\int VdP \qquad (III.10)$$

Isobaric Transformation (P=constant): In an isobaric process (constant pressure), the work done is $W=-P\Delta V=-P(V2-V1)$.

From the First Law, $\Delta U=Q+W$, so: $\Delta U=Qp-P(V_2-V1)$ (where Qp denotes heat at constant pressure).

For the enthalpy change, $\Delta H=\Delta U+\Delta(PV)=\Delta U+P\Delta V$.

Substituting $\Delta U=Qp-P\Delta V$:

$$\Delta H=(Qp-P\Delta V)+P\Delta V$$

Therefore: $\Delta H=Q_p$ *(III.10)*

III.6.4 Standard Quantities:

a) **Standard State:** This is the physical state in which a pure substance is most stable at standard atmospheric pressure (1 atm).

b) **Standard Enthalpy of a Pure Element**

The standard enthalpy of formation **(ΔH°_f)** for a **pure element** in its standard state **is defined as zero.**

Examples:

- ΔH°_{298} of H2(g)) =0
- ΔH°_{298} of (O2(g))=0
- ΔH°_{298} of (C(graphite))=0

c) **Standard Enthalpy of Formation ΔH°_f :**

This is the enthalpy change accompanying the formation of one mole of a compound from its elements in their standard states (at T=298K and P=1atm).

The **standard state** refers to the most stable physical state of a substance under specific conditions, typically:

- **Pressure:** 1 atm (or 1 bar, depending on the convention used)
- **Temperature:** 25∘C (298 K)

It is denoted by the symbol ΔH°_f

Table III. 1. Values of Enthalpy of formation of some compounds

Compound	$\Delta H^{\circ}_{298,f}$ (kcal/mol)
CO (g)	-26.42
H_2O (L)	-57.80
H_2O (g)	-96.06

III.6.5 Heat of Chemical Reaction:

Many heats of reaction cannot be measured directly by calorimetry. We often use the principle that enthalpy is a state function, depending only on the initial state (IS) and final state (FS), to calculate them indirectly as follows (Hess's Law):

$$\Delta H^{\circ}_{R,298} = \sum ni\, \Delta H_{f\,(products)} - \sum nj \Delta H_{f\,(reactants)} \qquad (III.11)$$

Based on Hess's Law , the calculate the standard enthalpy change of a reaction using the standard enthalpies of formation of the products and reactants.

Remark on Reaction Enthalpy

- If $\Delta H^{\circ}_{R,298} <0$: The reaction **releases heat**; it is an **exothermic reaction**.
- If $\Delta H^{\circ}_{R,298} >0$: The reaction **absorbs heat**; it is an **endothermic reaction**.

III.6.6 Determination of the Heat of Reaction (ΔH°_{R}) from ΔH°_{f}:

To find the relationship between the heat of a chemical reaction at constant pressure and constant volume at 25°C **(ΔH°_{298})** and at a temperature T **(ΔH°_{T})**, t is necessary to use the properties of state functions.

III.6.7 Calculation of Heats of Reaction at Different Temperatures (Kirchhoff's Relation):

Consider the chemical reaction: A→B with a standard enthalpy change ΔH°_{298} at 298 K. To determine the standard enthalpy change **ΔH°_{T}** of this reaction at a temperature T, knowing C_p and C_v, we use the following relation (Kirchhoff's Law):

$$\Delta H^{\circ}_{T} = \Delta H^{\circ}_{298} + \int_{298}^{T} \Delta C_p\, dT \text{ , And :}$$

$$\Delta Cp = \sum Cp_{\,(products)} - \sum Cp_{\,(reactants)} \qquad (III.12)$$

III.6.8 Influence of Temperature on the Standard Enthalpy of Reaction

Enthalpy changes are typically provided at a standard temperature, T_1=298 K. However, we often need to determine the enthalpy value at a different temperature, T_2. **Kirchhoff's Law** allows us to do this:

$$\Delta H^\circ_T = \Delta H^\circ_{298} + \int_{298}^{T} \Delta C_{p(}(T)dT \qquad \text{(III.13)}$$

a) When Cp is Independent of Temperature

If the molar heat capacity (Cp) is considered to be independent of temperature over the range of interest, the integration simplifies:

$$\Delta H^\circ_T = \Delta H^\circ_{298} + \Delta C_p \int_{298}^{T} dT \qquad \text{(III.14)}$$

Here, ΔC_p represents the change in molar heat capacity for the reaction, calculated as the sum of the molar heat capacities of the products minus the sum of those for the reactants:

$$\Delta C_p = (\sum n_P C_p(products)) - (\sum n_R C_p(reactants))$$

b) When Cp is a Function of Temperature

When the molar heat capacity (C_p) is temperature-dependent, it's often expressed as a polynomial function of temperature, such as :

$$\Delta Cp(T)=a+bT+cT^2.$$

In this case, Kirchhoff's Law requires integrating the temperature-dependent expression:

$$\Delta H^\circ_T = \Delta H^\circ_{298} + \int_{298}^{T} \Delta C_{p(}(T)dT \qquad \text{(III.15)}$$

Where $\Delta C_{p(}(T)$ is the temperature-dependent change in molar heat capacity for the reaction:

$$\Delta C_{p(}(T)=(\sum n_P\, C_{p(}(T)products))-(\sum n_R\, C_{p(}(T)(reactants))$$

Substituting the polynomial form:

$$\Delta H^{\circ}{}_{T} = \Delta H^{\circ}{}_{298} + \int_{298}^{T} (a + bT + cT^{2})\,dT \qquad (III.16)$$

This integral can be broken down:

$$\Delta H^{\circ}{}_{T} = \Delta H^{\circ}{}_{298} + a \int_{298}^{T} dT + b \int_{298}^{T} (T)\,dT + c \int_{298}^{T} (T2)\ dT$$

Performing the integration yields:

$$\Delta H^{\circ}{}_{T} = \Delta H^{\circ}{}_{298} + a(T)_{298}^{T} + \left(\frac{T^{2}}{2}\right)_{298}^{T} + \left(\frac{T^{3}}{3}\right)_{298}^{T}$$

This allows for the calculation of the standard enthalpy of reaction at any desired temperature T_2, given the enthalpy at 298 K and the temperature dependency of the heat capacities.

Exercises and Solutions

Exercice 1

Calculate the standard enthalpy change for the following reaction at 25∘C:

$$Ca_3(PO_4)_2(s) + 3H_2SO_4(\ell) \rightarrow 3CaSO_4(s) + 2H_3PO_4(s)$$

Compound	$\Delta H^\circ_{f,298}$ (kcal mol−1)
$Ca_3(PO_4)_2(s)$	−986.2
$H_2SO_4(\ell)$	−342.42
$CaSO_4(s)$	−193.91
$H_3PO_4(s)$	−306.20

Solution

The standard enthalpy of reaction ($\Delta H^\circ_{R,298}$) is calculated using the standard enthalpies of formation ($\Delta H^\circ_{f,298}$) of the products and reactants:

$$\Delta H^\circ_{R,298} = (\sum ni,\ \Delta H^\circ_{f,298}\ (\text{products})) - (\sum nj,\ \Delta H^\circ_{f,298}\ (\text{reactants}))$$

For the given reaction, this translates to:

$\Delta H^\circ_{R,298} = 3\ \Delta H^\circ_{f,298}(CaSO_4(s)) + 2\ \Delta H^\circ_{f,298}(H_3PO_4(s)) - (\ \Delta H^\circ_{f,298}(Ca_3(PO_4)_2(s)) + 3\Delta H^\circ_{f,298}(H_2SO_4(\ell)))$

Upon calculation, the value obtained is:

$\Delta H^\circ_{R,298} = -71.73$ kcal

Since $\Delta H^\circ_{R,298} < 0$, this indicates an **exothermic reaction**.

Exercice 1

Calculate the standard enthalpy of reduction of iron(III) oxide by aluminum (Al) at 25°C.

Given the reaction :

$2\ Al_{(s)} + Fe_2O_{3\ (s)} \longrightarrow 2\ Fe_{(s)} + Al_2O_{3\ (s)}$

The standard enthalpies of formation at 298 K:

$\Delta H^{\circ}_{f,298\ (Fe2O3,s)} = -196{,}5\ Kcal.mol^{-1}$

$\Delta H^{\circ}_{f,298\ (Al_2O_3,s)} = -399{,}1\ Kcal.mol^{-1}$

Solution 1

$2\ Al_{(s)} + Fe_2O_{3\ (s)} \longrightarrow 2\ Fe_{(s)} + Al_2O_{3\ (s)}$

The standard molar enthalpy of reduction of iron oxide is:

$$\Delta H^{\circ}_{R} = \sum \Delta H_{f(\text{ products})} - \sum \Delta H_{f\ (\text{reactatnts})}$$

$$\Delta H^{\circ}_{R} = 2\Delta H^{\circ}_{f,298(Fe,S)} + \Delta H^{\circ}_{f,298(Al_2O_3,S)} - 2\Delta H^{\circ}_{f,298(Al,S)} - \Delta H^{\circ}_{f,298(Al_2O_3,S)}$$

Knowing that the standard molar enthalpy of formation of a pure element in its standard state is zero, therefore:

$$\Delta H^{\circ}_{f,298(Fe,S)} = 0\ et\ \Delta H^{\circ}_{f,298(Al,S)} = 0$$

$$\Delta H^{\circ}_{R} = \Delta H^{\circ}_{f,298(Al_2O_3,S)} - \Delta H^{\circ}_{f,298(Al_2O_3,S)} = -202{,}6\ kcal$$

Exercise 2

Consider the following combustion reaction under standard conditions:

$H_2S_{(g)} + O_{2\ (g)} \longrightarrow SO_{2\ (g)} + H_2O_{(g)}$

a) Is this reaction endothermic or exothermic?

b) Calculate the standard molar enthalpy of reaction at 800 K.

c) Calculate the standard molar internal energy change at 800 K.

Eléments (standrad state)	$\Delta H^{\circ}_{f,298}\ (KJ/mol)$	$Cp\ (KJ/mol)$
$H_2S_{(g)}$	-20,15	$26{,}71+23{,}87\ 10^{-3}\ T$
$H_2O_{(g)}$	-241,83	$30{,}20+9{,}933\ 10^{-3}\ T$
$SO_{2\ (g)}$	-296,90	$25{,}72+13{,}61\ 10^{-3}\ T$
$O_{2\ (g)}$	0	$25{,}50+57{,}91\ 10^{-3}\ T$

Solution 2

a) First, balance the chemical equation :

$2H_2S_{(g)} + 3O_{2\,(g)} \longrightarrow 2SO_{2\,(g)} + 2H_2O_{(g)}$

Calculate the standard enthalpy change of the reaction at 298 K ($\Delta H°_{R,298}$) using the standard enthalpies of formation 298 K :

$$\Delta H°_{\mathrm{R}} = \sum \Delta H_{\mathrm{f(\ products)}} - \sum \Delta H_{\mathrm{f\ (reactants)}}$$

$$\Delta H°_{\mathrm{R}} = 2\Delta H^{°}_{f,298(\mathrm{SO2\ ,g})} + 2\Delta H^{°}_{f,298(\mathrm{H2O\ ,g})} - 2\Delta H^{°}_{f,298(\mathrm{H2S\ ,g})} - 3\Delta H^{°}_{f,298(\mathrm{O2\ ,g\ })}$$

$$= -1036.0\ KJ/mol$$

Since $\Delta H^{°}_{f,298} < 0$, the reaction is **exothermic** under standard conditions.

b) Standard Molar Enthalpy of Reaction at 800 K ($\Delta H^{°}_{r,(800)}$):

We use Kirchhoff's Law:

$$\Delta H^{°}_{r,(800)} = \Delta H^{°}_{r,(298)} + \int \Delta Cp\ dT$$

With : $\Delta Cp = \sum Cp_{\text{(products)}} - \sum Cp_{\text{(reactants)}}$

$$\Delta Cp = (Cp_{\text{(H2O)}} + Cp_{\text{(S2O)}}) - \left(Cp_{\text{(H2S)}} + \frac{3}{2} Cp_{\text{(O2)}}\right) = -9{,}04 - 87{,}2010^{-3}T$$

$\Delta H^{°}_{r,(800)} = \Delta H^{°}_{r,(298)} + \int_{298}^{800} \Delta Cp\ dT = -547{,}15$ kJ/mol

c) Standard Molar Internal Energy Change at 800 K : $\Delta H^{°}_{r,(800)} = \Delta U_{(800)} + \Delta n$ RT

$\Delta U_{(800)} = \Delta H^{°}_{r,(800)} - \Delta n$ RT = -543,82 KJ/mol

Exercise 3

Calculate the enthalpy change for the reaction at 100°C:

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(\ell)$$

Data:

Cp (J/Kmol) of $H_{2\,(g)}$ = 27.3+3.3x10^{-3}T

Cp (J/Kmol) of $O_{2\,(g)}$ = 29.9+4.2×10^{-3}T

Cp (J/Kmol) of $H_2O_{(g)}$ = 75.2

$\Delta H^{°}_{r,(298)}\ (H2O)$ = -286.0 KJ/mol

Solution

We need to calculate ΔrH373∘. According to Kirchhoff's Law:

$$\Delta H^{\circ}_{373} = \Delta H^{\circ}_{298} + \int_{298}^{373} \Delta C_{p(}(T)dT$$

- Calculate $\boldsymbol{\Delta} H^{\circ}_{R,\ 298}$ using Hess's Law:

  $$\Delta H^{\circ}_{R,298} = \sum \Delta H_{f(\text{ products})} - \sum \Delta H_{f\ (\text{reactatnts})}$$

  $$\Delta H^{\circ}_{R,298} = -572.0\ KJ/mol$$

- Calculate $\boldsymbol{\Delta C}_{p(}(\boldsymbol{T})$:

  $\Delta C_{p(}(T)=(\sum n_P\, C_{p(}(T)\text{products}))-(\sum n_R\, C_{p(}(T)(\text{reactants}))$

  $\Delta C_{p(}(T)= 65.9-10.8\times 10^{-3}T$ (in J/K)

- Integrate $\Delta C_{p(}(T)$ to find the change in enthalpy due to temperature difference:

$$\Delta H^{\circ}_{373} = \Delta H^{\circ}_{298} + \int_{298}^{373}(T65.9 - 10.8\times 10^{-3}\mathrm{T})dT$$

$$\Delta H^{\circ}_{373} = \Delta H^{\circ}_{298} + 65.9(T)_{298}^{373} - 10.8\ 10^{-3}\left(\frac{T^2}{2}\right)_{298}^{T373}$$

$\Delta H^{\circ}_{373} = 567.33\ \mathrm{KJ/mol}$

Exercise 3

The standard molar enthalpy of combustion of methane at 25°C and 1 atmosphere is equal to -212.8 kcal. Given the enthalpies of the following reactions:

$C_{(\text{graphite})} + O_{2\,(g)} \longrightarrow CO_{2\,(g)}$ (1) $\Delta H^{\circ}_{r,(298)(1)} = -94{,}05\ kcal$

$H_{2\,(\text{graphite})} + 1/2\ O_{2\,(g)} \longrightarrow H_2O_{(g)}$ (2) $\Delta H^{\circ}_{r,(298)(2)} = -68{,}3\ kcal$

a-Calculate the standard molar enthalpy of formation of gaseous methane $\Delta H^{\circ}_{f,(298)}\ (CH_{4,}g)$.

b-Calculate the molar enthalpy of combustion of methane at 1 atmosphere and a temperature of 1273 K, using the cycle method (Hess's Law) and Kirchhoff's Law. Given the molar heat capacities (assumed constant between 298 K and 1273 K) for the following substances:

$c_p(CH_4, g)$ = 13,2 cal/mol/K

$c_p(O_2, g)$ = 7,6 cal/mol/K

$c_p(CO_2, g)$ = 11,2 cal/mol/K

$c_p(H_2O, g)$ = 9,2 cal/mol/K

$c_p(H_2O, l)$ = 18 cal/mol/K

The enthalpy of vaporization of water is: L_v(water) = $\Delta H^{\circ}_{vap,373(\mathrm{H2O\ ,L})}$= 9,7 kcal/mol

Solution 3

a) Standard Molar Enthalpy of Formation of Gaseous Methane ($\Delta H_f°(CH_4,g)$)

The combustion reaction of methane, assuming liquid water as a product at 25°C, is:

$$CH_{4\ (g)} + 2O_{2\ (g)} \longrightarrow CO_{2\ (g)} + 2\ H_2O_{(L)}\ ,\ \Delta H^{\circ}_{r,(298)(1)} = -212{,}8\ kcal$$

We use Hess's Law:

$$\Delta H°_{\mathrm{R}} = 2\Delta H^{\circ}_{f,298(\mathrm{H2O\ (L)})} + \Delta H^{\circ}_{f,298(\mathrm{CO2\ (g)})} - \Delta H^{\circ}_{f,298(\mathrm{CH4\ (g\ )})} - 2\Delta H^{\circ}_{f,298(\mathrm{O2\ ,g\ })}$$

$$\Delta H^{\circ}_{f,298(\mathrm{CH4\ (g\ )})} = 2\Delta H^{\circ}_{f,298(\mathrm{H2O\ (L)})} + \Delta H^{\circ}_{f,298(\mathrm{CO2\ (g)})} - \Delta H°_{\mathrm{R}} = -16{,}3\ kcal/mol$$

b) Molar Enthalpy of Combustion of Methane at 1273 K

On applique la méthode de Kirchhoff avec le changement d'état :

We apply Kirchhoff's Law**,**

$$\Delta H^{\circ}_{r,(1273)} = \Delta H^{\circ}_{r,(298)} + \int_{298}^{373} \Delta Cp\ dT + \Delta H^{\circ}_{vap,373(\mathrm{H2O\ ,L})} + \int_{373}^{1273} \Delta C'_p\ dT$$

$$with : \Delta Cp = \sum Cp_{\ (\text{ produits})} - \sum Cp_{\ (\text{réactifs})}$$

$$\Delta C_p = C_p(\mathrm{CO2\ (g)}) + 2C_p(\mathrm{H2O\ (L)}) - C_p(\mathrm{CH4\ (g\ )}) - 2C_p(\mathrm{O2\ (g)}) = 18{,}8\ \mathrm{cal/mol/K}$$

$$\Delta C'_p = C_p(\mathrm{CO2\ (g)}) + 2C_p(\mathrm{H2O\ (g)}) - C_p(\mathrm{CH4\ (g\ )}) - 2C_p(\mathrm{O2\ (g)}) = 1{,}2\ \mathrm{cal/mol/K}$$

The molar enthalpy of combustion of methane at 1273 K, producing gaseous water, is approximately: $\Delta H^{\circ}_{r,(1273)} = -194{,}6\ kcal/mol$

Exercise 4

Calculate the standard enthalpy of the following reaction:

$$C_2H_{4\ (g)} + 2O_{2\ (g)} \longrightarrow CO_{2\ (g)} + 2\ H_2O_{(L)}$$

a) From standard molar enthalpies of formation.

b) From bond energies.

c) Explain the results obtained.

Data given :

$\Delta H^{\circ}_{f,298}$ (C_2H_4, g) = 33,6 kcal/mol

$\Delta H^{\circ}_{f,298}$ (CO_2, g) = - 94.05 kcal/mol

$\Delta H^{\circ}_{f,298}$ (H_2O, g) = -242,4 kcal/mol

Bond	H-H	C-H	C-C	O-H	C-O	C=C
$\Delta H^{\circ}_{f,298}$ (KJ/mol)	-434,7	-413,8	-263,3	-459,8	-313,5	-611,8

Solution 4

The balanced chemical equation for the reaction is:

$$C_2H_{4\,(g)} + 3O_{2\,(g)} \longrightarrow 2CO_{2\,(g)} + 2\,H_2O_{(L)}$$

a) Calculation from Standard Molar Enthalpies of Formation :

The standard enthalpy of reaction (ΔH°_r) is calculated using Hess's Law:

$$\Delta H^{\circ}_r = \sum \Delta H_{\text{f(produits)}} - \sum \Delta H_{\text{f (réactifs)}}$$

$$\Delta H^{\circ}_r = (2\Delta H^{\circ}_{f,298\,(CO2,g)} + 2\Delta H^{\circ}_{f,298\,(H2O,g)}) - \left(\Delta H^{\circ}_{f,298\,(C2H4,g)}\right) = -356{,}9\,kJ/mol$$

b) Calculation from Bond Energies:

The enthalpy change of a reaction using bond energies is given by:

ΔH°_r=∑(Bond energies of bonds broken)−∑(Bond energies of bonds formed)

$$\Delta H^{\circ}_r = (2\,\Delta H^{\circ}_{f,298\,(CO2,g)}) + 2\,\Delta H^{\circ}_{f,298\,(H2O,g)}) - \left(\Delta H^{\circ}_{f,298\,(C2H4,g)} + 3(\Delta H^{\circ}_{f,298\,(O2,g)})\right)$$

$$\Delta H^{\circ}_r = [\Delta H(C-C) + 4\Delta H(C-H) + \Delta H(C-O) + \Delta H(O-H)] - [\Delta H(C=C) + 4\Delta H(C-H)] - [2\Delta H(O-H)] = -312\,kcal/mol$$

c) The values for ΔH°_r obtained by the two methods are different because the enthalpies derived from bond energies are calculated using approximate methods**.** These methods assume that the bond energies for identical types of bonds (e.g., all C-H bonds) are constant and possess the same value across various molecules, which is a simplification.

Chapter IV

The Second Law of Thermodynamics

Chapter IV: The Second Law of Thermodynamics

IV.I The Necessity of a Second Principle

The **First Law of Thermodynamics**, which postulates the **conservation of energy**, enables us to establish an energy balance for systems without imposing conditions on the types of possible exchanges. However, this energy balance does not allow for the prediction of the direction of system evolution. For instance, it cannot predict the direction of chemical reactions, natural transformations, or the spontaneous transfer of heat from a hot body to a cold one.

The First Law, by its very nature, does not exclude the transfer of heat from cold to hot (which is thermodynamically impossible), nor does it explain the **irreversibility** of certain spontaneous or natural transformations. Consequently, it became necessary to introduce a **Second Law of Thermodynamics**, also known as the **principle of evolution**. This principle, derived from experimental observations, allows for the prediction of system evolution (and thus the **stability of states**).

III.1 The Second Law of Thermodynamics

Rudolf Clausius was a German physicist, and he developed another statement of the Second Law which says *"**Heat does not flow spontaneously from a cool body to a hotter body**."* Or "*Heat generally **cannot flow spontaneously** from a material at a lower temperature to a material at a higher temperature*."

The Second Law of Thermodynamics allows us to predict the direction of a spontaneous transformation. For this purpose, there exists an extensive property, a state function denoted as S (entropy), such that for a given system:

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} \frac{\delta Q}{T} \qquad (IV.1)$$

The change in entropy of the system (ΔS_{syst}) can be broken down into two parts:

$$\Delta S_{syst} = (S_{EF} - S_{EI})_{created} + (S_{EF} - S_{EI})_{exchanged} \qquad (IV.2)$$

where $(\Delta S)_{created}$ represents the entropy generated internally due to irreversibilities within the system, and $(\Delta S)_{exchanged}$ is the entropy transferred between the system and its surroundings.

The Second Law applies to a closed system and between two equilibrium states. Irreversible processes are always accompanied by an increase in entropy, while for reversible processes**,** entropy (S) is conserved (remains constant for the universe).

- If $\Delta S_{universe} = 0 \rightarrow$ reversible process
- If $\Delta S_{universe} > 0 \rightarrow$ irreversible transformation

IV.3 Entropy of Reversible and Irreversible Transformations:

a) During a Reversible Process

The amount of entropy supplied to the system by the surroundings is equal to the amount of entropy lost by the surroundings:

$$dS_{ext} = -\frac{\eth\, Q_{rev}}{T} \qquad (IV.3)$$

and

$$dS_{syst} = \frac{\eth\, Q_{rev}}{T} \qquad (IV.4)\ ,$$

Therefore, during a reversible transformation, the total change in entropy of the universe is zero because:

$$dS_{univ} = dS_{syst} + dS_{ext} = 0 \qquad (IV.5)$$

b) During an Irreversible Process

The amount of entropy gained by the system is greater than the amount of entropy lost by the surroundings..

$$dS_{univ} = dS_{syst} + dS_{ext} > 0 \qquad (IV.5)$$

IV.4 Entropy During an Isothermal Expansion:

a) Reversible Isothermal Expansion:

For an isothermal transformation, the temperature T is constant, so ΔT=0, which implies ΔU=0 for an ideal gas.

$\Delta T=0 \Rightarrow \Delta U = 0$

From the First Law of Thermodynamics,

⇨ $\Delta U = \eth\, Q_{rev} + W_{rev} = 0 \Rightarrow \eth\, Q_{rev} = -\, W_{rev}$,

We have : $\Delta S_{syst} = \frac{\eth\, Q_{rev}}{T} = -\frac{W_{rev}}{T} = \frac{nRT}{T}\, ln\frac{v1}{v2} \Rightarrow \Delta S_{syst} = nR\, ln\frac{v2}{v1} \qquad (IV.6)$

Since $Q_{sys} = -\, Q_{ext}$, therefore, $\Delta S_{ext} = -\, nR\, ln\frac{v2}{v1} \qquad (IV.7)$

Therefore, for this reversible transformation, the total entropy change of the universe is zero: $\Delta S_{univ} = \Delta S_{syst} + \Delta S_{ext} = 0 \qquad (IV.8)$

b) Irreversible Isothermal Expansion:

For an irreversible process, the **entropy change of the system is the same as if the process were reversible** between the same initial and final states, because entropy is a state function:

$$\Delta S_{syst(irrev)} = \Delta S_{syst(rev)} = nR\ ln\frac{v2}{v1} \qquad (IV.9)$$

For an isothermal transformation, T is constant and $\Delta T=0$ => $\Delta U=0$ for an ideal gas. This means => $Q_{irrev} = -W_{irrev}$

The entropy change of the surroundings is:

$$\Delta S_{ext} = -\frac{\eth\, Q_{irrev}}{T} = -\frac{W_{irrev}}{T} = -\frac{P_{ext}\ (v_2 - v_1)}{T} \qquad (IV.10)$$

For an irreversible expansion : $P_{irrev} < P_{rev}$, this implies : $Q_{irrev} < Q_{rev}$

The entropy of the universe for an irreversible expansion is:

$$\Delta S_{univ} = \Delta S_{syst} + \Delta S_{ext} \Rightarrow \Delta S_{univ} = nRln\left(\frac{V_2}{V_1}\right) - \frac{W_{irrev}}{T} \geq 0\ . \qquad (IV.11)$$

This inequality holds because for an irreversible expansion, $W_{irrev} > W_{rev}$ (less negative work is done by the system, so the surroundings do more work *on* the system or the system does less work *on* the surroundings). Also, $Q_{irrev} < Q_{rev}$, meaning the system absorbs less heat from the surroundings. Since ΔS_{syst} is fixed by the initial and final states, the "missing" entropy is created within the universe due to the irreversibility, leading to $\Delta S_{univ} > 0$.

IV.5 Variation of Entropy with Temperature T:

The entropy value of a substance at any given temperature can be determined, provided its specific heat capacity, as well as the temperatures and latent heats of phase changes, are known.

If Pressure (P) is constant and Heat Capacity (C_p) is constant:

$P = C^{te}$, $C_p = C^{te}$, => $\Delta S = nCp\ ln\frac{T2}{T1}$ (IV.12)

If there is a physical phase change at temperature T:

The change in entropy during the phase transition is:

$$\Rightarrow \Delta S = \frac{\Delta H}{T} \qquad (IV.13)$$

where $\Delta H_{phasechange}$ is the latent heat (e.g., heat of fusion or vaporization) at temperature T.

To calculate the standard entropy change of a reaction at a temperature T ($\Delta S_T°$):

This is often done using an integrated form of Kirchhoff's Law for entropy:

$$\Delta S_R^{\circ} = \Delta S_{298}^{\circ} + \int_{298}^{T} \frac{nC\text{p}}{T}\, dT \qquad (IV.14)$$

where ΔS_R° is the standard entropy change at a reference temperature T_0, and $\Delta C°_p$ is the change in standard molar heat capacities of the products minus reactants.

IV.6 Entropy as a Function of Variables T and V

From the First Law of Thermodynamics**,**

⇨ $dU=dQ+dW$

For work done by pressure-volume changes:

⇨ $dW=-PdV$

According to the Second Law of Thermodynamics**,** for a reversible process:

⇨ $dS = \frac{dQ_{rev}}{T}$

Substituting $dQ_{rev} = dU - dW = dU + PdV$ into the entropy equation:

⇨ $dS = \frac{dU+PdV}{T}$

This can be rearranged to

⇨ $dS = \frac{dU}{T} + \frac{P}{T} dV$

For an ideal gas, the change in internal energy (dU) is given by:

$dU=nCvdT$ (where n is the number of moles and Cv is the molar heat capacity at constant volume)

Substitute this expression for dU into the entropy equation:

⇨ $dS = nC_v \frac{dU}{T} + \frac{P}{T} dV$

dS=nCvTdT+TPdV

Using ideal gas law => ($PV=nRT$), => $TP=VnR$

n=1 mole => $\frac{P}{T} = \frac{R}{V}$

Substituting this into the entropy equation for 1 mole:

$$dS = C_v \frac{dT}{T} + R\frac{dV}{V} \qquad (IV.15)$$

This equation allows us to calculate the infinitesimal change in entropy for an ideal gas in terms of changes in temperature and volume.

IV.7 Entropy as a Function of Variables T and P

To express entropy (S) in terms of temperature (T) and pressure **(**P), we start with the enthalpy definition:

⇨ $H=U+PV$

⇨ $dH=dU+PdV+VdP$.

Substituting $dU=TdS-PdV$ (from the Second Law), we get:

⇨ $dH= TdS-PdV +PdV+VdP$.

⇨ $dH=TdS+VdP$.

For an ideal gas, $dH=nCpdT$ and $TV=PnR$. For one mole of an ideal gas (n=1):

$$dS = C_v \frac{dT}{T} + R\frac{dP}{P} \qquad (IV.16)$$

This equation shows how an ideal gas's infinitesimal entropy change relates to changes in its temperature and pressure.

IV.8 Entropy as a Function of Variables P and V

From the entropy equation as a function of temperature and pressure:

⇨ $dS = C_v \frac{dT}{T} + R\frac{dP}{P}$

According to Mayer's Law for ideal gases, the relationship between Cp, Cv, and R is:

⇨ $R=C_p-C_v$

Substitute this expression for R into the entropy equation:

⇨ $dS = C_v \frac{dT}{T} + (C_p - C_v)\frac{dP}{P}$

⇨ dS=CpTdT−(Cp−Cv)PdP

⇨ PV=nRT => For one mole (n=1): PV=RT

⇨ $ln(PV)=ln(RT)$ => $lnP+lnV=lnR+lnT$

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

⇨ $dS = C_p\left(\frac{dP}{P} + \frac{dV}{V}\right) - \left(C_p - C_v\right)\frac{dP}{P} = C_p\left(\frac{dV}{V}\right) - \left(C_v\right)\frac{dP}{P}$

⇨ $dS = C_p\left(\frac{dP}{P} + \frac{dV}{V}\right) - \left(C_p - C_v\right)\frac{dP}{P}$

$$dS = C_p\left(\frac{dV}{V}\right) + (C_v)\frac{dP}{P} \tag{IV.17}$$

This equation shows how an ideal gas's infinitesimal entropy change can be expressed in terms of changes in volume and pressure.

IV. 9 Reaction Entropy Balance

The entropy balance for a reaction, for example, the reaction: aA+bB⟶cC+dD, is given by:

ΔSR∘=∑S∘(products)−∑S∘(reactants)

Specifically, this expands to:

$$\Delta S_R^{\circ} = \sum ni\ S_{(\text{ produits})} - \sum ni\ S_{(\text{réactifs})} \qquad (IV.18)$$

Where ΔS_R° represents the standard molar entropy of each substance.

Exercises and Solutions

Exercise 1

One mole of an ideal gas in contact with a heat source at a temperature of 25 °C undergoes a reversible expansion from 100 atm to 1 atm. Calculate:

a- The change in entropy of the source.

b- The change in entropy of the gas.

c- The total change in entropy and discuss its sign.

Data given : The heat supplied by the source is equal to 2730 cal.

Solution 1

The process described is a reversible isothermal expansion.

- Change in Entropy of the Source **(ΔS_{source})**

The heat given off by the source is $Q_{source} = -2730$ cal. The temperature of the source is $T=25°C=298.15K$.

a- $\Delta S_{source}= \frac{Q\ source}{T} = \frac{2730}{298} = -9{,}16$ cal.K^{-1}

- Change in Entropy of the Gas **($\Delta Sgas$)**

The entropy change of the gas is:

b- $\Delta S_{gaz} = nR \ln \frac{Pi}{Pf} = 9{,}2$ cal.K^{-1}

c) Total Change in Entropy (ΔS_{total})

$$\Delta S_T = \Delta S_{source} + \Delta S_{gaz} \approx 0 \Rightarrow \Delta S_T = 0$$

$$\Delta S_{total} = (-9.16\ cal\cdot K^{-1}) + (9.16\ cal\cdot K^{-1}) = 0\ \ cal\cdot K^{-1}$$

The total change in entropy of the universe is **zero**. This result is characteristic of a **reversible transformation**, aligning perfectly with the statement of the Second Law of Thermodynamics, which dictates that for any reversible process, the total entropy of the universe remains constant.

Exercise 2

Calculate the entropy change of 2 moles of perfect gas expanding from 30 to 50 liters adiabatically, reversibly and irreversibly. Given T_1= 300K; C_v = 5 cal.mol^{-1}.K^{-1}

Solution 2

Entropy Change of Ideal Gas Expansion :

Given: n=2 mol ; V1=30 L ; V2=50 L ; T1=300 K ; Cv1=20.92 J mol^{-1}K^{-1};
R=8.314 J mol^{-1}K^{-1}

1. Adiabatic and Reversible Expansion:

For any adiabatic process, $dQ=0$.

For a reversible process, $dS = \frac{dQ_{rev}}{T}$

=> $dQ_{rev}=0$.

$\Delta S_{system}=0$

$\Delta S_{surroundings}=0$

$\Delta S_{total}=\Delta S_{system+}\Delta S_{surrounding}s=0$

2. Adiabatic and Irreversible Expansion (Free Expansion):

For an adiabatic process, dQ=0.

For free expansion into a vacuum, dW=0.

From $dU=dQ+dW)$ => $dU=0$.

$\Delta S_{system}=nRln(\frac{v2}{v1})$

- ⇨ ΔS_{system} = 8.494 J K^{-1}
- ⇨ $\Delta S_{surroundings}$ = 0
- ⇨ $\Delta S_{total}=\Delta S_{system+}\Delta S_{surrounding}s$ = 8.494 J K^{-1}

Exercise 3

1) Calculate the change in entropy (ΔS) of the system in each case.

-Mix 600 g of petroleum at 76 °C with 1260 g of petroleum at 13 °C.

2) In a water bath at an invariable temperature (T = 40 °C), mix 400 g of ice at -25 °C with 785 g of liquid water at 100 °C.

3) A solid with constant heat capacity C, initially at T_0, is brought into thermal contact with a heat source (reservoir) at temperature T. T_0=650 °C, T=37 °C, C=36.84cal/K.

4) Calculate the total change in entropy (ΔS) to transform 330 g of ice from -10°C to 127°C.

5) A piece of iron with mass m=200g is immersed at 89°C in a lake at 17°C.

a-Calculate the entropy variation of the solid (iron).

b-Calculate the entropy change exchanged between the piece of iron and the lake.

c-Deduce the total entropy change created (of the universe).

Given data: Cp (H_2O,l)= 2 $cal\cdot g^{-1}\cdot K^{-1}$; Cp(H_2O,s)= 1$cal\cdot g^{-1}\cdot K^{-1}$; Cp(H_2O, g) = 8 $cal\cdot mol^{-1}\cdot K^{-1}$; $L_{fus\ (ice)}$ = 80 cal/g at 0°C ; L_{vap} (H_2O, l) = 540 cal/g at 100°C ; $C_{p(petroleum)}$= 2.1$J\cdot g^{-1}\cdot K^{-1}$; $C_{p(iron)}$ = 0.46 $J\cdot g^{-1}\cdot K^{-1}$

Solution 3

1) Calculate ΔS of the system when mixing 600g of petroleum at 76°C with 1260g of petroleum at 13°C.

This is a mixing problem where two quantities of the same substance at different temperatures reach a final equilibrium temperature. We have data : m_1= 600g ; T_1= 76°C= 76+273.15= 349.15 K ; m_2= 1260g ; T_2= 13°C= 13+273.15 = 286.15K ; $c_{petroleum}$= 2.1 $J\cdot g^{-1}\cdot K^{-1}$

To calculate the final equilibrium temperature (T_f):

$Q_{lost} + Q_{gained} = 0 \Rightarrow m_1 c_p (T_f - T_1) + m_2 c_p (T_f - T_2) = 0 \Rightarrow m_1 (T_f - T_1) + m_2 (T_f - T_2) = 0 \Rightarrow 1860\ T_f = 570039$

Thus, T_f = **306.47** K (or 33.32 °C)

Calculate the entropy change for each part of the petroleum:

$\Delta S_1 = \frac{Q\,1}{T} = \int_{T1}^{Tf} m1Cp\ \frac{dT}{T} = \ m1Cp\ \ln\frac{Tf}{T1} = \ \mathbf{-164.88}$ J/K

$\Delta S_2 = \frac{Q\,2}{T} = \int_{T2}^{Tf} m2Cp\ \frac{dT}{T} = \ m2Cp\ \ln\frac{Tf}{T2} = \ \mathbf{181.25}$ J/K

Calculate the total entropy change of the system (**ΔS_{system}**).

$\Delta S_{system} = \Delta S_1 + \Delta S_2$

$\Delta S_{system} = -164.88 J/K + 181.25 J/K = 16.37$ J/K

Since $\Delta S_{system} > 0$, this irreversible mixing process is spontaneous.

2) In a water bath of invariable temperature (t = 40°C), mix 400g of ice at -25°C with 785g of liquid water at 100°C. Data : $m_{ice} = 400g$; $T_{ice,i} = -25°C$; $m_{water} = 785g$; $T_{water,i} = 100\ °C$; $Cp(H_2O, s) = 1 cal \cdot g^{-1} \cdot K^{-1}$; $Cp(H_2O, l) = 2 cal \cdot g^{-1} \cdot K^{-1}$; $L_{fus\ (ice)} = 80$ cal/g at 0°C.

Calculate heat needed to raise ice to 0 °C, to melt all ice at 0 °C and heat released by cooling water to 0 °C.

$Q_1 = m_{ice} \cdot c_{p,ice}\ (0°C - T_f) = 400 \times 1 \times (0 - (-25)) = 400 \times 25 = 10000cal$

$Q_2 = m_{ice} L_{fus} = 400 \times 80 = 32000cal$

$Q_3 = m_{water} c_l \Delta T = 785g \times 2 \times (0 - 100) = 1570 \times (-100) = -157000cal$

which the available heat from cooling water to 0°C is 157000cal (Q_3).

$Q_1 + Q_2 = 10000 + 32000 = 42000$ cal. Since 157000 cal > 42000 cal, all the ice will melt, and the final temperature will be above 0°C.

Calculate the final equilibrium temperature (**T_f**) of the water mixture (if isolated).

$Q_1 + Q_2 + m_{ice} \cdot c_{p,ice}\ (T_f - 0) + m_{water} c_l\ (T_f - 100) = 0$

➔ $10000 + 32000 + 400 \times 2 \times T_f + 785 \times 2 \times (Tf - 100) = 0$

➔ $T_f = 48.52°C$

Calculating ΔS_{system} (ice + water) and $\Delta S_{surroundings}$ (water bath):

Process steps for the 400g ice:

- Ice at -25°C to Ice at 0°C: $T_{i\,1} = 248.15$ K, $T_{f1} = 273.15$ K

➔ $\Delta S_1 = miceCs \ln\frac{Tf}{T1} == \mathbf{38.04}$ cal/K

- Ice at 0°C to Liquid at 0°C (melting): $T_{melt}=273.15K$

➔ $\Delta S_2 = \frac{m\ ice\ L_{fus}}{T_{melt}} =$ **117.15** cal/K

- Liquid water (from melted ice) at 0°C to Liquid water at 40°C: $T_{i3}=273.15K$, $T_{f3} =313.15K$

➔ $\Delta S_3 = miceCs \ln\frac{Tf3}{T13} == \mathbf{109.08}$ cal/K

➔ $\Delta S_{ice \rightarrow water(40C)} = \Delta S1 + \Delta S2 + \Delta S3 = 38.04+117.15+109.28 =$ **264.47** cal/K

Process steps for the 785g liquid water:

Liquid water at 100°C to Liquid water at 40°C: $T_{i4}=373.15K$, $T_{f4}=313.15K$

➔ $\Delta S_4 = miwater.Cl. \ln\frac{Tf4}{T14} = \mathbf{-275.46}$ cal/K

Total entropy change of the system (ice + original water):

$\Delta S_{system} = \Delta S_{ice \rightarrow water(40C)} + \Delta S_{water(100C) \rightarrow water(40C)}$ ➔ $\Delta S_{system} = (264.47) + (-275.46) = \mathbf{-10.99}$ cal/K

Total heat change of the system (ice + initial water) when it goes from its initial state to 40°C.

$Q_{system} = [m_{ice}c_s(0-(-25))] + [m_{ice}L_{fus}] + [m_{ice}c_l(40-0)] + [m_{water}c_l(40-100)]$

$Q_{system} = [400 \times 1 \times 25] + [400 \times 80] + [400 \times 2 \times 40] + [785 \times 2 \times (-60)]$

Qsystem=10000+32000+32000−94200

Qsystem=74000−94200= **−20200** cal

This is the heat *released* by the system (ice + water) to the bath. So,

$Q_{bath} = -Q_{system} = +20200$ cal.

Calculate the entropy change of the water bath ($\Delta S_{surroundings}$).

T_{bath}=40∘C=313.15K

$\Delta S_{surroundings}$= Q_{bath}/ T_{bath} = **64.49**cal/K

Calculate the total entropy change (ΔS_{total}).

ΔS_{total} =ΔS_{system}+$\Delta S_{surroundings}$

ΔS_{total}=−10.99cal/K+64.49cal/K = **53.50**cal/K

Since $\Delta S_{total}>0$ ➔ the process is spontaneous and irreversible, as expected for heat transfer between bodies at different temperatures.

4) Calculate ΔS to transform 330g of ice from -10°C to 127°C.

This involves multiple phase changes and temperature changes.

Given data: m_{H2O}=330g ; Initial T_i=−10°C=263.15K ;Final T_f =127°C=127+273.15=400.15K ; $C_{p(H2O,\ s)}$ =1cal·g^{-1}·K^{-1} ; $C_{p(H2O,\ l)}$ =2 cal·g^{-1}·K^{-1} ; $C_{p(H2O,\ g)}$ =8 cal·mol^{-1}·K^{-1} ; M_{H2O} = 18 g/mol ; $C_{p(H2O,\ g)}$ =188=0.444 cal·g^{-1}·K^{-1}); $L_{fus\ (ice)}$ = 80cal/g at 0°C (273.15K); $L_{vap\ (H2O,\ l)}$ = 540 cal/g at 100°C(373.15K)

Processes involved:1) Heating ice: −10°C →0°C, 2) Melting ice: 0°C (solid) →0°C (liquid), 3) Heating liquid water: 0∘C→100∘C, 4) Vaporizing water: 100°C (liquid) →100°C (gas), 5) Heating steam: 100°C →127°C.

ΔS_1 (Heating ice) ➔ $\Delta S_1 = mH2O.Cps.\ln\frac{Tmelt}{Ti} = \mathbf{12.31}\ \text{cal/K}$

ΔS_2 (Melting ice) ➔ $\Delta S_2 = \frac{m\ H2O\ L_{fus}}{T_{melt}} = \mathbf{96.65}$cal/K

ΔS_3 (Heating liquid water) ➔ $\Delta S_3 = mH2O.Cps.\ln\frac{Tboil}{Tmelt} = \mathbf{205.85}\ \text{cal/K}$

ΔS_4 (Vaporizing water) ➔ $\Delta S_4 = \frac{m\ H2O\ L_{Vap}}{T_{boil}} = \mathbf{477.56}$ cal/K

ΔS_5 (Heating steam) ➔ $\Delta S_5 = mH2O.Cps.\ln\frac{Tf}{Tboil} = \mathbf{10.24}\ \text{cal/K}$

ΔStotal : $\Delta S_{total} = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5$

➔ ΔS_{total} = 12.31+96.65+205.85+477.56+10.24 = **802.61**cal/K

5) A piece of iron with mass m=200g is immersed at 89°C in a lake at 17°C.

Data: m_{iron}=200g ; $T_{iron,i}$=362.15K; T_{lake}= 290.15K ; $C_{p(iron)}$ =0.46J·g^{-1}·K^{-1}

The lake is a very large reservoir, so its temperature remains essentially constant at 17°C. The iron will cool down to 17°C.

2) Calculate the entropy variation of the solid (iron**).**

$\Delta S_{iron} = miron.\,Cpiron.\ln\frac{TLake}{Tiron} = \mathbf{-20.39}$ J/K

b) Calculate the entropy change exchanged between the piece of iron and the lake**.** This refers to the entropy change of the lake, which acts as the surroundings.

Q_{iron}:

. $Q_{iron} = m_{iron} C_{p(iron)} (T_{lake} - T_{iron,i})$ = **+6624** J.

ΔS_{lake}: . $\Delta S_{lake} = Q_{lake} / T_{lake}$ = **22.83** J/K

- Deduce the entropy change created (total entropy change, $\Delta S_{universe}$).

$\Delta S_{total} = \Delta S_{iron} + \Delta S_{lake}$ ➔ ΔS_{total} = −20.39J/K+22.83J/K = **2.44** J/K

Since **$\Delta S_{total} > 0$**, this heat transfer process is **spontaneous** and **irreversible**.

Exercice 4

One mole of oxygen (O_2 : an ideal gas) undergoes an irreversible adiabatic expansion from an initial state A (P_A =10atm; T_A =300K) to a final state B (P_B =P_{ext} =1atm). Calculate:

a) The temperature T_B and the volume V_B

b) The work and heat exchanged by the gas with its surroundings.

c) The change in entropy of the gas and that of the surroundings (the temperature of the surroundings is constant and equals 300 K).

Given data:

Cv= 18,91 J.K^{-1}.mol^{-1} ; R= 8,32 J.K^{-1}.mol^{-1}

Solution 4

The process is an **irreversible adiabatic expansion** from initial state A to final state B.

Initial state A: $\begin{cases} P_A = 10\ atm \\ T_A = 300\ k \\ V_A = nRT_A/P_A \end{cases}$ === irreversible adiabatic ==> Final state B: $\begin{cases} P_B = 1\ atm \\ T_B = ? \\ V_B = ? \end{cases}$

a) Calculation of T_B and V_B

Since the process is **adiabatic**, Q=0 therefore, according to the First Law of Thermodynamics, ΔU = W

=> nCv ΔT = -P_{ext} ΔV

So, we have the equality:

=> nCv (T_B-T_A) = -P_{ext} (V_B-V_A)

=> $\mathbf{T_B} = \frac{P_B V_A + nCvT_A}{nCv + nR} = 217.51$ k

Now calculate V_B:

$P_B V_B = nRT_B \Rightarrow \boldsymbol{V_B} = \frac{nRT_B}{P_B} = 17{,}08\ l$

a) Calculation of Work (W) and Heat (Q)

As the process is **adiabatic**, by definition, no heat is exchanged with the surroundings.

Q = 0 J

Since ΔU=W:

W= -Pext ΔV=-Pext (V_B-V_A) =>

W= −1559 J

b) Calculation of Entropy Change (ΔS_{gas})

Since entropy is a state function, we can calculate ΔS_{gas} using a reversible path. A common approach is to use a two-step reversible path:

- Isothermal process from A to an intermediate state I (at T_A) such that P_I=P_B.
- Isobaric process from I to B (at P_B).

Stat (A)$\begin{cases} P_A = 10\,atm \\ T_A = 300\,k \\ V_A = 2{,}46\,l \end{cases}$ ➔ intermediate state (I)$\begin{cases} P_I = 10\,atm \\ T_I = \frac{V_I P_I}{nR} = 2082{,}9K \\ V_I = 17{,}8\,l \end{cases}$ ➔ Stat (B)

$$\begin{cases} P_B = 1atm \\ T_B = 208{,}31k \\ V_B = 17{,}8\,l \end{cases}$$

$$\Delta S_T = \Delta S_1 + \Delta S_2$$

$$\Delta S_1 = \int_{T1}^{TI} nCp \frac{dT}{T} = nCp \ln \frac{TI}{T1} = 52{,}7\,J\,K^{-1}$$

$$\Delta S_2 = \int_{TI}^{T2} nCv \frac{dT}{T} = nCv \ln \frac{TB}{TI} = 43{,}5\,J\,K^{-1}$$

$$\Delta S_T = \Delta S_1 + \Delta S_2 = 9{,}2\,J\,K^{-1} > 0$$

Since $\Delta S_{total} > 0$, this confirms that the process is **irreversible**. The increase in the total entropy of the universe is a characteristic of all spontaneous, irreversible processes.

Exercice 5

Calculate the entropy change ΔS during the reversible expansion of 3 moles of an ideal gas, initially at 36 °C, from an initial pressure of 4 atm to a final pressure of 1 atm:

a) In the case of an isothermal expansion.

b) In the case of an adiabatic expansion (calculate the final volume and final temperature).

Given:

$Cp=3{,}5R$ et $R= 2$ cal. mol^{-1} K^{-1}

Solution 5

a) In the case of an isothermal expansion:

For an isothermal process, the temperature T is constant (T1=T2=309.15K). For an ideal gas, the entropy change is given by:

$$\Delta S_1 = nCp \ln \frac{Pi}{Pf} = 8{,}31 \text{ cal.K}^{-1}$$

b) In the case of an adiabatic expansion (calculate the final volume and final temperature)

Stat (A) initial $\begin{cases} P_A = 14\,atm \\ T_A = 309\,k \\ V_A = 19\,l \end{cases}$ ➔ Stat (B) final $\begin{cases} P_B = 1atm \\ T_B = ? \\ V_B = ? \end{cases}$

$$P_A V_A^{\gamma} = P_B V_B^{\gamma} \Rightarrow \frac{V_B}{V_A} = \left(\frac{P_A}{P_B}\right)^{1/\gamma} \Rightarrow V_B = V_A \cdot \left(\frac{P_A}{P_B}\right)^{1/(\gamma)} = 51{,}14l$$

Calculate the final temperature (T2):

$$P_B V_B = nRT_B \Rightarrow T_B = \frac{V_B P_B}{nR} = 207{,}88\,K$$

Calculate the variation of entropy (**ΔS**) for adiabatic expansion:

For any reversible adiabatic process, the entropy change is **zero**. $\Delta S=0$

Exercice 6

A piece of lead (Pb) with a mass of 2590 grams, initially at 38°C, is brought into contact with an infinite heat source (thermostat) at a temperature of 400°C. Calculate:

a) The heat received by the lead.

b) The change in entropy of the lead.

c) The heat given off by the source.

d) The change in entropy of the source.

e) The total change in entropy (or entropy created).

Given :

M_{pb}=207,2 g/mol ; $T_{f \text{ of } Pb}$= 327°C ; $Cp_{\text{ of } Pb}$ (solid)= 6,52 cal. mol^{-1} K^{-1}; $Cp_{\text{of } Pb}$ (liquid)= 7,50 cal. mol^{-1} K^{-1} ; Latent heat of fusion of Pb : 1440 cal. mol^{-1}

Solution 6

a- The heat received by the lead (Q_{Pb})

$Q=Q_1+Q_2+Q_3 = n\, c_{p\,s}\,(T_2 - T_1)+ n\Delta H_f + n\, c_{p\,l}\,(T_3 - T_2)= 48{,}23\ 10^3$ cal

b- The variation of entropy of the lead (ΔS_{Pb})

$\Delta S_T=\Delta S_{Pb} + \Delta S_{source}$

$\Delta S_{Pb}=\Delta S_1 + \Delta S_2 + \Delta S_3 = nCp \ln\frac{T2}{T1} + \frac{\Delta Hf}{Tf} + nCp \ln\frac{T3}{T2} = 94{,}09\ cal.K^{-1}$

c- The heat given off by the source (Q_{source})

$Q_{source} = - Q_{system} = - 48{,}23 10^3$ cal

d- The variation of entropy of the source (ΔS_{source})

$$\Delta S_{source} = \frac{Q_{source}}{T_{source}} = -71{,}9\ cal.K^{-1}$$

e- The total variation of entropy (or entropy created) (ΔS_{total} or $\Delta S_{universe}$)

$\Delta S_T=\Delta S_{Pb} + \Delta S_{source} = 22{,}18\ cal.K^{-1}$

Since ΔStotal=22.36cal/K is **greater than zero**, this confirms that the process is **irreversible**

Chapter V:

The Third Law of Thermodynamics and Gibbs Free Energy

Chapter V: The Third Law of Thermodynamics and Gibbs Free Energy.

V.1 The Third Law of Thermodynamics:

The Third Law of Thermodynamics, first enunciated by Nernst in 1906, states that at the limit of absolute zero temperature (0 K), the entropy of a perfect crystalline system in equilibrium is zero:

$$S_{0K} = 0 \qquad (V.1)$$

V.2 Gibbs Free Energy, Gibbs Function, Condition for Spontaneity:

V.2.1 Gibbs Free Energy G :

The total energy contained within a molecule is called enthalpy, H. The portion of this energy that can perform useful work is called free energy (or Gibbs function, denoted as G). This function is very important in the study of chemical reactions as it allows us to predict their direction of evolution (spontaneity).

V.2.2 Gibbs Function:

Gibbs free energy is represented by a state function, known as the **Gibbs relation:**

$$\Delta G = \Delta H_{sys} - T\Delta S_{sys} \qquad (V.2)$$

$$Or \qquad \Delta G^0_{298} = \Delta H^0_{298} - T\Delta S^0_{298} \qquad (V.3)$$

Conditions for Spontaneity at Constant Temperature and Pressure:

- If $\Delta G<0 \Rightarrow$ Gibbs free energy decreases for irreversible (spontaneous) transformations.
- If $\Delta G>0 \Rightarrow$ Gibbs free energy increases for non-spontaneous transformations (the reverse reaction is spontaneous).
- If $\Delta G=0 \Rightarrow$ Gibbs free energy is constant at equilibrium for reversible transformations.

V.2.3 Gibbs-Helmholtz Relation:

The variation of Gibbs free energy with respect to temperature at constant pressure is expressed by the following relation:

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_p = -\frac{H}{T^2} \qquad (\ V.4)$$

This is known as the **Gibbs-Helmholtz Relation**.

For a change in Gibbs free energy (e.g., for a chemical reaction, ΔG), the relation is often expressed as:

$$\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right)_p = -\frac{\Delta H}{T^2} \qquad (\ V.4)$$

This equation is crucial in chemical thermodynamics as it connects the temperature dependence of Gibbs free energy (and thus the spontaneity and equilibrium of a reaction) to its enthalpy change (ΔH).

V.2.4 Condition for Spontaneity

The criterion for spontaneity, dSint≥0 (where dSint is the entropy created internally due to an irreversible process), can therefore be translated as $\boldsymbol{\Delta G^{\circ}_{r}}$ **≤0 at constant pressure (P=C^{te})**.

The sign of dG allows us to predict the spontaneity of an isothermal transformation:

- If $\boldsymbol{\Delta G^{\circ}_{r}}$**<0** : The system can evolve **spontaneously** in the direction of 1 (reactants) → 2 (products).
- If $\boldsymbol{\Delta G^{\circ}_{r}}$**= 0** : The system is at **equilibrium** (reversible); 1 (reactants) ↔ 2 (products).
- If $\boldsymbol{\Delta G^{\circ}_{r}}$**>0** : Evolution in the direction of 1 (reactants) → 2 (products) is **non-spontaneous**. Instead, the reverse reaction (2 (products) → 1 (reactants)) may be spontaneous.

V.3 Variation of Gibbs Free Energy and Standard Gibbs Free Energy of Formation

V.3.1 Variation of G with State Parameters

The state function **Gibbs free energy (G)** can be described as a function of the state variables such as pressure (P), temperature (T), and the number of moles of each component (ni).

Thus, $G=f(P,T,n_1,n_2,\dots)$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,ni} dT + \left(\frac{\partial G}{\partial P}\right)_{P,ni} dP + \sum\left(\frac{\partial G}{\partial ni}\right)_{P,T,ni} \qquad (V.5)$$

a) **Variation of G with Temperature::**

At constant pressure (P) and constant number of moles (ni) (i.e., no transformation): P and ni = C^{tes})

Starting from the definition $G=H-T.S$ => the differential form is: $dG = dH-T.dS-S.dT$

At constant pressure, $P = C^{tes}$

From the First Law, $dH = dU+P\,dV = \partial Q - PdV + PdV$

$$dH = \partial Q \leq \partial Q_{rev} = TdS$$

For a reversible process (where dG = −SdT at constant P and n), or for an infinitesimal change:

$$\left(\frac{\partial G}{\partial T}\right)_{P,ni} = -S \qquad (V.6)$$

This equation shows that at constant pressure and composition, Gibbs free energy decreases with increasing temperature, as entropy (S) is always a positive value.

b) **Variation of G with Pressure:**

At constant temperature (T) and constant number of moles (ni) (i.e., no transformation): à (T and ni = C^{tes})

Starting from $G=H-T.S$ => the differential form is: $dG = dH-T.dS$

À $T= C^{tes}$

$$dH = dU+P\,dV + V\,dP = \partial Q - PdV + PdV + V\,dP$$

$$\partial Q \leq \partial Q_{rev} = TdS$$

$$dG=P\,dV$$

So, for a reversible process (or for an infinitesimal change)::

$$\left(\frac{\partial G}{\partial P}\right)_{T,ni} = V \qquad (V.\ 7)$$

This equation shows that at constant temperature and composition, Gibbs free energy increases with increasing pressure, as volume (V) is always a positive value.

Let the free energy of a system be G_1 in the initial state and G_2 in the final state ,when an apprediable change in pressure has takes place, at constant temperature. Then, integrating Eq (IV.7), the free energy change, $\Delta \boldsymbol{G}$, is given by:

$$\Delta \boldsymbol{G} = \boldsymbol{G2} - \boldsymbol{G1} = \int_{p1}^{P2} V dP \qquad (V.\ 8)$$

Where P_1 and P_2 are the initial and final pressures, respectively.

If one mole of an ideal gas is under consideration, then PV = RT

$$\Delta G = RT \int_{p1}^{P2} \frac{dp}{p} = RT \ln \frac{P2}{PI} = RT \ln \frac{V1}{V2} \qquad (V.\ 9)$$

Where V_1 and V_2 are the initial and the final volumes, respectively.

For *n* mole of gas,

$$\Delta G = RT \ln \frac{P2}{PI} = RT \ln \frac{V1}{V2} \qquad (V.\ 10)$$

c) Variation of G with Composition:

At constant pressure (P) and temperature (T):

The total differential of G considering changes in composition (number of moles, ni) for a multi-component system is:

$$dG = \sum \left(\frac{\partial G}{\partial ni}\right)_{P,T,ni} dn \qquad (V.\ 11)$$

At constant pressure and temperature,

$$\left(\frac{\partial G}{\partial ni}\right)_{P,T,ni} = \mu_i \qquad (V.12)$$

μ_i is called the chemical potential of component i in the system.

The chemical potential μi generally depends on the composition of the mixture, specifically on the different mole fractions (xi)..

V.3.2 Standard Gibbs Free Energy of Formation

The standard Gibbs free energy of formation $\Delta G^{\circ}_{\boldsymbol{R}}$ is the change in Gibbs free energy that accompanies the formation of one mole of a compound from its constituent elements in their standard states.

By convention, the standard Gibbs free energy of formation $\Delta \boldsymbol{G}^{\circ}_{\boldsymbol{f}}$ for an element in its most stable allotropic form at standard conditions is zero**:**

$$\Delta \boldsymbol{G}^{\circ}_{\boldsymbol{f}} = 0 \qquad (V.\ 13)$$

V.3.3 Standard Gibbs Free Energy of a Chemical Reaction:

For a chemical reaction occurring under constant pressure and temperature conditions, such as:

$$aA + bB \text{ ---------> } cC + dD$$

The **standard Gibbs free energy of reaction** ($\Delta G^{\circ}_{\boldsymbol{R}}$ is expressed as the difference between the sum of the standard Gibbs free energies of formation of the products and the sum of the standard Gibbs free energies of formation of the reactants:

$$\Delta G^{\circ}_{\boldsymbol{R}} = \sum \Delta G^{\circ}_{f\ (\text{produits})} - \sum \Delta G^{\circ}_{f\,(\text{réactifs})} \qquad (V.14)$$

This equation is fundamental for predicting the spontaneity of a chemical reaction under standard conditions.

Exercises and Solution

Exercise 1

Sulfur can be found in two crystalline forms: Sα (orthorhombic) and Sβ (monoclinic). Given that at standard pressure (P=P∘=1bar), for the process from Sα to Sβ:

Sα⟶Sβ

On peut trouver le soufre en deux formes cristallines S_a (orthorhormbique) et S_b (monoclinique) sachant que sous P=P° =1 bar, on a pour la process S_a à S_b , on a $\Delta G^{\circ}_{\boldsymbol{r(398K)}} = \mathbf{0}$; $\Delta H^0_{r(298)} = 296{,}8\, J.mol^{-1}$

a) Calculate $\Delta H^0_{r(T)}$ at temperature T for this change.

b) Calculate $\Delta G^{\circ}_{\boldsymbol{r(T)}}$ at temperature T for this change

Given :

$\Delta G^{\circ}_{\boldsymbol{r(398K)}} = \mathbf{0}$, $\Delta H^0_{r(298)} = 296{,}8\, J.mol^{-1}$

$Cp^0(S_a) = 17{,}2 + 19{,}7.10^{-3}T\ (J.K^{-1}.mol^{-1})$

$Cp^0(S_b) = 15{,}1 + 30{,}1.10^{-3}T\ (J.K^{-1}.mol^{-1})$

Solution 1

a-We apply Kirchhoff's law

$$\Delta H^0_{r(T)} = \Delta H^0_{r(298K)} + \int_{298}^{T} \Delta Cp^0 dT$$

$$\Delta Cp^0 = Cp^0(S_b) - Cp^0(S_a) = -2 + 30{,}1.10^{-3}T$$

Thus,

$$\Delta H^0_{r(T)} = \Delta H^0_{r(298K)} - 2{,}1\,(T - 298) + \frac{10{,}4\ 10^{-3}}{2}\,(T^2 - 298^2)$$
$$= 460{,}8 - 2{,}1T + 5{,}210^{-3}T^2$$

b-We apply the Gibbs relation

$$\left(\frac{\partial\left(\frac{\Delta G^{\circ}_{r}}{T}\right)}{\partial T}\right)_p = -\frac{\Delta H^0_{r(T)}}{T^2}$$

$$==>.\ d\left(\frac{\Delta G^{\circ}_{r}}{T}\right)_{p} = \frac{-460-2{,}1T+5{,}2\ 10^{-3}T^{2}}{T^{2}}\ dT$$

$$==>.\ \Delta G^{\circ}_{r(T)} = 460{,}8 - 11{,}16T + 2{,}1T\ lnT - 5{,}210^{-3}T^{2}$$

Exercise 2

Consider the following reaction:

$$F_{2(g)} + HCl_{(g)} \longrightarrow 2HF_{(g)} + Cl_{2(g)}$$

-Calculate ΔG°_{r} for this reaction.

Given : $\Delta G^{\circ}_{f}(HCl_{(g)}) = -95{,}18\ KJ.mol^{-1}$; $\Delta G^{\circ}_{f}(HF_{(g)}) = -276{,}21\ KJ.mol^{-1}$

Solution 2

The standard Gibbs free energy of reaction (ΔGR∘) is calculated using the standard Gibbs free energies of formation (ΔGf∘) of the products and reactants, weighted by their stoichiometric coefficients:

ΔGR∘=∑(stoichiometric coefficient×ΔG°_{f}(products)−∑(stoichiometric coefficient×ΔG°_{f}(reactants)

For the given reaction: $F_{2(g)} + HCl_{(g)} \longrightarrow 2HF_{(g)} + Cl_{2(g)}$

$\Delta G^{\circ}_{f}(HCl_{(g)}) = -95{,}18\ KJ.mol^{-1}$; $\Delta G^{\circ}_{f}(HF_{(g)}) = -276{,}21\ KJ.mol^{-1}$

$$\Delta G^{\circ}_{R} = 2\Delta G^{\circ}_{f}(HF_{(g)}) + \cancel{\Delta G^{\circ}_{f}(Cl_{2})} - \cancel{\Delta G^{\circ}_{f}(F_{2})} - 2\Delta G^{\circ}_{f}(HCl_{(g)})$$

$$\Delta G^{\circ}_{R} = -457.24\ kJ < 0 =>$$

Since the standard Gibbs free energy of reaction (ΔG°_{R})**is negative**, the reaction is **spontaneous** under standard conditions

Exercise 3

Under 1 atm pressure and at high temperature, the following equilibrium occurs::

$2\ CO(g) \quad \overset{1}{\underset{2}{\leftrightarrows}} \quad CO2(g) + C(s)$

a) Calculate the standard enthalpy, entropy, and Gibbs free energy of the reaction at 298 K. Deduce the equilibrium constant from these values.

b) Determine at what temperature (under 1 atm pressure) the following will occur::

a-90% moles of CO

b-50% moles of CO

Consider how this equilibrium will shift if :

a- The temperature is increased.

b- The pressure is increased.

c- Carbon (solid) is added.

d- An inert gas is added at constant pressure.

Given the following table :

Corps	CO(g)	$CO2(g)$	$C(s)$
$\Delta H^0_{f(cal.mol^{-1})}$	26400	94050	---
$S^0_{f(cal.mol^{-1}K^{-1})}$	47,32	51,06	1,36

Solution 3

P = 1 atm

$2\ CO(g) \quad \overset{1}{\underset{2}{\leftrightarrows}} \quad CO2(g) + C(s)$

A) According to Hess's Law

on a $\Delta H^0_{298} = -41250\ cal$; $\Delta S^{\circ}_{298} = -42,22 cal\ K^{-1}$

$$\Delta G^{\circ}_{298} = \Delta H^0_{298} - T\Delta S^{\circ}_{298}$$

⇨ $\Delta G^{\circ}_{298} = -28668,44\ cal$

$$K = e^{-\frac{\Delta G^{\circ}_{298}}{RT}} = 7,8\ 10^{20}$$

B) $\Delta Cp=0$ => $\Delta H_T^0 = \Delta H_{298}^0$; $\Delta S^\circ_T = \Delta S^\circ_{298}$

$\Delta G_{298}^0 = \Delta H_{298}^0 - T\Delta S_{298}^0 = -RT.\ln K$ =>

$$T = \frac{\Delta H_{298}^0}{\Delta S_{298}^0 - RT.\ln K}$$

a) 90% de CO => $X_{co} = 0{,}90$ et $X_{co2} = 0{,}10$

Or $K = \frac{P_{co2} . X_{co2}}{P_{co}^2 X^2_{co}} = 0{,}123$ thus, T=1084 K

b) For 50% moles of CO, we find

K=2 et T=946 K

3) Equilibrium Shifts

a) The **reverse reaction** (sense 2) is favored.

b) The **forward reaction** (sense 1) is favored.

c) There is **no effect**.

d) The **reverse reaction** (sense 2) is favored.

Chapter VI

Chemical Equilibrium

Chapter VI: Chemical Equilibrium

VI. 1. State of Equilibrium

In some reactions, reactants convert into products, but after a certain period, the products begin to react with each other to re-form the initial reactants. These are called **reversible reactions**. For such reactions, when the concentrations of both reactants and products become constant over time, we say that **equilibrium** has been reached.

Consider the following reaction:

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

Equilibrium is attained when the concentrations of the reactants and products remain constant; this is represented by the **double arrow** (⇌).

Note: A chemical equilibrium is **dynamic**. This means that at equilibrium, the rates of the forward and reverse reactions are equal but not zero; the reactions continue to occur, just at the same pace in both directions.

VI. 2. Guldberg and Waage's Law: The Equilibrium Constant

For a general reversible reaction:

$$aA + bB \rightleftharpoons cC + dD$$

The **equilibrium constant (K)** is defined as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \textit{(VI.1)}$$

Where:

- K is constant for a given reaction at a specific temperature.
- The bracketed terms **[ ]** represent the molar concentrations of the species in moles per liter (mol/L).
- The exponents for each substance correspond to their stoichiometric coefficients from the balanced chemical equation.

Note: The equilibrium constant, K, may possess units dependent on stoichiometric coefficients. K_c pecifically designates concentrations in mol/L.

VI. 3. Homogeneous Equilibrium

In a homogeneous equilibrium**,** all substances involved in the equilibrium exist in the same physical phase.

- Example 1 (Gaseous Phase):

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

- Example 2 (Liquid Phase):

$$CH_3CO_2H\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O\ (l)$$

a. Liquid Phase Equilibrium

For reactions occurring in the liquid phase, the **Law of Mass Action** uses molar concentrations. For Example:

$$CH_3CO_2H\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O\ (l)$$

The equilibrium constant, Kc, is written as:

$$kc = \frac{[CH_3CO_2C_2H_5][H_2O]}{[CH_3CO_2H][C_2H_5OH]}$$

b. Gaseous Phase Equilibrium: Relation between Kc and Kp

Consider a general reaction occurring in the gaseous phase:

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

In terms of concentrations, the equilibrium expression is:

$$Kc = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \textit{(VI.2)}$$

We can also express the equilibrium constant in terms of **partial pressures** (Pi). This is denoted as Kp:

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} \qquad (VI.3)$$

Using the ideal gas law,

$$P_i = \frac{ni}{V} RT$$

where [i] is the molar concentration of component i. Substituting these into the *Kp* expression:

$$Kp = \frac{[C]^c[D]^d}{[A]^a[B]^b} (RT)^{(c+d)-(a+b)} \qquad (VI.4)$$

Let's define Δn as the change in the number of moles of gas from products to reactants:

$\Delta n = (c+d)-(a+b) = (\sum \nu_{i,\text{products}}) - (\sum \nu_{j,\text{reactants}})$

Thus, the relationship between Kp and Kc becomes:

$$K_p = K_c(RT)^{\Delta n} \text{ or } K_p = K_c(RT)^{-\Delta n}$$

Note: When Δn=0, then $K_p = K_c$. This occurs when the total number of moles of gaseous products equals the total number of moles of gaseous reactants.

VI.4. Heterogeneous Equilibrium

A heterogeneous equilibrium involves a reversible reaction where substances are in different phases**.**

a. Solid-Gas Heterogeneous Equilibrium

For reactions like: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

The equilibrium constant expressions only include the gaseous component:

- In terms of concentration: $Kc=[CO_2]$
- In terms of partial pressure: $Kp=P_{CO2}$

Note: In solid-gas heterogeneous equilibria, pure solids and liquids are omitted from the equilibrium constant expression because their concentrations are considered constant.

b. Solid-Liquid Heterogeneous Equilibrium

For reactions involving solids and dissolved ions (in solution), such as:

$Co(s) + Ni^{2+}(aq) \rightleftharpoons Co^{2+}(aq) + Ni(s)$

The equilibrium constant (Kc) is expressed by considering only the species in the liquid (solution) phase:

$$Kc = \frac{[Co^{2+}]}{[Ni^{2+}]}$$

Note: In solid-liquid heterogeneous equilibria, the Law of Mass Action applies exclusively to the liquid (solution) phase. Pure solids (and pure liquids, if present) are not included in the equilibrium constant expression as their concentrations remain constant.

c. Liquid-Gas Heterogeneous Equilibrium

For reactions like:

$$H_2O(l) \rightleftharpoons H_2O(g)$$

The equilibrium constant expressions only include the gaseous component:

- $Kc=[H_2O]$
- $Kp=P_{H2O}$

Note: For liquid-gas equilibria, only the gaseous phase is included in the Law of Mass Action expression, as the concentration of the pure liquid is constant.

VI.5. Extent of Reaction

The magnitude of the equilibrium constant (**K**) provides insight into the extent of a reaction at equilibrium:

- If the value of K is **l**arge, it means the products are favored. In other words, the reactants have a strong tendency to convert into products.
- If the value of K is very large, the reaction can effectively be considered complete, meaning almost all reactants have transformed into products.
- Conversely, a very small value of K indicates that the reaction proceeds to a very limited extent; the reactants are favored over the products.

VI. 6. Direction of Reaction Evolution

When a reaction mixture contains both products and reactants, its position relative to **equilibrium** must be determined. Three states are possible:

- **At equilibrium:** The system is stable.
- **Shifting right:** Reactants convert to products to reach equilibrium.
- **Shifting left:** Products convert to reactants to reach equilibrium.

To predict this direction, the **reaction quotient (Q)** is calculated. Q has the same form as the equilibrium constant (K), but uses instantaneous (non-equilibrium) concentrations or partial pressures.

For example, for :

$$2A(g) \rightleftharpoons B(g) + C(g)$$

$$Q_c = \frac{[B][C]}{[A]^2} \qquad (VI.5)$$

Comparing Q with K indicates the direction of net reaction to achieve equilibrium.

VI.7. Gibbs Free Energy and Equilibrium

a. Equilibrium at Constant Temperature

For a chemical reaction :

$$aA + bB \rightleftharpoons cC + dD$$

involving ideal gases at constant temperature (T), the ***Gibbs free energy change of reaction*** ($\Delta_r G_T$) is given by:

$$\Delta_r G_T = \Delta_r G_T^\circ + RT \ln\left(\frac{P_C^c P_D^d}{P_A^a P_B^b}\right) \qquad \textit{(VI.6)}$$

Here, the term $\left(\frac{P_C^c P_D^d}{P_A^a P_B^b}\right)$ represents the **reaction quotient** (Q_p), which is expressed in terms of the partial pressures of reactants and products *before* the reaction reaches equilibrium.

Spontaneity Criteria:

- $\Delta_r G_T$ **<0**: Reaction proceeds spontaneously to the right.
- $\Delta_r G_T$ **>0**: Reaction proceeds spontaneously to the left.
- $\Delta_r G_T$ **=0**: Reaction is at **equilibrium**.

At equilibrium, Qp=Kp (the equilibrium constant). Therefore: $0 = \Delta_r G_T^\circ + RT \ln K_p$

This yields a fundamental relationship:

$$\Delta_r G_T^\circ = - RT \ln K_p \qquad \textit{(VI.7)}$$

K_p is the equilibrium constant expressed in terms of partial pressures at equilibrium.

8. Le Chatelier's Principle

Le Chatelier's Principle states: "Any change to a factor at equilibrium will cause the equilibrium to shift in a direction that opposes that change."

The factors that can influence an equilibrium are:

- Temperature
- Concentrations **or** partial pressures **of reactants/products**
- Total pressure

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