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Lessons and exercises in thermodynamics (chemistry-2)

2023-2024

Summary

Every nonfiction book has a purpose or mission. The mission of this book is to give the reader an overview of the important principles, concepts, and analytical techniques related to thermodynamics, written in such a way that this abstract and complex subject is relatively easy to understand and includes students of a common core of material sciences, sciences, techniques, and related disciplines who have scientific and mathematical backgrounds. The content is presented in a way that also allows many non-engineering professionals to follow the material and gain useful knowledge. For power engineers who have been away from direct engineering practice for a while.

This book will serve as a quick and effective update. Thermodynamics topics such as enthalpy, entropy, work, latent heat, heat, heat of fusion, heat of sublimation, etc. are explained in detail. Phases of matter, the law of conservation of energy, the first, second, and third laws of thermodynamics, ideal gas laws, and related formulas are also covered. The author examines various thermodynamic processes as well as heat and energy cycles such as Carnot. Case studies are used to illustrate various principles of thermodynamics.

Each chapter concludes with a list of questions and problems for self-assessment, with brief answers provided. The publication was also provided with some assignments and exams as models for the review process and assessment of its level, which enables students to evaluate themselves effectively before exams and increase their chances of success.

Keywords: thermodynamics, energy, heat, lessons, and exercises.

كل كتاب غير روائي له هدف أو مهمة. مهمة هذا الكتاب هي إعطاء القارئ نظرة عامة على المبادئ والمفاهيم والتقنيات التحليلية المهمة المتعلقة بالديناميكا الحرارية، مكتوبة بطريقة تجعل هذا الموضوع المُجرد والمُعقد سهل الفهم نسبيًا، ويشمل طلبة جذع مشترك علوم المادة وعلوم وتقنيات والشعب القريبة منها والذين لديهم خلفيات علمية ورياضية. يتم تقديم المحتوى بطريقة تسمح أيضًا للعديد من المهنيين غير الهندسي بمتابعة المواد واكتساب معرفة مفيدة. بالنسبة لمهندسي الطاقة الذين كانوا بعيدًا عن الممارسة الهندسية المباشرة لفترة من الوقت.

سيكون هذا الكتاب بمثابة تحديث سريع وفعال. يتم شرح وتوضيح مواضيع الديناميكا الحرارية مثل الأنتالبيه، الأنتروبيا، الشغل، الحرارة الكامنة، الحرارة، حرارة الانصهار، حرارة التسامي... بالتفصيل. يتم أيضًا تغطية مراحل المواد، وقانون حفظ الطاقة، والقانونين الأول، الثاني والثالث للديناميكا الحرارية، وقوانين الغاز المثالي، والصيغ ذات الصلة. يفحص المؤلف العمليات الديناميكية الحرارية المختلفة، بالإضافة إلى دورات الحرارة والطاقة مثل كارنو... يتم استخدام دراسات الحالة لتوضيح مبادئ الديناميكا الحرارية المختلفة.

ويختتم كل فصل بقائمة أسئلة ومشاكل للتقييم الذاتي، مع توفير الإجابات مختصره. كما تم تزويد المطبوعة ببعض الفروض والامتحانات كنماذج لعملية المراجعة وتقييم مستواه، والتي تمكن الطلاب من تقويم أنفسهم بشكل فعال قبل الامتحانات وزيادة فرص نجاحهم.

الكلمات المفتاحية: الديناميكا الحرارية، الطاقة، الحرارة، دروس وتمارين

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General Introduction

There are many types of energy, such as thermal energy, electrical energy, mechanical energy, chemical energy, magnetic energy, kinetic energy, surface energy, etc., and under certain conditions, these types of energy can transform into each other.

Energy production is one of the most important advantages that accompany and characterise chemical reactions. Every chemical reaction is subject to two main laws: the law of conservation of matter and the law of conservation of energy. When someone eats candy, its contents, especially sugar, react with oxygen to produce H2O and CO2, and as a result of this reaction, thermal energy is emitted that helps the body move its muscles and maintain a suitable body temperature. There are many examples in this life of exothermic or endothermic reactions. For example, great heat is emitted when burning coal, natural gas, and other petroleum derivatives, and this heat or energy is used in various aspects of life. There are also some chemical reactions that absorb heat, including the dissociation of water to prepare oxygen and hydrogen. Humans on planet Earth produce more than 90% of their energy from chemical reactions, especially those resulting from burning coal, oil, and natural gas.

The science that investigates energy and its changes is called thermodynamics. This science is studied in chemistry, physics, engineering, pharmacy, and other sciences. What interests us about thermodynamics in this chapter is the part that links energy changes to chemical reactions, and this science is called thermochemistry.

This science was built on the basis of the great human experience that energy exists and cannot be created or destroyed. From this fact, it was possible to derive various mathematical relationships between the properties of the material, which involve the absorption of heat.

The study of thermodynamics relies mainly on three generalisations known as the three laws of thermodynamics, which are: the first law, the second law, and the third law of thermodynamics. These three laws do not depend on any model or theory of atomic or molecular structure or the nature of matter. Therefore, any development that occurs in current ideas and theories regarding the nature of molecules will not affect in any way the validity of any thermodynamic result.

It is worth noting that the prevailing thermodynamic references in our country relied on the French language in presenting them.

Due to the lack of references in Arabic that first-year students may need, a common core is material sciences, sciences, and techniques, and the branches related to them that rely on the basic concepts in chemistry in general.

A publication of lessons and exercises in thermodynamics (Chemistry-2) has been prepared in accordance with the pedagogical programme for common basic education for the first year, a common core, material sciences, sciences, and technologies, which is ruled and specified by the Ministry of Higher Education and Scientific Research for the content of the standard, through the preparation of a publication of detailed lessons and a group. One of the exercises was solved in an analytical manner based on demonstrating relationships and methods of linking them.

On the other hand, this publication includes additional exercises so that the student can develop his thinking and evaluation methods, making him an expert in solving other situations and knowing how to evaluate. This has been taken into account in these exercises.

The programme was meticulous, as was the use of precise scientific terminology for thermodynamics, while maintaining the link between these exercises and making them a tool for deepening the theoretical understanding presented in the lectures delivered. The level of students' reception and comprehension ability was also taken into account by using simple academic language. The publication was also provided with some assignments and exams as models for the review process and level assessment, which enable students to evaluate themselves effectively before exams and increase their chances of success.

This publication covers five chapters:

- Chapter One: Introduction to Thermodynamics.

- Chapter Two: The First Principle of Thermodynamics.
- Chapter Three: Applications of the First Principle of Thermodynamics.
- Chapter Four: The Second and Third Principles of Thermodynamics.
- Chapter Five: An Introduction to Chemical Equilibria.

I hope that all students aspire to higher grades and first ranks. This is a legitimate right for everyone and is not limited to anyone. Know, dear student, that your self-effort and intellectual activity are the basic foundation for your success and excellence, so be sure to do what you can and cooperate with your teachers to achieve your goal.Finally, we hope that we have contributed, even if only a little, to removing some of the mistakes and obstacles that the student encounters in his academic journey.

Chapter one

I.1. Introduction

Thermodynamics is one of the branches of physical chemistry that is concerned with studying the changes in thermal energy that accompany various chemical and physical transformations. The information obtained from studying thermal movement helps predict whether a chemical or physical change will occur spontaneously or whether it will not occur spontaneously. The term thermodynamics consists of an English word that comes from Greek origins: thermos, meaning heat, and dynamic, meaning energy. As a result, this term refers to the process of moving heat from one form to another (such as converting heat into work).

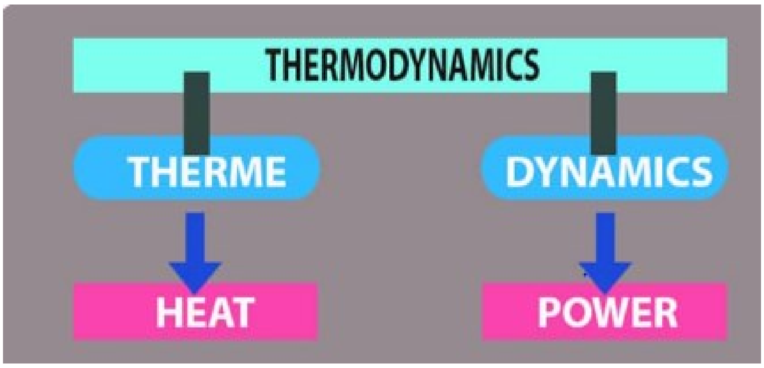


Fig. I.1 explains the meaning of thermodynamics

I.2. History of thermodynamics

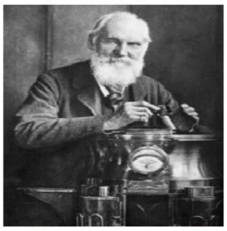
The history of thermodynamics is regarded as a major branch of the history of physics, the history of chemistry, and the history of science in general. The development of classical mechanics, quantum mechanics, magnetism, and chemical kinetics are closely associated with the history of thermodynamics. The technological development of steam engines and internal combustion engines, low-temperature physics, and electricity generation also benefited from its influence. The study of engines led to the origins of thermodynamics. Otto von Guericke, a German

Robert Boyle
1691-1627

scientist, designed the first signs of engines in 1650.Shortly thereafter, the Irish physicist and chemist Robert Boyle studied Otto's designs, and in 1656, in collaboration with the English scientist Robert Hooke


Thomas Savery
1650 -1715


Sadi Carnot
1796-1832


William Thomson
1907-1824

They built an air pump, said Robert Hooke. Using this pump, Boyle and Hooke examined the relationship between pressure and volume, which showed that pressure multiplied by volume equals a constant. Following the invention of the thermometer, it became possible to study temperature properties quantitatively. This invention gave the scientist Lussac the opportunity to derive his law, which led shortly thereafter to knowledge of the ideal gas law. In 1698, engineer Thomas Savery designed the first steam engine. Although these primitive engines were simple and had low efficiency, they attracted the attention of the pioneering scientists at that time. Sadi Carnot, "the father of thermodynamics," is among these scientists. In 1824, he published the research paper "Reflections of the Kinetic Power of Fire," which was a lecture on heat, energy, and the efficiency of engines, and it is considered one of the important signs in the beginning of the transformation of thermodynamics. a subject of modern science. In 1834, James Joule experimentally introduced the principle of heat-equivalent mechanical potential. Joule reported on his most famous experiment in 1845, where he used a dropped weight from above to turn a pedal wheel inside a barrel of water. Estimation of heat-equivalent mechanical capacity. This led to the emergence of the theory of energy conservation, which explained why heat can do work. In the 1850s, the famous mathematical physicist Rudolf Clausius defined the term entropy as heat lost or converted into exhaust. However, the word "thermodynamics" was not known until 1854. In that year, the British physicist and mathematician William Thomson (Lord Kelvin) coined the term thermodynamics in his research paper on "The Dynamic Theory of Heat. "In 1871, the Scottish physicist and mathematician James Clerk Maxwell, together with Clausus, formulated a new branch of thermodynamics called statistical thermodynamics, which analyzes a large number of particles under equilibrium.

Shortly thereafter, in 1875, the Austrian physicist Ludwig Eduard Boltzmann formulated a precise relationship between entropy and molecular motion. In 1876, an important point in the development of human concepts occurred. During this period, chemical engineer Willard Gibbs published a 300-page research paper entitled On the State of Equilibrium in Heterogeneous Substances, in which he formulated one of the major equations, the caged equation for free energy, which gives the amount of useful work that can be obtained from chemical reaction systems. Gibbs also established the principle we now know as enthalpy and called it the “temperature function of constant pressure.”


Willard Gibbs
1903–1839

I.3. Benefits of thermodynamics:

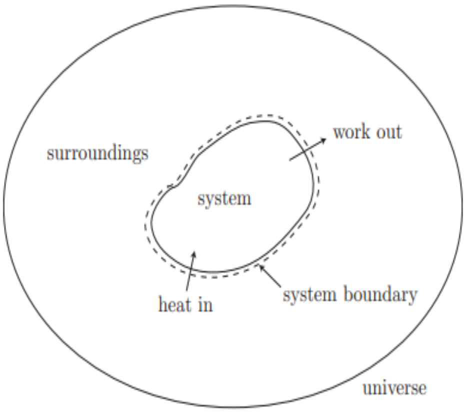
The science of thermodynamics answers important questions, such as:

- ✓ Why do chemical reactions occur?
- ✓ Why do some reactions spontaneously occur until they complete, while others only partially complete, and some reactions never occur under the same conditions?
- ✓ What are the energy changes associated with chemical reactions, whether in the reactions themselves or in the surrounding environment?

The science of thermodynamics is one that does not care about the time factor in reactions. It only predicts whether a specific chemical change or, in general, a change is likely to occur or not without indicating the speed at which this change will occur. The reaction, for example, may be spontaneous and occur very slowly, such as iron rusting. Some reactions may require simple stimulation to occur, such as the combustion of hydrogen with oxygen, where the reaction only begins in the presence of a spark of fuel. The irreversible nature of spontaneous reactions, such as the inability to disassemble a water molecule after formation, is one of their characteristics.

I.4. Some Thermodynamic Terms

1. The System: That part of the universe on which we focus our attention or on which the experiment is conducted, and everything below it is called the surroundings or the external environment (Surroundings), and the system's boundaries separate it from the surroundings.



- The surrounding middle (the perimeter of the sentence): is everything outside the sentence.

- System boundary: This is the real or imaginary surface that surrounds the sentence and separates it from its surroundings.

The sentence can be of the following types: ?

✍ An open system: is like an uncovered cup containing a boiling liquid, is a sentence in which both matter and energy can pass through its limit. The liquid absorbs energy from the external environment until it boils, and in return, it releases its vapor into the external environment.

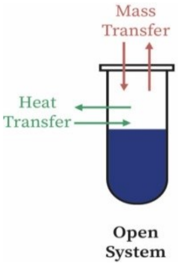
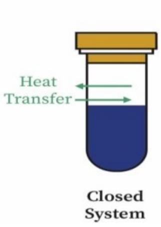
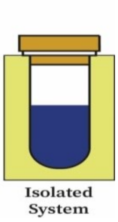
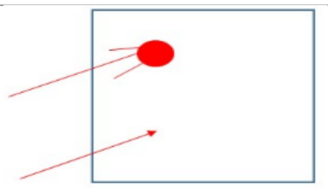
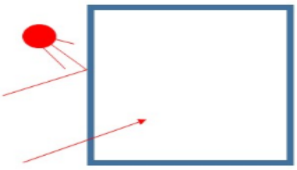
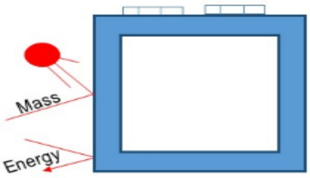
✍ A closed system: is a sentence in which matter cannot permeate the term of the sentence while energy can permeate the term of the sentence, such as a liquid boiling in a tightly covered cup.

✍ An isolated system: is a sentence in which both matter and energy cannot escape from the limit of the sentence, such as an ideal thermos containing coffee, where the coffee remains hot without loss in quantity or energy.

Comparison between the exchange of matter and energy between the system and the external environment

System	Exchange of matter	Exchange of energy
Isolated	No	No
Closed	No	Yes
Open	Yes	Yes

Comparing different patterns of thermodynamic system

		
		
Open system	**Closed system**	**Isolated system**

2. Homogeneous and heterogeneous systems:

A system is homogeneous if it consists of only one phase or state, and this phase may be either gaseous, liquid, or solid. If it contains more than one phase, it is a heterogeneous sentence.

- ✓ In the case of gases, the system is always homogeneous because the gases are miscible with each other.
- ✓ In the case of liquids, it is based on their physical and chemical properties.

3. State Variables:

When describing a physical chemical change, we need to determine the properties of the system (the set of variables that accurately describe the system) before and after the change. These variables are called the thermodynamic state of the system. The dynamic state of the system is described by measuring the amounts of a group of physical variables of the system called state variables. The most important state variables are:

- ✍ Temperature: It is what describes the degree of hotness or coldness of a substance, and we symbolize it with the symbol (T), and it is measured with two scales, usually in Kelvin (K) and other times in Celsius (°C). There are also scales that are still used in some cases. Countries to this day, perhaps the most famous of which are the Fahrenheit (°F) and rankine (R) scales, where

$$\mathbf{T(K) = T(^{0}C) + 273{,}15 \;;\quad T(R) = 1{,}8T(K)}$$

$$\mathbf{T(°F) = 1{,}8T(^{0}C) + 32 \quad;\quad T(R) = T\,(^{\circ}F) + 459{,}67}$$

- ✍ Pressure: It is the force applied to a unit of area, and we symbolize it with the symbol (P), as it is measured in the international unit of the pascal ($Pa = N/m^2$). However, due to their small size, we replace these units with larger ones, such as the bar (bar), which equals 10^5 Pa. The atmospheric pressure unit (atm) also measures it, and the height of a mercury column 760 mm long over an area of 1 cm^2 is a common method.

atm	Pa	bar	mmHg
1	1,10325×105	1,01325	760

- Volume: The amount of space that this solid occupies in space, and we symbolize it with the symbol (V). It is measured in the international unit of cubic meters(m^3 or cm^3). There are other special units used to measure volume, such as the liter (L), cup, and gallon. (Gallon), but it is mostly derived from units of length, where:

L	m^3	dm^3	cm^3	Gallon americain
1	10^{-3}	1	10^3	0,264

- The number of moles of a substance (number of moles): It is the ratio of its mass given in a chemical reaction to the mass of one mole of that substance. We symbolize it with the symbol (n_i), and it is measured in the unit (mole), and one mole of any substance is equal to Ovogadro's number (N_A), i.e., $N_A = 6,023\times10^{23}$.
- Mass: It is defined as the amount of matter a body contains, and we symbolize it with the symbol (m), as it is measured in the international unit kilogram (Kg). There are multiple sub-units for measuring mass in the international system, including the gram (g) and the milligram (mg), and the units of mass measurement in the English system are the pound and the ounce.

Kg	g	mg	Pound (Ibs)	Ounce (oz)
1	103	106	2,204	35,274

I.5. Properties of a System:

State variables can be divided into two groups:

1. Extensive properties (inclusive or external): These are the properties that depend on the amount of matter present in the system, such as mass, volume, number of moles, length, etc.
2. Intensive Properties (intensive or internal): These are the properties that do not depend on the amount of matter present in the system, such as pressure, temperature, density, surface tension, electromotive force, and electric potential. All of these properties are characteristic of the substance but do not depend on its quantity.

So, expansive quantities are quantities that are proportional to the amount of matter in the sentence, while condensative quantities are quantities that are not related to the amount of matter in the sentence.

Important note:

If we divide an extensional property by an extensional property, it gives us a focal property.

$$\boxed{\text{Intensive} = \frac{\text{Extensive}}{\text{Extensive}}}$$

Illustrative example:

Volumetric mass (ρ) is a concentration property (Intensive), where Intensive=$\rho = \frac{m}{V}$.

I.6. Thermodynamic Equilibrium:

The sentence is in a state of dynamic equilibrium (Hariri dynamics) when the state variables are constant at every point and change with time. The study of equilibrium in physical and chemical systems is of great importance in thermal motion. There are three types of equilibrium:

1. Mechanical Equilibrium: This type of equilibrium occurs when there is no microscopic change in the system over time.
2. Chemical Equilibrium: This type of equilibrium occurs when the concentration of a substance does not change over time.
3. Thermal equilibrium: This type occurs when the temperature is equal to the surrounding medium. This type of equilibrium is represented by the zeroth law of thermodynamics, which states that if two systems are in a state of equilibrium with the third system, then the two systems are in a state of equilibrium with each other.

I.7. Different transformations of the system (types of processes in thermodynamics):

When one or more properties are changed, we say that there has been a change in state (1) to (2). The path between (1) and (2) is called a transformation or process. If the sentence goes through transformations that return it to its initial state, we say that the sentence has gone through a cycle.

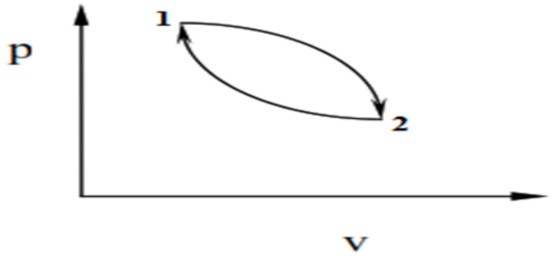


Fig. I.2: A cycle consisting of two operations

1. Reversible processes: (slow, perfect, imaginary, etc)

The reversible transformation is the transformation that moves the sentence away from its initial state or returns it to it so that the sentence is at one stage in a state of equilibrium. These are slow transformations, and the external pressure is equal to the internal pressure ($P_{ext} = P_{int}$). It passes through many equilibrium states to reach its final state, and it is possible to return from the final state to the initial state. Example: heating an object and then cooling it.

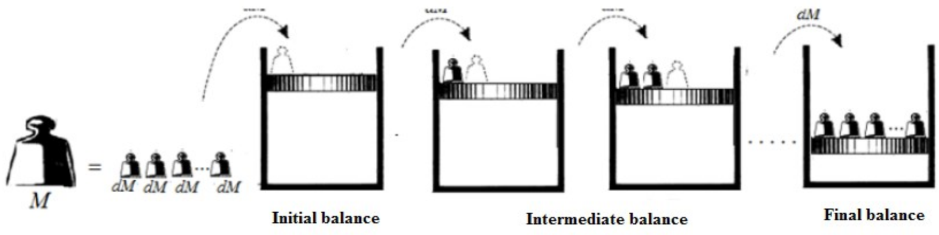


Fig. I.3: Reversible transformations in thermodynamics

2. Irreversible processes: (one-way, natural, fast...)

Irreversible transformations are spontaneous transformations and are distinguished from reversible transformations in that they do not go through a state of equilibrium at every moment and do not return them to the same starting point. The system transitions from the initial state to the final state quickly, but without returning to the initial state. Such as combustion and life. Whether reversible or irreversible, transformations fall into the following categories:

Fig. I.4: Irreversible transformations in thermodynamics

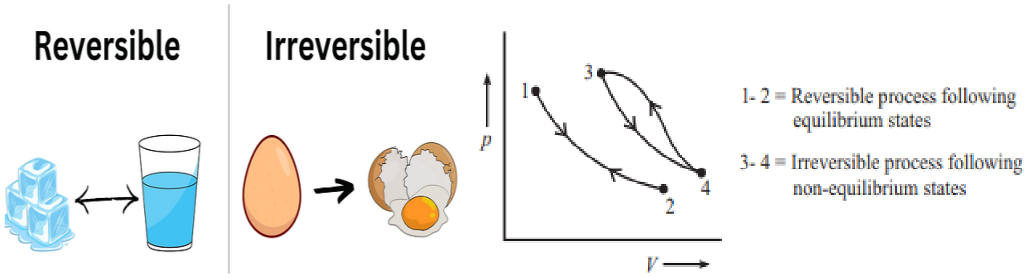


Fig. I.5: Differences between reversible and irreversible

- Constant heat transformations (isothermal process): $T = C_{ste}$

These are the processes that occur when the temperature (T) is constant, and as a result, there is no change in the internal energy of the system ($\Delta U = 0$).

- Constant pressure transformations (isobaric process): $P = C_{ste}$

These are the processes that occur when the pressure (P) is constant, usually the normal atmospheric pressure, and as a result, expansion or contraction of the gases in the system can occur, thus changing its volume changes (V).

- Constant volume transformations (isochoric processes): $V = C_{ste}$

These are the processes that occur in a closed system with a fixed volume (V), and as a result, no work can occur in or on the system ($W = 0$).

- Adiabatic transformations(adiabatic process):

These are the processes that occur in an isolated system (such as a calorimeter, for example); that is, no heat transfer occurs to and from the system, i.e., $Q = 0$.

Important note:

We have used the term transformations instead of reactions because it is more inclusive of chemical reactions and physical transformations.

All objects can exist, depending on the conditions of temperature and pressure, in one of three states: solid, liquid, or gas. The passage from one state to another constitutes a change in physical state or a change in phase.

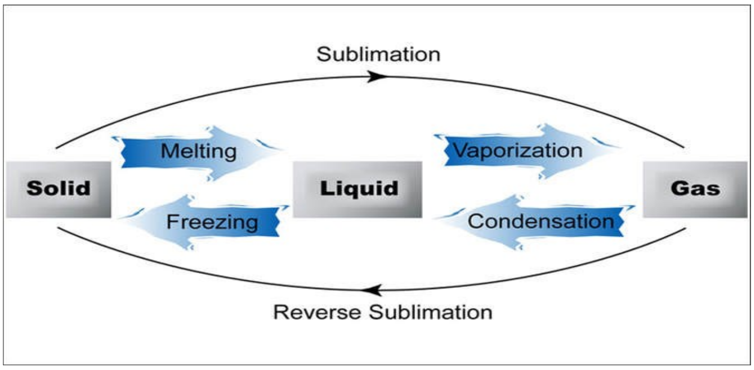
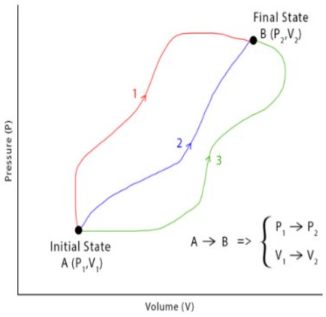


Fig. I.6: Diagram of transformation states of

I.8. State Functions:

We say about a function that it is a “state function” if the amount of change in the function does not depend on the method (path) by which the change or interaction took place, but rather depends only on the initial state before the initial change and the final state after the change (FS). Whatever path is followed (1, 2, or 3) to move from the initial state (IS) to the final state (FS), the change in the value of the function describes the difference between the two states, that is, the initial state and the final state of the system, and the amount of change in the value of the function does not depend on the path on which the chemical reaction or physical change occurred. The change in the state function is symbolized by the symbol Δ and is read Delta. For example, it refers to the change in temperature as ΔT, the change in pressure as ΔP, and the change in volume as ΔV. This change is equal to the difference between the final value of the function and its initial value $\Delta V = V_f - V_i$. Pressure, temperature, volume, mass, amount of matter, electric charge, and amount of heat are all state functions because their change during a transformation is not related to the path taken by this transformation, while work and the amount of heat are not state functions because they are related to the distance of the transition (i.e., related to the path).

I.9. Gases:



Matter in the gaseous state is similar to matter in the solid and liquid states in that it consists of small particles (particles) in a state of continuous movement, but the gases differ from liquids and solids in the following:

- The distance between the molecules in a gas is very far apart.
- Weakness and exchange between molecules, attraction and repulsion, to a degree that can be neglected.
- The movement of gas molecules is random, which leads to the size and shape of the gas not being determined.
- The volume of a gas is greatly affected by pressure and temperature.

1. Perfect or ideal gas:

An ideal gas can be characterized by the following properties:

- Single molecules are similar in mass and size.
- Gas molecules move randomly (indefinitely in size and direction). During their movement, they collide with the wall of the vessel, resulting in pressure.
- Gas molecules are spherical in shape and completely elastic.

Experimentally, it was found that gases follow three laws related to gas volume, pressure, and temperature, and the gas that follows these laws is called an ideal gas.

The concept of an ideal gas: is that it is a gas composed of elastic molecules that ignore mass and size, and the force of cohesion (forces of mutual influence) does not affect between its molecules.

Boyle-Mariotte Law:

When the temperature is constant, the pressure of an ideal gas is inversely proportional to the volume, where $V \alpha \frac{1}{P} \leftrightarrow T= C^{ste}$

$$P_1V_1=P_2V_2 \leftrightarrow P\times V= n\,.R.T= \text{Constant}$$

Gay-Lussac's Law:

When the pressure is constant, the volume of an ideal gas is directly proportional to the temperature, where $V \alpha T \leftrightarrow P= C^{ste}$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \leftrightarrow \frac{V}{T}=\text{Constant}$$

Charles-Amontons's Law:

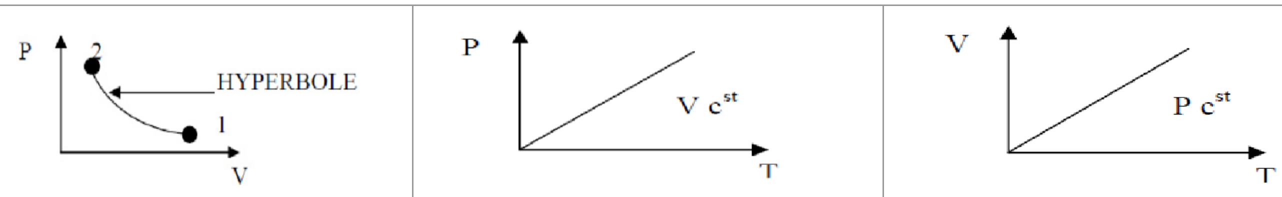
When the volume is constant, the pressure of an ideal gas is directly proportional to the temperature, where $P \alpha T \leftrightarrow V= C^{ste}$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \leftrightarrow \frac{P}{T}=\text{Constant}$$

Avogadro's Law:

Equal volumes of different gases that have the same temperature and pressure. It contains the same number of m n $\leftrightarrow V \alpha n.P.T.Cste$ $V= C^{ste}$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \leftrightarrow \frac{V}{n}=\text{Constant}$$



Boyle-Mariotte Law **Charles-Amontons's Law** **Gay-Lussac's Law**

Fig.I.7: Relationship between state variables

The general law for ideal gases:

It is the relationship between the three properties (T, P, and V), which is written as follows:

$$P.V = n.R.T$$

Where: P: gas pressure (Pa) or (atm), V: volume (L) or (m3), T: temperature (K), n: number of moles of gas (mol), and R: ideal gas constant, constant values Ideal gases change units with the three variables (T, P, and V).

Constant values and units for ideal gases

R (atm.L/mol. K)	R (J/mol. K)	R (Cal/mol. K)	R (mmHg.L/mol. K)
0,082	8,314	≃2	62,363

2. Real Gas Law (Van der Waals Equation for a Real Gas)

The general equation for ideal gases applies to the so-called ideal gas, and gases follow ideal behavior at low pressure and high temperatures. It was noted that the further we move away from these conditions, the more the gas deviates from the previous laws, as Vander Waals arrived at the following equation:

$$\left(P + \frac{a.n^2}{V^2}\right)(V - n.b) = nRT$$

where a: an approximation factor to fix the pressure effect and b: an approximation factor to fix the volume effect.

$$a = \frac{27.T^2.R^2}{64.P} \quad , \; b = \frac{R.T}{8.P}$$

The values of the constants (a, b) depend on the nature of the gas because the sizes and molecular attractions change from one gas to another, and their numerical value is determined from practical experiments.

Values of Van der Waals constants for some gases		
Gas	**a (atm.L^2.mol^{-2})**	**b (L.mol^{-1})**
He	**0,034**	**0,0237**
Ne	**0,211**	**0,0171**
H_2	**0,244**	**0,0266**
NO	**1,34**	**0,0279**
CO	**1,35**	**0,0322**
CH_4	**1,36**	**0,0318**
N_2	**1,39**	**0,0391**
H_2O	**5,46**	**0,0305**

I.10. Dalton's Law of Partial Pressures:

When a number of gases are mixed in one container (provided that no reaction occurs), each gas spreads, occupies its volume, and creates a pressure called partial pressure. The total pressure of the gaseous mixture in a certain volume is equal to the sum of the molecular pressures of the gases that make up the mixture:

$$P_T = \sum_i^n P_i = P_1 + P_2 + P_3 \ldots P_n$$

Where

P_T: total pressure

P_1: partial pressure of gas (1)

P_2: partial pressure of gas (2)

Assuming that all gases are ideal and that the mixture occupies a volume V at a temperature T, then:

$$P.V=n.R.T \leftrightarrow P = \frac{n.R.T}{V}\ , P = \frac{R.T(\,n_1+n_2 \ldots + n_k\,)}{V}$$

$$P_T = P_1 + P_2 + \cdots + P_k = \frac{n_1.R.T}{V} + \frac{n_2.R.T}{V} + \cdots . \frac{n_k.R.T}{V}$$

$$\boxed{P_i = \chi_i \times P_T}$$

Where $\chi_i = \frac{n_i}{n_T}$

So: $\sum \chi_i = 1$

Where n_i: the number of moles of gas

P_i: the appropriate partial pressure of the gaseous component present in the mixture.

χ_i: the mole fraction.

Exercise series
(Introduction to Thermodynamics)

Exercise -1-:

Use the following systems or sentence structures:

A. The solid material of a burning candle is present.
B. Boiling liquid water.
C. Electric motor in operation.
D. A burning lamp.

In each case, determine whether the system is open or closed.

Answer: open systems (A, D) and closed systems (B, C)

Exercise -2-:

An ideal gas is transformed into: Under a constant temperature, from the initial state marked by (P_1 = 5atm, V_1 = 20 L) to the final state, where does the volume become 50l?

- Calculate the final pressure of the gas.

Under constant pressure from the initial state marked by (T_1 = 100 K, V_1 = 10 L) to the final state, where does the temperature become 300 K?

- Calculate the final volume of the gas.

Under a constant volume from the initial state marked by (P_1 = 2atm, T_1 = 27°C) to the final state, where the temperature becomes 227 °C.

- Calculate the final pressure of the gas.

Answer: P_2 = 2atm ،V_2= 30L ، P_2'= 3,33 atm.

Exercise -3-:

A metal flask with a capacity of 1.8 liters is filled with the nitrogen gas N_2 at a temperature of T_1=10°C and a pressure of P_1 = 100 bar.

- Calculate the mass of nitrogen gas in the bottle.
- The flask is left exposed to the sun. What is the new pressure?
- We want the gas pressure to remain at P = 100 bar at the temperature T = 38°C.

- What is the amount of nitrogen that needs to exit the bottle?

It is given: M_N = 14 g/mol, R = 8.31 J/mol.

Answer: m_1 = 214,19 g, P_2 =109,99 bar, m' = 19,27 g.

Exercise -4-:

We consider an ideal container to hold 10g of oxygen gas at a pressure of 15 atm and a temperature of 57°C. After a while, we find that the pressure drops to 3/4 (three-quarters) of the initial value and the temperature is 27°C as a result of its leakage.

- What's the size of the bowl?
- What is the amount of oxygen in grams that leaked? R = 0.082 L atm/mol K

Answer: m_2 = 8,25 g, m' = 1,75 g.

Exercise -5-:

In a 100-liter container, there are the following gases: 2800 grams of N_2, 800 grams of O_2, 110 grams of CO, and 54 grams of water vapor. We consider all gases to be ideal and below the 273K temperature.

- Find the total pressure, mole fractions, and partial pressures of each gas.

Answer: $P_T = 29{,}9\times 10^5$ Pa ، χ_{N2}=0,758 , χ_{O2}=0,189 , χ_{CO}=0,03, χ_{H2O}0,023، P_{N2}=22,38atm ،P_{O2}=5,58atm ،P_{CO}==0,886atm ،P_{N2}=0,679atm

Additional exercises

Exercise -1-:

Identify open, closed, and isolated systems among the following sentences, explaining and justifying your answer.

a. Explosive motor in working order
b. Organism
c. Tree-growing
d. A closed pot of boiling water
e. A car is in motion.
f. The alarm is ringing.
g. Coffee in a thermos flask
h. The universe as a whole

Exercise -2-:

Which of the following statements most accurately describes the state of an ideal (perfect) gas?

a. Hydrogen gas.
b. A mole of hydrogen gas under a pressure of 1 atm.
c. A mole of hydrogen gas at a pressure of 1 atm and a volume of 22.4 L.
d. A mole of hydrogen gas at a temperature of 0 °C and a volume of 22.4 L.
e. A mole of hydrogen gas at a pressure of 1 atm, a temperature of 0 °C, and a volume of 22.4 L.

Exercise -3-:

An ideal gas exists in a closed system at 680 °C and a temperature of 45°C, occupying a volume of 3200 ml.

- What volume does it occupy when both the manometer and thermometer indicate the regular conditions of pressure and temperature?

Exercise -4-:

Let there be two vessels, one containing hydrogen (H_2) and the other methane gas (CH_4), where the initial conditions are as follows:

Calculate the mass of hydrogen and methane.

a. We heat the two vessels to a temperature of 350 K. Deduce the pressure for both H_2 and CH_4.
b. Using a tap, we mix the gases from the two vessels. What happens to the gases?

   - Calculate the partial pressures and total pressure after mixing.
c. The tap is closed. Calculate the mass of the two gases in each container.

Exercise -5-:

A group of gases is placed in a container with a volume of 10 dm^3 to give a total pressure of 107 kPa at a temperature of 30°C. If the mixture contains 8g of CO_2, 6g of O_2, and x g of N_2, Calculate the following:

- The number of total moles in the mixture and the mole fraction of each gas.
- The partial pressure of each gas.
- The mass of N_2 in the gaseous mixture.

Exercise -6-:

Dry air at sea level consists roughly of the following mass proportions: N_2=75.52%, O_2=23.15%, Ar=1.28%, CO_2=0.046%

- What is the molecular pressure of each component when the atmospheric pressure is 1 atm?

Given: M_O=16g/mol, M_C=12g/mol, M_N=14g/mol, M_{Ar}=40g/mol

Exercise:- 7-

The rubber wheels of a car are filled with air until they reach a pressure of 3 atm at a temperature of 25°C, and when exposed to the sun, their temperature rises to 50 °C.

- Will the wheel withstand this temperature, or will it explode? (Note that the wheel does not resist a pressure of 6 atm. We assume the size of the wheel is constant and air is an ideal gas).

Chapter Two

II.1. Introduction

Energy exists in many forms, such as thermal, mechanical, electrical, chemical, and nuclear. Even mass can be considered a form of energy. Heat and work are two distinct forms of energy transfer to or from a closed system (static mass). Mass flow can also transfer energy. If a temperature difference causes the transfer of energy to or from a closed system, we refer to it as heat; otherwise, we refer to it as work, which is the result of a force acting over a distance.

Otherwise, it is work produced by a force acting across a distance.

II.2. Energy

In every chemical reaction (or physical transformation), energy absorption or emission occurs. When the system transfers energy to the external medium (the surroundings), it becomes an exothermic heat emitter. When the system absorbs energy from the ocean, it transforms into an energy absorber (endothermic).

- The energy value is positive for the endothermic system.
- The energy value is negative for the exothermic system.

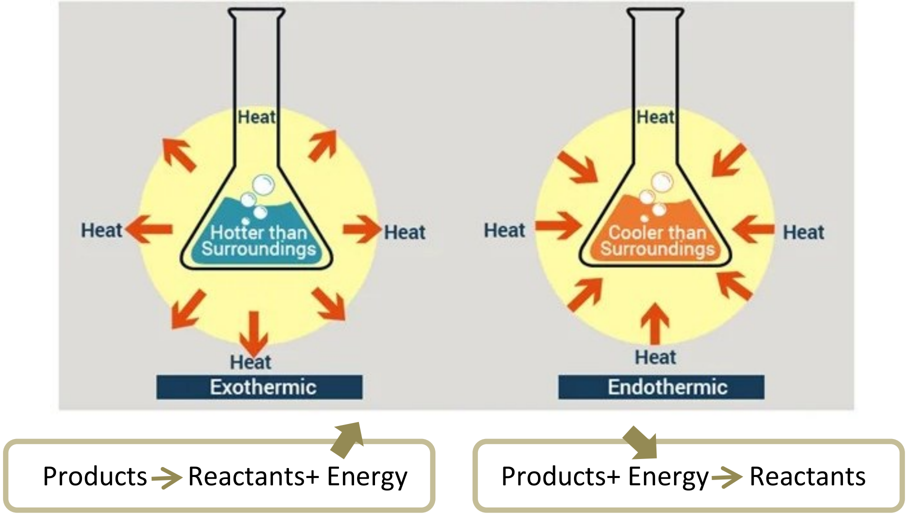


Fig.II.1:The endothermic system and the exothermic

II.3. Work and amount of heat:

Macroscopic physical systems exchange energy with the external environment in two different ways: work and heat.

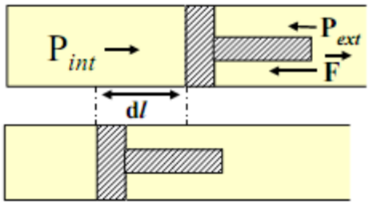
1. Work exchanged:

It is a mechanical energy exchange in microscopic form. If there is an exchange of energy that results in thermodynamic variables other than temperature, then we call it an exchange of work.

Mutual action with the external environment is of great importance in the case of a gaseous mass because the mechanical energy (W) in the case of a liquid or solid-phase mass is negligible.

Let us have a cylinder with a frictionless, moving piston.

By definition, mutual work with the environment is equal to:



$$|\delta W| = |\boldsymbol{F}.\mathbf{dl}| = |P_{ext} \cdot S \cdot dl|$$

$$\delta W = P_{ext} \cdot dV$$

As we already said, the sentence is earned, so (W>0) is the result of the force acting on the piston (F_{ext}). In this case, ($\Delta V = V_2 - V_1$) after integration ($dV < 0$), which means that there must be a connection between the work relationship and its sign (W >0). The work relationship must look like this:

$$\boxed{\delta W = -P_{ext} \cdot dV}$$

δW is called elemental work and is measured in the joule and is symbolized by the symbol (J) if P_{ext} is in the pascal (Pa), and dV is in the unit (cm^3), or in the unit of calorie (Cal), where 1 Cal = 4.18 J.

The system provides work that moves from the initial state (1) to the final state (2), and the following formula then provides that work:

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

✍ Work for reversible transformation of $T = C^{ste}$ (W_{rev})

During a reversible transformation $\mathbf{P \neq C^{ste} = P_{ext} = P_{syst}}$

$$\delta W_{rev} = -P_{ext} \cdot dV = -P\,dV \quad ; \quad P = \frac{n.R.T}{V}$$

Substituting, we find:

$$\int_1^2 W = -\int_{V1}^{V2} \frac{nRT}{V} \cdot dV \leftrightarrow \delta W_{rev} = -\frac{n.R.T}{V}.dV$$

$$W_{1-2} = -\int_1^2 n.R.T\,\frac{dV}{V} = -n.R.T\int_1^2 \frac{dV}{V}$$

So:

$$\boxed{W_{rev} = n.R.T\ ln\frac{P_2}{P_1}} \qquad \boxed{W_{rev} = \mathrm{n.R.T}\ ln\frac{V_1}{V_2}}$$

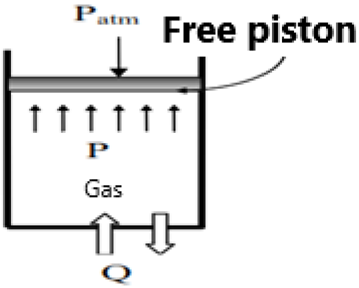


Fig.II.2: The process involves expanding or contracting under constant

✍ Work for irreversible transformation of P = C^{ste} (wire)

When the system undergoes an irreversible transformation, $\mathbf{C^{ste} = P_{final} = P_{syst}}$.

$$\delta W_{irre} = -P_{ext}\,.\,dV = -P_{final}\,.\,dV \leftrightarrow W_{irre} = -\int_1^2 P\ dV = -P\int_1^2 dV$$

$$\boxed{W_{rev} = -P\,(V_2 - V_1)}$$

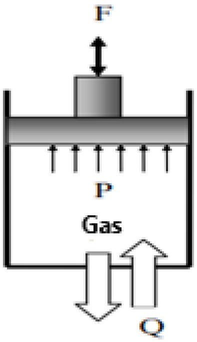


Fig.II.3:The process of expansion or contraction occurs at a constant

✍ **Work to shift from V = C^{ste}**

$$W_{irre} = -\int_1^2 P\ dV = 0 \qquad \boxed{W_{rev}=0}$$

Illustrative example:

a. Calculate the work exchanged with the external medium during the isotope compression of 56g of nitrogen (N_2) from pressure P_1 = 1 atm to P_2 = 20 atm under a temperature of 25 °C.

b. Compression occurs in a reversible manner.

c. Compression occurs irreversibly.

d. Compare the two results.

The solution:

a. Calculating the mutual work with the external medium:

We have $W = -\int_{V_1}^{V_2} PdV \qquad n = \frac{m}{M} = \frac{56}{28}$ =2 mole

b. Reversible condition: ($P \neq C^{ste}$)

$$W_{rev} = -\int_{V_1}^{V_2} P.dV = -n.R.T.ln\frac{P_1}{P_2} = -2.8{,}31.298{,}15\ ln\frac{1}{20} = \mathbf{14.844KJ}$$

c. Irreversible condition: (P = Cste)

$$W_{irre} = -\int_{V_1}^{V_2} PdV = -nRT\left(1-\frac{P_2}{P_1}\right) = -2 * 8.31 * 298.15\left(1-\frac{20}{1}\right) = \mathbf{94{,}149\ KJ}$$

d. Comparison: We note that $\boldsymbol{W_{rev}} >> \boldsymbol{W_{irre}}$.

The system always gains more work in the irreversible state ($\boldsymbol{W_{irre}}$) than it does in the reversible state ($\boldsymbol{W_{rev}}$).

2. **Amount of heat (energy)**

It is a microscopic exchange of energy in the form of heat. We exchange energy, resulting in only heat. The rest of the thermodynamic variables remain equal to their values. We say that there is an exchange of the amount of heat.

☒ Expression of the amount of heat: For a small shift, the amount of heat dQ represents the amount of heat received by the system, whether heating or cooling:

$$\boxed{\mathbf{dQ} = \boldsymbol{n.c.dT}} \qquad \boxed{\mathbf{dQ} = \boldsymbol{m.c.dT}}$$

We have :

$$\boxed{c = \frac{C}{m}} \leftrightarrow \boxed{dQ = C.dT}$$

Where:

dT represents the change in temperature

C: heat capacity (J/K)

c: Specific heat capacity (J/kg) or (J/mol)

dQ: It is called the amount of heat exchanged, measured in joules (J) or calories (Cal).

The amount of heat (Q) required to raise the temperature of the mg from T_1 to T_2 without a change in the physical state is equal to:

$$\boxed{Q = \int_{T_1}^{T_2} m.c.dT = m.c.(T_2 - T_1)}$$

In the case of a change in the physical state occurring at a constant temperature (evaporation or melting), where L is the latent heat of boiling, fusion, sublimation, freezing, or condensation.

$$\boxed{Q = m.L}$$

- ✍ Latent heat is defined as the amount of heat required to change the state of 1 gram or 1 mole of a pure substance at a constant temperature.

3. Heat Capacity and Specific Heat Capacity:

Heat capacity (C) is the amount of heat that a substance gains or loses with the external environment when the temperature changes 1 g by one temperature. Or it is the amount of heat needed to raise the temperature of 1 gram of a substance by one degree Celsius.

Since the heat capacity is directly proportional to the mass of the substance, we will therefore divide the heat capacity by the mass until we obtain a new physical quantity that does not depend on the mass, which is the specific heat capacity, which depends only on the type of substance; its symbol is (c), and the unit of specific heat capacity Mass (J/kg/°C), while molarity (J/mol/°C).

The specific heat of water is equal to 1 $\frac{Cal}{g.°C}$ or $\frac{4{,}18\ J}{g.°C}$ so $\mathbf{c}_{\mathbf{water}} = \frac{\mathbf{1\ Cal}}{\boldsymbol{g.°C}} = \frac{\mathbf{4{,}18\ J}}{\boldsymbol{g.°C}}$

4. The amount of heat generated while heating an object:

Let m be the mass of a pure body at temperature T_1 heated to T_2, where $T_1 < T_{Fus}$ and $T_2 > T_{Vap}$

- Calculate the amount of heat generated during this heating.

Solution: The amount of heat required for this process is equal to

$$Q = \sum_i^n Q_i = Q_1 + Q_2 + Q_3 + Q_4 + Q_5$$

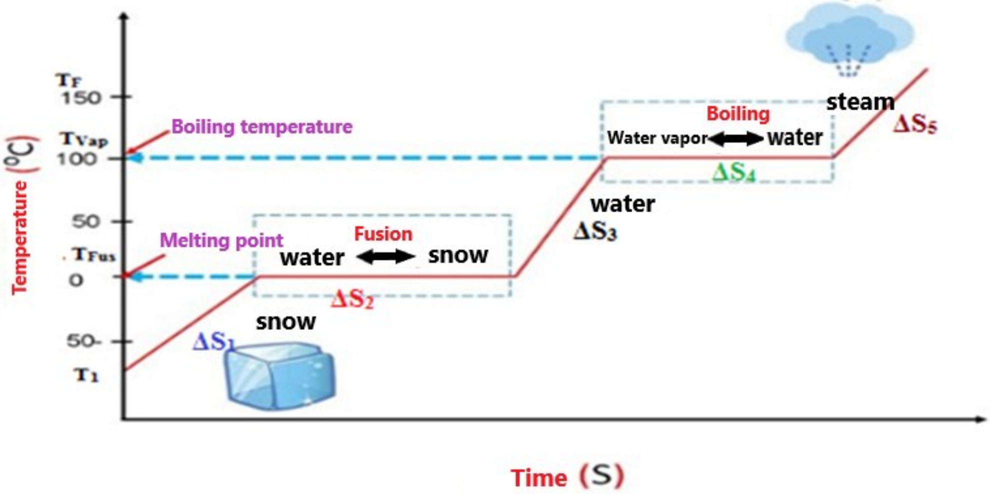


Fig.II.4: The state of matter changes with temperature

we've got:

☒ Heating without a change in physical state

$C_{(s)}$: mass-specific heat in the solid state (Cal/gK) $Q_1 = m.c_{(s)}.(T_{Fus} - T_1)$

☒ Change in physical state with constant temperature (melting)

L_{Fus}: Latex heat of fusion (Cal/g) $Q_2 = m.L_{(Fus)}$

☒ Heating without a change in physical state

$C_{(l)}$: mass-specific heat in the liquid state (Cal/gK) $Q_3 = m.c_{(l)}.\left(T_{Vap} - T_{Fus}\right)$

☒ Change in physical state with constant temperature (melting)

L_{Vap}: Latent heat of evaporation (Cal/g) $Q_4 = m.L_{(Vap)}$

☒ Heating without a change in physical state

$C_{(g)}$: mass-specific heat in the gaseous state (Cal/g.K) $Q_5 = m.c_{(g)}.(T_2 - T_{Vap})$

So :

$$\boxed{Q = m.c_{(s)}.(T_{Fus} - T_1) + m.L_{(Fus)} + m.c_{(l)}.(T_{Vap} - T_{Fus}) + m.L_{(Vap)} + m.c_{(g)}.(T_2 - T_{Vap})}$$

5. Equilibrium temperature:

When mixing in a thermally insulated vessel a mass m_1 of a pure body at a temperature of T_1 with another mass m_2 of a pure body at a temperature of T_2, where $T_2 > T_1$, the equilibrium temperature will be equal to:

A thermally insulated container: $Q_T = Q_1 + Q_2 = 0 \Rightarrow Q_1 = -Q_2$

Where: $Q_1 = \int_{T_1}^{T_{eq}} m.c.dT = m_1.c.(T_{eq} - T_1)$

$$Q_2 = \int_{T_{eq}}^{T_2} m.c.dT = m_2.c.(T_2 - T_{eq})$$

So: $m_1.c.(T_{eq} - T_1) = -m_2.c.(T_2 - T_{eq})$

Therefore, it will be:

$$\boxed{T_{eq} = \frac{m_1.T_1 + m_2.T_2}{m_1 + m_2}}$$

In the case of two different materials:

$$\boxed{T_{eq} = \frac{m_1.c_1.T_1 + m_2.c_2.T_2}{m_1.c_1 + m_2.c_2}}$$

C_1: Capacitance of Body 1

C_2: Capacitance of Body 2

II.4. First law of thermodynamics

The first law of thermodynamics is nothing but the conservation of energy. This principle states, based on experimental observations, that energy is neither destroyed nor created from nothing but is transformed from one form to another according to the conservation of energy. The closed system that does not...

Any change occurs, and its total energy remains constant. When the state of the system changes as a result of a process, the magnitude of the surrounding medium must equal zero, meaning that it is not possible to separate the first law of thermodynamics, the system, and the surrounding medium.

$$\Delta\text{Total energy of the system} + \Delta\text{Total energy of surroundings} = 0$$

The change in the total energy of the system is the sum of the change in internal energy, the change in kinetic energy, and the change in potential energy of the system, while the change in the total energy of the surrounding medium is the algebraic sum of the work done in all its forms and the heat lost to or from the surrounding medium. But the change in kinetic energy and potential energy for closed systems is usually neglected, considering the energy that governs the previously agreed-upon signs of work and heat.

1. Text of the First Principle of Thermodynamics:

The first principle states that the total amount of energy exchanged between the system (the system) and the surroundings during a cyclic transformation (or during a cycle) is zero. The energy exchanged between the system and the external medium is in the form of mechanical energy (work, W) and heat energy (Q), that is:

$$W_1 + Q_1 + W_2 + Q_2 + \cdots + W_i + Q_i = 0 \Rightarrow \sum_{i=1}^{n} W_i + \sum_{i=1}^{n} Q_i = 0 \Leftrightarrow$$

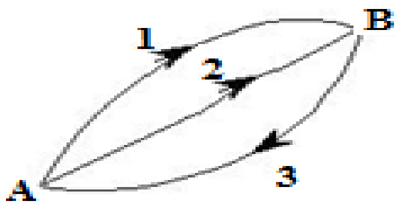
$$\boxed{\boldsymbol{W_T + Q_T = 0}}$$

Important note:

A cyclic transformation is a transformation in which the initial state is identical to the final state, meaning that the initial and final states have the same characteristic values of the state variables.

2. Total energy of an acyclic transformation:

Let the following transformation be:



- ✍ Episode One: Transformation (1) and Transformation (3)

$$W_1 + Q_1 + W_3 + Q_3 = 0 \qquad (\boldsymbol{i})$$

- ✍ Episode Two: Transformation (2) and Transformation (3)

$$W_2 + Q_2 + W_3 + Q_3 = 0 \qquad (\boldsymbol{ii})$$

From the relationships (i) and (ii), we find that $\boldsymbol{W_1 + Q_1 = W_2}$

So:

$$\boxed{\mathbf{W + Q = Const}}$$

Conclusion:

Whatever the type of method or path, the amount of energy exchanged (W+Q) remains constant; that is, it relates only to the initial state and the final state; that is, it is a state function.

3. Internal Energy:

The internal energy of the system, symbolized by the symbol (U), is the sum of the energies possessed by the system and is represented by:

- Kinetic energy of molecules
- Kinetic energy of electrons
- The energy of the vibration of atoms
- Potential and kinetic energy of the components of the nucleus.

It is noted that it is not possible to calculate the value of this internal energy for a system in a particular state. But during the transformation of a system from one state to another, the amount of total energy exchanged with the surroundings represents the change in internal energy (ΔU), so U is a state function and is equal to:

$$\Delta U = U_1 + U_2 = W_{1-2} + Q_{1-2}$$

The final form of the first law of thermodynamics applied to closed systems is:

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

$$\boxed{\mathbf{\Delta U = \delta W + \delta Q}}$$

Internal energy is a function of the system's measurable state. The joule is an international unit for internal energy.

Terms for signs of magnitudes W, Q, and ΔU

ΔU	Q	W
ΔU>0 then T increases	Q>0 if heat enters the system	W>0 if the system shrinks
ΔU<0 then T decreases	Q<0 if heat leaves the system	W<0 if the system expands
ΔU=0 if T remains constant	Q=0 if there is no heat exchange	W=0 if the volume remains constant

✍ Transformation under constant volume (isochoric): $V = C_o^{nst}$

definition: $V = C_o^{nst} \Rightarrow \Delta V = 0$, $dU = \delta W + \delta Q$,$\partial W = -PdV \Rightarrow W = 0$

So:

$$\boxed{\Delta U = Q_V}$$

Where Q_V : represents the amount of heat exchanged during the isoelectric transformation.

✍ Molar or mass heat capacity at constant volume (C_v)

If we raise the temperature of a pure body from T_1 to T_2 at a fixed volume without causing any change in its physical state, then

$$dQ_V = m.c_V.dT = n.c_V\ .dT$$

$$Q_V = \int_{T_1}^{T_2} n.c_V.dT = \int_{T_1}^{T_2} m.c_V.dT$$

So

$$\boxed{\begin{gathered} dU = dQ_V = m.c_V\,.dT = n.c_V\,.dT \\ c_V = \frac{\partial Q_V}{\partial T} = \left(\frac{\partial U}{\partial T}\right)_V \end{gathered}}$$

✍ Transformation under constant pressure (isobaric): $P = C_o^{nst}$ and Enthalpy

definition: $P = C_o^{nst}$, $dU = W + Q$

Then: $dW = -P.dV \Rightarrow W = -P.dV$

$$\Delta U = Q_P + W = Q_P - P(V_2 - V_1)$$

$$U_2 - U_1 = Q_P - P.V_2 + P.V_1$$

So $$Q_P = (U_2 + P.V_2) + (U_1 + P.V_1)$$

Where The Q_P: represents the exchange between the system and the external medium during the isobar transformation.

Most chemical reactions and physical variables take place under constant pressure, not constant volume. The symbol (H) represents the important property of enthalpy, also known as heat content, emitted or absorbed at a fixed volume. The first to introduce the concept of enthalpy was the Dutch scientist Kamerlingh Onnes.

Kamerlingh Onnes
1853-1926

It has an energy dimension, as it represents the thermal energy exchanged during a chemical reaction or physical transformation, and it is a state function where:

$$Q_V = \Delta H = H_2 - H_1 = (U_2 + P.V_2) + (U_1 + P.V_1)$$

That is, $H_1 = U_1 + P.V_1$ and $H_2 = U_2 + P.V_2$

In general, the change in enthalpy is equal to:

$$\boxed{\Delta H\ dU + d\,(P.V)}$$

✍ Molar or mass heat capacity at constant pressure (C_P)

It is the amount of heat that a substance gains or loses with the external environment when the temperature changes 1 g or 1 mole by one temperature.

$$Q_P = \int_{T_1}^{T_2} n.c_P.dT = \int_{T_1}^{T_2} m.c_P.dT$$

Among them:

$$\boxed{c_P = \frac{\partial Q_P}{\partial T} = \left(\frac{\partial H}{\partial T}\right)_P}$$

Important note:

The value of both C_P and C_V can be a function of temperature: $C_P = f(T)$, $C_V = f(T)$.

✍ Isothermal transformation $T = C_o^{nst}$

Joule's Law: Joule experimentally demonstrated that internal energy and enthalpy solely depend on temperature, indicating that

James Prescott Joule
1818-1889

changes in each of them are solely dependent on temperature changes.

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad ، \quad \left(\frac{\partial U}{\partial P}\right)_T = 0 \quad ، \quad \left(\frac{\partial H}{\partial V}\right)_T = 0 \quad ، \quad \left(\frac{\partial H}{\partial P}\right)_T = 0$$

And that ∀ type of transformation, then:

$$\boxed{\begin{aligned} dH &= m.c_P.dT \\ &= n.c_P.dT \end{aligned}} \qquad \boxed{\begin{aligned} dU &= m.c_V.dT \\ &= n.c_V.dT \end{aligned}}$$

Conclusion:

When the temperature is constant for a reversible transformation, then:

$$\Delta U = Q + W = 0 \Rightarrow Q = - W$$

$$\boxed{\begin{aligned} Q &= n.R.T.\ln\frac{V_2}{V_1} \\ &= R.T.\ln\frac{P_1}{P_2} \end{aligned}}$$

✍ Relationship between C_V and C_P:

Given that $H= U+P.V \Rightarrow dH= dU +d(P.V)$

$$dH = dU +d(n.R.T) \Rightarrow n.c_p.dT =n.c_v.dT + n.R.dT$$

$$C_p.\ dT = C_v.\ dT + n.R.\ dT \Rightarrow C_p = C_v + R$$

After rearranging the above equation, we get the following Mayer relationship:


Robert Von Mayer
1814-1878

✍ For 1 mole of an ideal gas,

$$\boxed{C_p - C_v = R}$$

✍ For a mole of an ideal gas

$$\boxed{C_p - C_v = n.R}$$

we've got:

$$\gamma = \frac{C_P}{C_V} \Rightarrow C_P = \gamma.C_V$$

$$C_P - C_V = \gamma.C_V - C_V = R$$

$$C_V\ (\gamma - 1) = R$$

From it, we find:

$$\boxed{C_P = \frac{\gamma.R}{\gamma-1}} \qquad \boxed{C_V = \frac{R}{\gamma-1}}$$

✍ Adiabatic transformation (reversible):

☜ The relationship between state variables:

Definition of adiabatic transformation: Q = 0 (the amount of heat exchanged is zero). And accordingly

$$dU= \delta W \Rightarrow C_v.\, dT + PdV=0 \;....\; (1)$$

From the ideal gas equation: $P.V = n.R.T \quad \Rightarrow \quad P.dV+V.dP= n.R.\, dT$

So $$dT = \frac{P.dV+V.dP}{n.R} \ldots (2)$$

Substituting (2) into (1), we find: $C_v.\left(\frac{P.dV+V.dP}{n.R}\right) + PdV=0$

However, we already have $C_V\text{-}C_p\text{=}n.R$ and $\gamma = \frac{C_P}{C_V}$

$$C_v.P.dV + C_v.V.dP = C_P.P.dV - C_v.P.dV$$

So $$\frac{dP}{P} = -\frac{C_P}{C_V}.\frac{dV}{V}$$

Thus, the previous relationship becomes:

$$\boxed{\gamma.\frac{dV}{V} + \frac{dP}{P} = 0}$$

Pierre-Simon de Laplace
1749-1827

This relationship is known as the Laplace relationship.

$$\int \frac{dP}{P} = \gamma.\int \frac{dV}{V} \Rightarrow \quad \ln P + \gamma.\ln V = \ln.K$$

Where $ln.K$ is the constant of integration, and by raising the natural logarithm, we get:

$$\boxed{P^{\frac{1}{\gamma}}.V = C_o^{nst}} \text{ or } \boxed{P.V^{\gamma} = K = C_o^{nst}}$$

Based on the general relationship between ideal gases,

$$\boxed{T^{\frac{1}{\gamma-1}}.V = C_o^{nst}} \text{ or } \boxed{T.V^{\gamma-1} = C_o^{nst}}$$

$$\boxed{T.P^{\frac{\gamma-1}{\gamma}} = C_o^{nst}} \text{ or } \boxed{T^{\frac{\gamma}{1-\gamma}}.P = C_o^{nst}}$$

Working for Kazumi's reversible transformation:

Definition: ∂W_{rev}= -$P.dV$

And that $P.V^{\gamma} = C_o^{nst} \Rightarrow P_1.V_1{}^{\gamma} = P_2.V_2{}^{\gamma} = \cdots = P.V^{\gamma}$

That is: P = $\frac{P_1.V_1{}^{\gamma}}{V^{\gamma}} = \frac{P_2.V_2{}^{\gamma}}{V^{\gamma}}$

So

$$\partial W_{rev} = -\frac{P_1.V_1{}^{\gamma}}{V^{\gamma}}\, dV \quad \Rightarrow \quad W_{rev} = -P_1.V_1{}^{\gamma}.\int_{V_1}^{V_2}.\frac{dV}{V^{\gamma}}$$

The form includes the work relationship during Kazumi's transformation.

$$\boxed{W_{rev} = \frac{1}{\gamma - 1}\left(P_2.V_2 - P_1.V_1\right)}$$

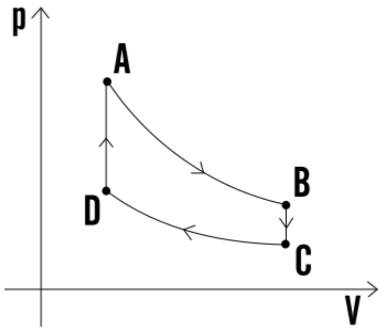
The work and heat generated by the loop cycle

The loop's total work is equal to its own work.

$$W_{cycle} = \sum W_i$$

The amount of heat in the ring is equal to the sum of the amounts of heat that occurred through the ring.

$$Q_{cycle} = \sum Q_i = -\sum W_i$$



According to the cycle in the figure, $W_{Cycle} = W_{A-B} + W_{B-C} + W_{C-D} + W_{D-A}$

$$Q_{Cycle} = Q_{A-B} + Q_{B-C} + Q_{C-D} + Q_{D-A}$$

Calculate ΔU and ΔH for the loop cycle:

When a system undergoes a cyclic transformation and returns to its basic state, the internal energy and enthalpy become delta states.

$$\Delta U_{Cycl} = W_{cycl} + Q_{cycl} = 0 \Rightarrow Q_{cycl} = -W_{cycl}$$

The enthalpy of the ring remains constant $\boldsymbol{\Delta H_{Cycl} = 0}$.

The return of the episode

$$\boxed{R=-\frac{W_{Cycle}}{Q_{rece}}}$$

Where: R<0 0<R<1

The relation between U and H for an ideal gas: is as follows

We have: H = U + P.V.

$$Q_P = Q_V + \Delta n_g \,.\, R.T \quad \text{or} \quad \Delta H = \Delta U + \Delta n_g \,.\, R.T$$

Where Δn_g is the amount of change in the number of moles of initial and final gas ($\Delta n_g = \sum \mathbf{n}_{\mathbf{(g)products}} - \sum n_{\mathbf{(g)reactants}}$)

Note: If the transformation is isothermal, then ΔT = 0, and hence ΔH = ΔU.

- ☜ Received work during cyclic transformation

We impose two successive evolutions or transformations, $A \overset{1}{\rightarrow} B$ and $B \overset{2}{\rightarrow} A$, represented by the (P,V) Clapeyron diagram.

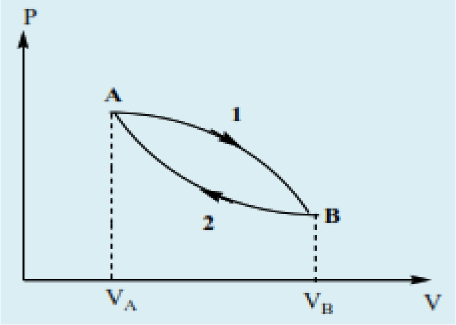


Fig.II.5: The (P,V) Clapeyron diagram

Exercise series
(First Principle of Thermodynamics)

Exercise - 1-:

A mole of an ideal gas expands during a constant-temperature reversible transformation from state 1 (298 K, 5 atm) to state 2 (1 atm, T_2)

- Calculate the final temperature T_2
- Change in internal energy ΔU
- Work done by gas W
- The amount of heat during the reaction Q
- Change in enthalpy ΔH

It is given: R=0.082 $J.mol^{-1}.K^{-1}$

Answer: T_2=298 K, $\Delta H = \Delta U = 0$, Q= -W= -3,98 KJ

Exercise - 2-:

Calculate the heat absorbed by 360 g of $C_6H_{12}O_6$ when the temperature increases from 273 K to 25 C° under normal pressure.

It is given: $C_p = 1{,}884.10^{-2} + 92.10^{-5}T$cal /mol. K, M (C) = 12 g/mol, M (H) = 1 g/mol, M (O) = 16 g/mol.

Answer: Q= 27,208 Kcal

Exercise - 3-:

Calculate the amount of heat that converts a piece of ice with a mass m = 1 kg, temperature T = -20 °C, to the point of complete evaporation T = 100 °C.

Data:

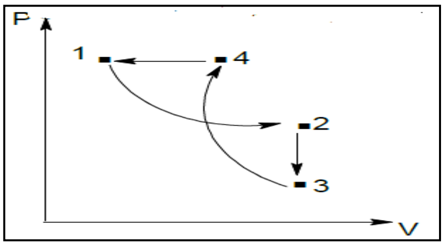
$C_{(s)}$(ice)	**$C_{(l)}$(water is liquid)**	**$C_{(g)}$(water is vapor)**	**L_{fus}**
2,1× 10^3 $J.kg^{-1}$. K^{-1}	4187 $J.kg^{-1}$. K^{-1}	1930 $J.kg^{-1}$. K^{-1}	3,3×10^5 $J.kg^{-1}$
	L_{vap}	**T_{Fus}**	**T_{vap}**
	2,3×10^6 $J.kg^{-1}$	0 °C	100°C

Answer: Q_T= 3092 KJ

Exercise - 4-:

Let the following Clapeyron diagram represent a series of transformations for 0.2 moles of an ideal gas that we consider to be reversible. With the data listed in the table:

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



- Calculate the work, the amount of heat, and the internal energy for each transformation and for a complete cycle?

It is given: R= 2 cal/mol. K, C_V= 3.03 cal/mol.K, C_P= 5.03 Cal/mol.K

Answer: W_{Cycle}= -267,82 Cal ،Q_{Cycle}=267,82 Cal ،ΔU_{Cycle}= 0 Cal

Exercise - 5-:

A sample of an ideal gas in state A, where A (P_A = 1 atm, V_A = 12 L, T_A = 293 K) undergoes the following transformations, which we consider to be reversible:

- Adiabatic (Kaziomi) compression to point B, where T_B = 400K.
- Compression under constant temperature to point C where V_c = 1 L.
- Adiabatic expansion to point D, where $T_D = T_A$.
- Expansion under constant temperature to the initial state A.
- Calculate the unknown pressures, volumes, and temperatures.
- like the previous transformations in Clapeyron's parameter.
- Calculate ΔH, ΔU, Q, W for each transformation and period.
- Verify the validity of the first law of thermodynamics.

Answer: :ΔH_{cyc} = 0 , ΔU_{cyc}= 0 ،Q_{cyc}=- 1300,56 J ،W_{cyc}= +1301,48 J.

Additional exercises

Exercise - 1-:

The calorimetric coefficients λ and μ are defined by the following relationships:

$$\mu = C_v\left(\frac{\delta T}{\delta V}\right)_P \quad ، \quad \lambda = C_p\left(\frac{\delta T}{\delta V}\right)_P$$

Deduce the values of λ and μ in terms of γ for an ideal gas, knowing that $\frac{C_P}{C_V} = \gamma$ and $C_p - C_V = nR$.

Exercise - 2-:

One mole of an ideal gas goes from the state $T_1 = 273K$, $P_1 = 2atm$ to the final state $P_2 = 4atm$, through a reversible transformation in which $\frac{P}{V} = C_o^{nst}$.

- Calculate T_2, V_2, V_1.
- Calculate the change in internal energy, ΔU, in calories.
- Calculate the change in enthalpy ΔH.
- Calculate the work w during the shift in joules.
- Calculate the amount of heat exchanged during the transformation in calories.

Given: $C_V = (3/2)R$, R= 2 cal/mol. K

Exercise - 3-:

Calculate the amount of heat needed to heat 2kg of aluminum from 0C° to 700C°.

It gives: T_{fusion}= 658C° , L_f= 86,6Kcal/Kg , $c_{PAl(s)}$= 0,9 J/g.C° , $c_{PAl(l)}$=0,259Kcal/Kg.K

Exercise - 4-

One mole of an ideal gas undergoes four reversible transformations.

- From the first case (1) to the second case (2) adiabatic compression.
- From the second state (2) to the third state (3) it expands under constant pressure.
- From the third state (3) to the fourth state (4) adiabatic expansion.
- From the fourth state (4) to the first state (1) cooling under constant volume.

Note that $\frac{V1}{V2} = a$, $\quad \frac{V4}{V3} = b$, $\quad \gamma = \frac{Cp}{Cv}$

1. Draw the previous transformations according to Clapeyron's diagram.
2. Write expressions for each of the pressures, volumes, and temperatures in each case in terms of b, a, T_1, P_1, V_1.
3. Calculate the previous values (pressures, volumes, and temperatures).
4. Calculate in each case Q, W

- Data:

$\gamma = 1{,}4$ $P_1 = 1\text{x}10^5$ Pa , $T_1 = 300$ K , a = 9 , b = 3 , Cv = 20,8 J. K^{-1}. mol^{-1}

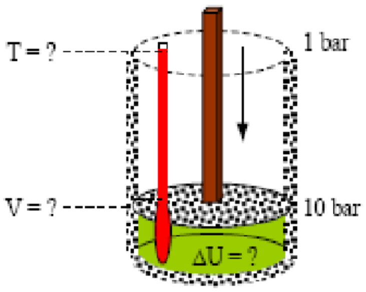
Exercise - 5-:

A thermometer contains 500 g of water at 19 °C. We add a quantity of water with a mass of m = 150 g at 25.7 °C, so the equilibrium temperature becomes 20.5 °C, and the heat capacity of the water is: $C_{p\ eau} = 4180$ J/ Kg.K

1. Calculate the heat capacity of a calorimeter.
2. In the same calorimeter that now contains 750 g of water at 19°C, we place a piece of copper with a mass of m = 550 g at 92°C, so the final temperature becomes 23.5°C.
   - ✓ Calculate the mass heat capacity of copper.
3. What is the amount of soda needed to be cooled from 30°C to 10°C using a block of ice m = 25 g at a temperature of 0°C? gives: $cp_{soda} = 4180$ J. K^{-1}.kg^{-1} ; $L_{f\ (glace)} = 335$ kJ.kg^{-1}.

Exercise - 6-:

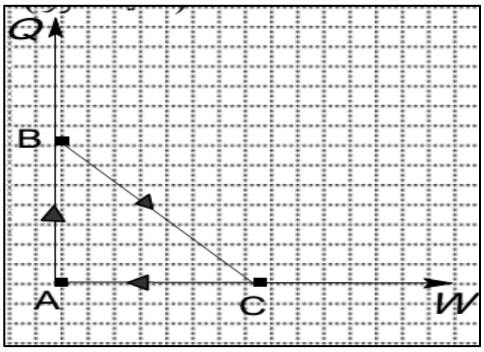
A compression process is achieved from 1 bar to 10 bar for a volume of air (we consider air to be an ideal gas) of 1 liter, the initial temperature. 20°C This process takes place so quickly that any heat exchange with the surroundings is negligible.



1. Calculate the final temperature of the air mass.
2. Deduce its final size and the amount of change in internal energy.

Given: The average molar mass of air is 29 g/mol R = 8,31 J. mol^{-1}. K^{-1} . Cv = 720 J. Kg^{-1}. K^{-1} $\gamma = 1{,}4$

Exercise - 7-:



A 22.4 g mass of carbon monoxide (CO) occupying an initial volume of (V_A = 10 L) under pressure (P_A = 2 atm) undergoes a series of reversible transformations, as shown in the figure Q = f (W).

Knowing that the pressure at C (Pc =6 atm) and the transformation (B→C) achieve ($W_{B\to C} = - Q_{B\to C}$)

1. State the type of each transformation.
2. Calculate the state variables for points A, B and C
3. Draw the transformations in Clapeyron's landmark
4. Calculate ΔH, Q, W for each transformation and period.

It is given: $C_p = 7$ cal . $mol^{-1}.K^{-1}$.

Chapter Three

III.1. Introduction

For a chemical reaction to occur, energy must be needed to break some of the bonds between the atoms in the molecules and the ions of the reactants. In thermochemistry, which is concerned with the thermal changes associated with chemical reactions by measuring the amount of heat released (liberated) or absorbed and knowing the nature of these variables, thermochemistry is closely linked to the branch of thermochemical movement, which is concerned with finding the relationship between the amount of matter as one of the types of energy, work, as well as other types.

III.2. Heat of Reaction

Thermal changes are generally measured either under constant pressure (Q_P) or constant volume (Q_V). Thermal changes as a result of a chemical reaction in an aqueous medium do not include the use or formation of gaseous substances. They are measured at constant pressure using a device that measures calories, or calorie units, which is called a calorimeter. Thermal or calorimeter. Such a calorimeter can be used to measure temperature changes for many reactions, such as reactions of acids with bases or modification reactions. Since the measurements are made under constant pressure (atmospheric pressure), the change in temperature (Q_P) is equal to the enthalpy (ΔH)., where $Q_P = \Delta H$.

In order to calculate the change in temperature (Q_P) or (ΔH), the change in temperature of a known mass of solution must be known, as well as the amount of heat absorbed by the calorimeter, which is usually determined before the reaction is carried out by using the calorimeter with a known amount of heat.

In the case of a physical transformation of matter (a change in its physical state)

- Melting: is the transformation of a substance from a solid state to a liquid state, such as: $H_2O_{(s)} \rightarrow H_2O_{(l)}$

  The enthalpy of this transformation is represented by ΔH°_{fus} or ΔH°_{fus}, and the reverse process of this transformation is freezing.

- Evaporation: is the transformation of a substance from a liquid state to a gaseous state, such as: $H_2O_{(l)} \rightarrow H_2O_{(g)}$

The enthalpy of this transformation is represented by ΔH°_{vap} or L_{vap}, and the reverse process of this transformation is liquefaction.

- Sublimation: is the transformation of a substance from the solid state directly to the gaseous state without passing through the liquid state. Such as: $I_{2(s)} \rightarrow I_{2(g)}$ The reverse process of this transformation is condensation. We can also include changes in the crystalline structure of the substance within the change of physical state. Such as: $C_{(g)} \rightarrow C_{(d)}$ turns graphite into diamond.

Important note: The enthalpy of any physical transformation differs from the enthalpy of its reverse state only in sign, while it is equal in magnitude. For example, if $L_{fus} = -248\ kJ/mol$, then the enthalpy of the reverse transformation is equal to: $\Delta H_{fus} = +248\ kJ/mol$.

Illustrative example:

When 50 ml of 0.5M HCl are placed with 50 ml of 0.5M NaOH in a thermometer at constant pressure, its heat capacity is 335 J/°C. The initial mixture temperature was 22.5°C and the final temperature was 24.9°C

- Calculate the change in enthalpy of the reaction, assuming that the density and specific heat of the solution are equal to the density and specific heat of the water.

The solution

Since the sentence is isolated: $\Sigma Q_i = 0$ $Q_{sol} + Q_{Cal} + Q_p = 0 \Rightarrow Q_p = \Delta H = -(Q_{sol} + Q_{Cal})$

- Calculate the heat gained by the solution (HCL + NaOH) Q_{sol}

$$Q_{sol} = C^{`}_{solution}.(T_{eq} - T_1)$$

$$C^{`}_{solution} = (m_{HCL} + m_{NaOH})\ c_{solution}$$

We have that $c_{H2O} = c_{solution} = 4{,}184$ J/g.°C

$$Q_{sol} = (50+50) \times 4{,}184 \times (24{,}9 - 22{,}5) = 2{,}1 \times 103\ J$$

- Calculate the heat gained by the Q_{cal} calorimeter

$$Q_{Cal} = C_{cal}.(T_{eq} - T_1) = 335 \times (24.9 - 22.5) = 804\ J$$

So $$Q_p = -(2.1 \times 103 + 804) = -2.81\ KJ$$

Since $Q_p = \Delta H$, we find that the heat of reaction (ΔH) is -2.81 KJ= ΔH

Heat of Reaction Measurement

Thermal changes resulting from the combustion of any substance are measured at a fixed volume, using what is called a calorimeter or bomb calorimeter. (Bomb Calorimeter) The thermometer is a device used to measure thermal changes (the amount of heat absorbed or released) associated with chemical reactions. The type of thermometer to be used is determined according to the type.

The chemical reaction is studied, meaning whether the reaction takes place at a constant pressure or at a fixed volume, and the bomb calorimeter is used to measure the heat released during the combustion processes.

Description of the calorimeter device

The calorimeter usually consists - as shown in the figure opposite - of:

1. An external container with good thermal insulation to prevent heat leakage from inside or outside this container. A certain amount of water with an accurately known weight is placed in this external container, and the vessel in which the reaction will take place is immersed in it.
2. perature scale.
3. A source of ignition.
4. Engine.

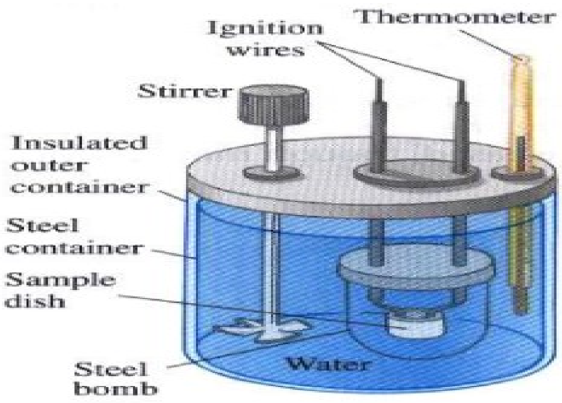


Fig. III.1 : Calorimeter

- ✓ But how is the heat released as a result of the combustion of a substance measured in the calorimeter?

Steps:

1. A precise amount of the reactant whose heat of combustion is to be measured is weighed and placed in the reaction vessel.
2. The reaction vessel is filled with oxygen gas under high pressure.
3. Place the reaction vessel in the insulated vessel.
4. The reaction vessel (calorimeter) is immersed in a certain amount of precisely weighed water, which is placed in a completely insulated container.
5. The water is stirred with a stirrer in order for the water temperature to be homogeneous with the rest of the parts of the calorimeter.
6. Record the temperature of the initial group (sample temperature) and let it be (T_1).
7. The reaction (combustion process) is initiated by an ignition source or by electrical heating of the material (an electrical wire immersed in the material).
8. The heat released as a result of the reaction is absorbed by the calorimeter and its components, and as the temperature of the assembly rises, the final temperature (T_2) is recorded.
9. Since both the water and the calorimeter absorb heat, the total heat capacity (C_{total}).

   The sum of the heat capacities of the calorimeter and the water is equal to:

   $$C_{total} = C_{H2O} + C_{cal}$$

   C_{H2O}: The heat capacity of water is calculated from the mass of water used and the specific heat of the water, as previously explained.

   C_{cal}: The heat capacity of the calorimeter. It is estimated practically by measuring the increase in the temperature of the calorimeter as a result of heating it with a known amount of heat.
10. The amount of heat released in the experiment (Q) is calculated from the total heat capacity (C_{total}) and from the increase in temperature (T_2-T_1) using the equation:

    $$Q= C_{total} \times \Delta T$$

Illustrative example:

A chemical reaction was carried out in a calorimeter containing 1.2 kg of water. The temperature rose from 20°C to 25°C. Calculate the amount of heat produced by the reaction. Note that the heat capacity of the calorimeter is 2.21 $KJ.K^{-1}$ and the specific heat of water is 4.184 J/g.°C.

Solution:

$$Q = -(Q_{H2O}) + Q_{Cal}$$

$$Q = -[\grave{c}_{H2O} \times m_{H2O}(T_2 - T_1)] + [\grave{C}_{Cal}(T_2 - T_1)]$$

$$Q = -[4{,}184 \times 1{,}2 \times 10^3\ (25 - 20\ )] + [2{,}21\ \times 10^3 (25 - 20)]$$

$$Q = -36{,}154\ KJ$$

III.3. Standard Enthalpy of Reaction

The change in enthalpy for a chemical reaction is called the enthalpy of the reaction and is symbolized by the symbol (ΔH_R). It is equal to the heat of the reaction released or absorbed at constant pressure. The values of the enthalpy of the reaction are often written in the balanced chemical equation and this type of thermochemical equations is called Thermochemical Equations.

Illustrative example: Let the following reactions take place at 25°C

✍ Exothermic reactions:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}\ \Delta H_R = -393\ KJ$$

$$H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(g)}\ \Delta H_R = -241{,}8\ KJ$$

$$H_{2(g)} + 1/2Br_{2(g)}\ HBr_{\ (g)}\ \Delta H_R = -36{,}4\ KJ$$

✍ Endothermic reactions:

$$1/2N_{2(g)} + 1/2O_{2(g)} \rightarrow NO_{(g)}\ \Delta H_R = +90{,}25\ KJ$$

$$CuCO_{3(s)} \rightarrow CuO_{(s)} + CO_{2\ (g)}\ \Delta H_R = +178\ KJ$$

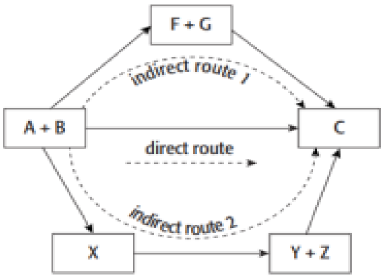
$$2CO_{2\ (g)} + 3H_2O_{\ (l)} \rightarrow C_2H_5OH_{(l)} + 3O_{2\ (g)}\ \Delta H_R = +1367\ KJ$$

III.4. Standard Molar Enthalpy of Formation

Standard molar formation enthalpy ($\Delta H°_f$) or formation ($\Delta H°$) is defined as the change in enthalpy (or state of reaction) when one mole of a substance is formed from its elementary elements in their standard state at atmospheric pressure ($P_{\ atm}$)

and normal temperature T (Generally equal to 298 K), and (ΔH°_f) is often called the standard molar heat of formation or, in short, the heat of formation.

III.5. Hess's Law



Hess's law (or the law of summation of heats of reaction) states that the amount of heat corresponding to a given reaction or the change in enthalpy for a given chemical reaction is a constant value whether the reaction occurs in a direct route during one step or indirectly (Indirect route 1,2). (through a number of steps) under a pressure of 1 atm, provided that the reactants and products are the same in each case. This is consistent with the change in enthalpy being a function of state - that is, its value does not depend on the path taken by the reaction. It was named after the Russian chemist Germain Hess. For example, if compound (D) is formed directly from compound (A), or compound (D) is formed from the same compound (A), but through steps during which intermediate compounds (B) are formed, And (C).

Germain Henri Hess
1803-1850

These interactions can be illustrated with the following diagram:

$$\begin{tikzcd}
A \arrow[r, "\Delta H_4"] \arrow[d, "\Delta H_1"'] & D \\
B \arrow[r, "\Delta H_2"'] & C \arrow[u, "\Delta H_3"']
\end{tikzcd}$$

It is noted from the figure that ΔH_4 represents the change in enthalpy for the direct reaction that leads to the formation of compound (D) in one step from compound (A), while ΔH_1, ΔH_2, ΔH_3 represent the change in enthalpy for three reactions that ultimately lead to the formation of compound (D) from compound (A), so according to Hess's law, ΔH_4 is equal to the sum of ΔH_1, ΔH_2, and ΔH_3.

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

in general:

$$\boxed{\Delta H_R = \sum \Delta H_i}$$

An important application of Hess's law is to calculate the change in enthalpy for a specific reaction (ΔH_R) by using the values of ($\Delta H°_f$) for the reactants and products.

Through the principle of the initial state and the final state, Hess's law can be written for the reaction in the form:

$$a\,A + b\,B \;\rightarrow c\,C \;+ d\,D$$

Where: $\Delta H°_R = - \left[\text{c.}\ \mathbf{\Delta H^o_{\mathit{f}}}\,(\text{C}) \;+ \text{d.}\ \mathbf{\Delta H^o_{\mathit{f}}}\,(\text{D}) \right] - \left[\text{a.}\ \ \mathbf{\Delta H^o_{\mathit{f}}}\,(\text{A}) \;+\; \text{b}\ \mathbf{\Delta H^o_{\mathit{f}}}\,(\text{B}) \right]$

Hess's law is written

$$\boxed{\Delta H°_R = \sum \boldsymbol{n_P}\ \ (\boldsymbol{\Delta H°f})\boldsymbol{Products} - \sum \boldsymbol{n_R}\ \ (\boldsymbol{\Delta H°f})\boldsymbol{Reactnts}}$$

Important note: The enthalpy of the standard formation in its standard state for simple elements is zero.

$$\Delta H°_f\ (H_{2,g}) = \Delta H°_f\ (O_{2,g}) = \Delta H°_f\ (N_{2\ ,g}) = \Delta H°_f\ (C_{,graphite}) = \Delta H°_f\ (Br_2, l\ )$$

Although we are talking about the same element, it is therefore very important to determine the state in which the element exists during its formation, for example

$$\Delta H°_f\ (C_{,diamond}) \neq 0 \quad ، \Delta H°_f\ (Br_2, g\ ) \neq 0$$

The following table gives the physical state of some elements in the standard state:

Element symbol	*Br*	*I*	*H*	*S*	*P*	*C*	*Na*	*N*	*O*
Pure body	Br_2	I_2	H_2	S_8	P_4	$C_{graphite}$	*Na*	N_2	O_2
Physical state	*(l)*	*(s)*	*(g)*	*(s)*	*(s)*	*(s)*	*(s)*	*(g)*	*(g)*

Illustrative example:

Calculate the standard enthalpy of the following reaction ($\Delta°H_R$) at a temperature of 25°C

$$2NaHCO_{3\ (s)} \rightarrow NaCO_{3\ (s)} + CO_{2\ (g)} + H_2O_{\ (g)} \ \ldots\ldots\ \Delta°H_R$$

$$\Delta H°_f\,(NaHCO_3, s) = -\ 947.7\ \text{kJ/mole}\ ;\ \Delta H°_f\,(NaCO_3, s) = -\ 1131\ \text{kJ/mole}$$

$$\Delta H°_f\,(CO_2, g) = -\ 394\ \text{kJ/mole}\ ;\ \Delta H°_f\,(H_2O, g) = -\ 242\ \text{kJ/mole}$$

The solution :

We previously mentioned the relationship between ΔH°f and ΔH°R

$$\Delta°H_R = \Delta H°_{f\,(Products)} - \Delta H°_{f\,(Reactants)}$$

$$\Delta°H_R = \Delta H°_f\,(NaCO_3, s) + \Delta H°_f\,(CO_2, g) + \Delta H°_f\,(H_2O, g) - \Delta H°_f\,(NaHCO_3, s)$$

$$\Delta°H_R = (-1131) + (-241) + (-394) - 2(-947{,}7)$$

$$\Delta°H_R = 128.4 \text{ KJ}$$

III.6. Bond Energy

You know bond energy or bond dissociation energy as the amount of energy absorbed or required to break one mole of a covalent bond between two atoms in a gaseous molecule and form atoms in the gaseous state in their standard state and temperature 25°C.

where:

$$\left.\begin{array}{lll} A + B \rightarrow A\text{---}B & & \Delta H^{o}_{f\,(A\text{---}B)} \\ A\text{---}B \rightarrow A + B & & \Delta H^{o}_{diss\,(A\text{---}B)} \end{array}\right\} \quad \boxed{\Delta H°_{f\ (A\text{--}B)} = E_{(H\text{-}H)} = -\,\Delta H_{diss\ (A\text{---}B)}}$$

$\Delta H^0_{f(A---B)}$: The enthalpy of bond formation (A---B) from atoms A and B in their gaseous state, and it is always negative.

$\Delta H^0_{diss(A---B)}$: The enthalpy of dissociation of the bond (A---B) into free atoms in the gaseous state, and it is always positive.

Important note on bond energy:

1. The reaction is exothermic if the value of (ΔH°) is negative
2. The reaction is endothermic if the value of (ΔH°) is positive
3. When calculating the interaction energy using the bond energies, it must be:
   - ✓ Put a positive sign in front of the bond breaking energy.
   - ✓ Placing a negative sign in front of the bond formation energy.

   This is because breaking a bond consumes energy (absorbent), while forming a bond produces energy (repellent).

For example, the bond energy for the dissociation of a hydrogen molecule is:

$$H_{2\,(g)}\ [or\ H - H] \rightarrow 2H_{(g)}\ ;\quad \Delta H_{(H\text{-}H)} = -436 \text{ KJ/mole},\ D_{(H\text{-}H)} = +436 \text{ KJ/mole}$$

The bond energy for the dissociation of chlorine gas is:

$$Cl_{2\,(g)}\ [or\ Cl - Cl] \rightarrow 2Cl_{(g)}\ ;\quad \Delta H_{(Cl\text{-}Cl)} = -436 \text{ KJ/mole},\ D_{(Cl\text{-}Cl)} = +498 \text{ KJ/mole}$$

It is noted that $D_{(Cl\text{-}Cl)} > D_{(H\text{-}H)}$, meaning that the covalent bond in the hydrogen molecule is much stronger than the covalent bond in the chlorine molecule. The heat of bond formation is defined as the amount of energy required to form 1 mole between gaseous atoms of the original elements in their gaseous state at A pressure of 1 atm.

Important note:

In the case of polyatomic molecules, the enthalpy of formation of these molecules from their atoms in the standard gaseous state is equal to the sum of the covalent bonds.

Illustrative example:

Calculate the standard enthalpy of reaction ($\Delta H°_R$) at 25°C for the formation of HCl

$$\frac{1}{2}H_2\,(g) \quad + \quad \frac{1}{2}\,Cl_2\,(g) \;\rightarrow\; HCl\,(g)$$

Where:

$\Delta H°f\,(HCl,g)$ =- 22 Kcal/mol, $E_{Cl\text{-}Cl}$ =- 58 Kcal/mol, $E_{H\text{-}H}$=- 104,2 Kcal/mol

The solution:

We have: $$\Delta H°_R = -\sum n_j.E_{j\,(Products)} - \sum n_i.E_{i\,(Reactants)}$$

$$\Delta H°f\,(HCl,g) = E_{H\text{-}Cl} - \left(\frac{1}{2}E_{H\text{-}H} + \frac{1}{2}E_{Cl\text{-}Cl}\right)$$

$$E_{H\text{-}Cl} = \frac{1}{2}E_{H\text{-}H} + \frac{1}{2}E_{Cl\text{-}Cl} + \Delta H°_f\,(HCl,g)$$

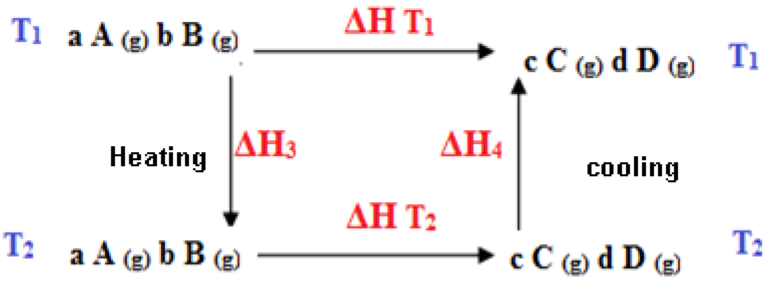
$$E_{H\text{-}Cl} = \frac{1}{2}(-104{,}2) + \frac{1}{2}(-58) + (-22) = -103{,}1 \text{ Kcal/mol}$$

$$E_{H\text{-}Cl} = -103{,}1 \text{ Kcal/mol}$$

III.7. Kirchhoff relationship

1. The enthalpy of the reaction as a function of temperature

   Let the following chemical reaction take place under constant pressure.



where

ΔH_{T_1}: represents the heat of reaction (enthalpy of reaction) at temperature T_1

ΔH_{T_2} : represents the heat of reaction (enthalpy of reaction) at temperature T_2

ΔH_3: represents the heat of heating of the reactants from T_1 to T_2

$$\Delta H_3 = \int_{T_1}^{T_2} \left(a.c_{p\,(A)} + b.c_{p\,(B)} dT\right)$$

ΔH_4 : represents the temperature of cooling of the products from T_2 to T_1.

$$\Delta H_4 = \int_{T_2}^{T_1} \left(c.c_{p\,(C)} + d.c_{p\,(D)} dT\right)$$

Since H is a state function, ΔH does not depend on the method, i.e

$$\Delta H_{T_1} = \Delta H_{T_2} + \Delta H_3 + \Delta H_4$$

$$\Delta H_{T_2} - \Delta H_{T_1} = -\Delta H_3 - \Delta H_4$$

$$\Delta H_{T_2} - \Delta H_{T_1} = -\int_{T_2}^{T_1}\left(c.c_{p\,(C)} + d.c_{p\,(D)} dT\right) - \int_{T_1}^{T_2}\left(a.c_{p\,(A)} + b.c_{p\,(B)} dT\right)$$

$$= \int_{T_1}^{T_2}\left(c.c_{p\,(C)} + d.c_{p\,(D)} dT\right) - \int_{T_1}^{T_2}\left(a.c_{p\,(A)} + b.c_{p\,(B)} dT\right)$$

$$\boxed{\Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_2} \Delta n.c_p\, dT}$$

Where $\Delta n.c_p = \sum n_i \ (c_p\ ) Products - \sum n_i \ (c_p\ ) Reactnts$

Kirchhoff's law $\boxed{\Delta n.c_p = \frac{d(\Delta H_T}{dT}}$

III.8. Heat of reaction under constant volume (ΔU) as a function of temperature:

With the same previous steps, we find that

$$\Delta U_{T_2} - \Delta U_{T_1} = \int_{T_1}^{T_2} \Delta n.c_V\, \mathrm{dT}$$

Where $\Delta n.c_V = \sum n_i \ (c_V\ ) Products - \sum n_i \ (c_V\ ) Reactnts$

Exercise series
(Applications of the first principle in chemical)

Exercise - 1-:

Calculate the standard enthalpy of formation ($\Delta°H_f$) for (H_2S,g) at 25°C using the following reactions:

$$2\ H_2S_{(g)} + SO_{2(g)} \rightarrow 3S_{(s)} + 2\ H_2O_{(g)} \qquad ;\ \Delta^{\circ}H_1 = -144\ kJ$$

$$H_2S_{(g)}\ +\ 3/2\ O_{2(g)} \rightarrow H_2O_{(l)} + SO_{2(g)} \qquad ;\ \Delta^{\circ}H_2 = -561\ kJ$$

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \qquad ;\ \Delta^{\circ}H_3 = +42{,}5\ kJ$$

$$H_{2\ (g)} + 1/2\ O_{2\ (g)} \rightarrow H_2O_{(g)} \qquad ;\ \Delta^{\circ}H_4 = -58\ kJ$$

Answer: $\Delta°H_R$ (H_2S,g) = 162.83 KJ

Exercise - 2-:

Calculate the difference in enthalpy of the reaction between the temperatures of 273 K and 823 K at constant pressure for the following reaction:

$1/2\ N_{2(g)} + 3/2\ H_{2(g)} \rightarrow NH_{3(g)}$

$Cp\ (H_2) = 27.25 + 3.2 \times 10^{-3}\ T\ \ J.\ K^{-1}.mol^{-1}$.

$Cp\ (N_2) = 27.84 + 4.2 \times 10^{-3}\ T\ \ J.\ K^{-1}.\ mol^{-1}$.

$Cp\ (NH_3) = 29.72 + 2.5 \times 10^{-2}\ T\ \ J.\ K^{-1}.\ mol^{-1}$.

Answer: $\Delta H_{823} - \Delta H_{273} = -8.3\ KJ.mole^{-1}$

Exercise - 3-:

Let the combustion reaction of ethylene be:

$$C_2H_{4(g)} + 3O_{2(g)} \quad \rightarrow \quad 2CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H°_{comb,\ 298} = -1387{,}8$$

Using the enthalpies of formation and sublimation of the following compounds:

$$\Delta H°_{sub}\ (C,\ s) = 171{,}2\ \ kcal.mol^{-1}$$

$$\Delta H°_{f,298}\ (CO_2\ ,g) = -393\ kJ.mol^{-1}$$

$$\Delta H°_{f,298}\ (H_2O\ ,l) = -284{,}2\ kJ.mol^{-1}$$

1. Calculate the enthalpy of formation of gaseous ethylene

2. Calculate the binding energy of C=C in ethylene C_2H_4

   The enthalpies of binding energies are given in the following table:

Bond	H-H	C-H	C-C
E ($KJ.mol^{-1}$)	- 434,7	- 413,8	- 263,3

Answer: ΔH_R (C_2H_4,g)=33.6 $KJ.mole^{-1}$, $E_{C=C}$ =-611.8 $KJ.mol^{-1}$

Exercise -4-:

Let the glucose reaction be as follows:

$$\text{(glucose) } C_6H_{12}O_{6\,(s)} \overset{\Delta H^\circ_1}{\rightleftharpoons} 2C_3H_6O_{3\,(l)} \text{ (lactic acid)}$$

1. Write the equations for the combustion reaction of glucose and lactic acid.
2. Calculate the standard enthalpy of conformation of glucose taken in the solid state and lactic acid taken in the liquid state.

   Note that:

   - The enthalpy of combustion of glucose $\Delta H^\circ_{comb,\,(C1)} = -2816\ kJ.mol^{-1}$
   - The enthalpy of combustion of lactic acid $\Delta H^\circ_{comb,\,(C2)} = -1364\ kJ.mol^{-1}$

   The standard enthalpy of water in the liquid state and carbon dioxide is given

   $\Delta H^\circ_{f,298}$ (CO_2 ,g) = -393 $kJ.mol^{-1}$ ، $\Delta H^\circ_{f,298}$ (H_2O ,l) = -284,2 $kJ.mol^{-1}$.
3. Calculate the standard enthalpy ΔH°_1 for the glucose reaction.

   Answer: $\Delta H^\circ f$($C_6H_{12}O_6$,g)=-1247,2 $KJ.mole^{-1}$ ، ΔH°_1 =88 KJ.

Exercise - 5-:

We mix inside a calorimeter with a heat capacity of 200.64 J. K_{-1}, 100 ml of sulfuric acid solution (H_2SO_4) and 200 ml of soda (NaOH), where the temperature is 22.50°C, which is the same temperature as the calorimeter, and then The temperature of the mixture rises to 30.14°C, noting that the heat capacity of the solution is 4.0755 $J.g^{-1}.k^{-1}$ and its volumetric mass is 1,036 $g.cm^{-3}$.

1. Calculate the enthalpy of modification for one mole of H_2SO_4.
2. Under the same conditions, he derived the enthalpy of modification for one mole of HCl.

Answer: ΔH_R (H_2SO_4)=-112,1Kj.mole^{-1} ، ΔH_R (HCl)=- 56 Kj.mole^{-1}

Additional exercises

Exercise - 1-:

Calculate the enthalpy of formation for sulfuric acid using the following three equations:

$$SO_{3\,(g)} + H_2O_{(l)} \rightarrow H_2SO_{4\,(l)} \qquad \Delta H°_1 = -80\ kJ$$

$$S_{(s)} + 3/2\ O_{2\,(g)} \rightarrow SO_{3\,(g)} \qquad \Delta H°_2 = -395\ kJ$$

$$H_{2\,(g)} + O_{2\,(g)} \rightarrow H_2O_{(l)} \qquad \Delta H°_3 = -286\ kJ$$

Exercise - 2-:

Let the following reaction be: $\frac{1}{2}\ N_{2(g)} + \frac{3}{2} H_{2(g)} \rightarrow NH_{3(g)}$

At a temperature of 0°C and under constant pressure, the heat of ammonia formation is $\Delta H°_{f,273\ (NH3)} = -12,2$ kcal

1. Calculate the heat of formation of ammonia (NH_3) under constant pressure at 400 °C and 600 °C.
2. Deduce the heat of formation of ammonia (NH_3) under constant volume at 400 °C and 600 °C.

It is given: $cp_{(H2)} = Cp_{(N2)} = 6,8 + 10^{-3}.T$ $cal.mol^{-1}.K^{-1}$

$cp_{(NH3)} = 8,25 + 7 \times 10^{-3}.T$ $cal.mol^{-1}.K^{-1}$

Exercise - 3-:

Acrolein CH_2=CH-CHO is a liquid under normal conditions.

1. Calculate the standard enthalpy of the formation of acrolein using the enthalpy of combustion.
2. Calculate the standard enthalpy of acrolein formation using binding energies.

Data:

- Enthalpy of combustion of acrolein: $\Delta H°_R = -1630\ kJ.mol^{-1}$
- Enthalpy of water formation: $\Delta H°_f (H_2O,l) = -285.3\ kJ.mol^{-1}$
- Enthalpy of coal gas formation: $\Delta H°_f (CO_2,g) = -393.5\ kJ.mol^{-1}$
- Enthalpy of sublimation for hard coal: $\Delta H°_{sub} (C, S) = 716.7\ kJ\ mol^{-1}$
- Enthalpy of evaporation of acrolein: $\Delta H°_{vap} (C_3H_4O, l) = 20.9\ kJ.mol^{-1}$

Bond	H-H	O=O	C=O	C-H	C=C	C-C
E (kJ/mol)	– 435	– 498	– 720 and – 804 in CO_2	– 415	– 620	– 340

Exercise - 4-

Consider the combustion of ethane, $C_2H_{6\,(g)}$, at 25°C and atmospheric pressure:

$$C_2H_{6\,(g)} + \frac{7}{2}O_{2\,(g)} \rightarrow 2CO_{2\,(g)} + 3H_2O_{\,(l)} \quad \Delta H^\circ_{r,298} = -373{,}8$$

Deduce the standard molar heat of formation of gaseous ethane $\Delta H^\circ_{f,298}$ (C_2H_6, g)

Given:

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

$$H_2\,(g) + \frac{1}{2}O_2\,(g) \rightarrow H_2O(l) \qquad \Delta H^\circ_{r,\,298\,(2)} = -68{,}3 \text{ kcal}$$

Exercise - 5-:

Parts 1 and 2 are independent of each other

1. Let us consider the following reaction:

$$SO_{2(g)} + ½\, O_{2(g)} \rightarrow SO_{3(g)}$$

-If you know that:

$$S_{\,(s)} + O_{2(g)} \rightarrow SO_{2(g)} \qquad \Delta H^\circ_{\,298K} = -70{,}96 \text{ kcal}$$

$$S_{\,(s)} + \frac{3}{2}O_{2(g)} \rightarrow SO_{3(g)} \qquad \Delta H^\circ_{\,298K} = -94{,}48 \text{ kcal}$$

a. Draw the diagram corresponding to the previous reaction, indicating the initial state and final state.
b. Calculate $\Delta H^\circ_{r\ 298K}$ for the previous reaction

2. Calculate the internal energy change of dissociation of 1 mol of calcium carbonate at 0°C

A table of the enthalpies of the formation of the following compounds is given:

$$CaCO_{3\,(S)} \rightarrow CaO_{\,(S)} + CO_{2\,(g)}$$

Compound	CaO	CO_2	$CaCO_3$
$\Delta H°_f$ (Kcal.mol-1)	- 152	- 94,3	- 270

Exercise - 6-:

The molar heat of reaction to form ZnO is set according to the following reaction:

$$Zn_{(s)} + ½\, O_{2(g)} \rightarrow ZnO_{(s)}\ \Delta H_R$$

We measured the molar heat of the intermediate or elemental reactions in the laboratory that this reaction undergoes and applied the principle of the initial state and the final state using Hess's law. This is done through the following interactions:

Reaction 1	$ZnO_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_2O_{(l)}$	ΔH_1=?
Reaction 2	$Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$	ΔH_2=-170,31KJ
Reaction 3	$H_{2(g)} + ½\, O_{2(g)} \rightarrow H_2O_{(l)}$	ΔH_3 =-285,8 KJ

- Calculate the molar enthalpy of the reaction 1 ΔH_1 (kJ/mol)

Where it gives:

μ= 10 g	Mass ZnO m_{ZnO}= 2,2g	Final temperature (T_f) = 28,5°C	Initial temperature (T_i) = 20,4°C	Mass of HCl solution m_{HCl} = 70 g
	$c_{eau}=c_{solution}= c_{cal}$ = 4.18 J/K.g		$M_{(O)}$=16 g/mol	$M_{(Zn)}$=65.38g/mol

Chapter Four

IV.1. Introduction

The first principle, which stipulates equality between different forms of energy, cannot predict the most expected direction in which the transformation of a system will occur, or, in simple terms, how it will evolve. It can be deduced from the heat or enthalpy of the reaction (Q) that the heat or enthalpy of the reverse reaction is (-Q), as shown in the following two reactions:

$$A + B \text{ -------> } C + D \quad H_1 = Q$$

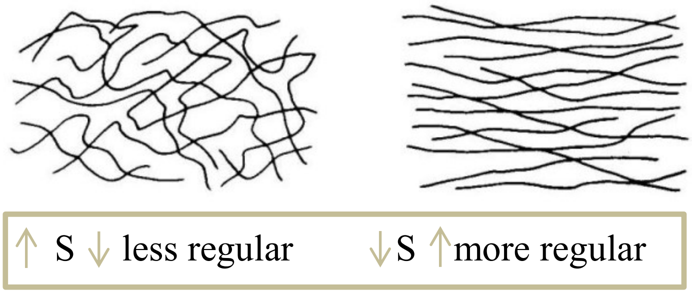
$$C + D \text{ -------> } A + B \quad H_2 = - H_1 = - Q$$

In this case, it is also worth noting that the sign (ΔH) never represents a criterion for the spontaneity of a transformation or reaction.

On the other hand, experience has shown that some of the transformations that are subject to the first principle and achieve it do not occur in reality. Heat does not transfer automatically from the body with the highest temperature to the lowest, and the opposite does not happen. For example, when a rock falls from the top of a mountain, it does not roll back up to the top of the mountain. Likewise, the scent of goodness spreads in the room when a perfume bottle is opened, and it is impossible for the dispersed particles to return to the bottle automatically.

The content of the above indicates that spontaneous events point in a direction and cannot be reversed. The spontaneity of a transformation or reaction simply means that it is irreversible. This is what can be considered a general law of nature, which is not referred to at all by the first principle of thermodynamics. The latter is not sufficient alone to frame and explain all thermodynamic phenomena. Therefore, it was urgent to introduce and define another principle that takes this concept into account, namely, that it can describe the changes that occur in any system, especially spontaneous and non-spontaneous changes. Clausius (1865) stated, based on the previous observations and indications, that no matter what type of system it is (open, closed, or isolated), and regardless of the nature of the transformation, reversible or irreversible, its state can be distinguished by a new state function, which is the entropy function.

IV.2. Entropy



Entropy is a physicochemical property related to the degree of chaos or increased disarrangement, and it is a measure of the lack of order or randomness of a system (system) designated by the symbol (S) and its unit (J. mol^{-1}.K^{-1})

The less regular the system is (greater the randomness), the larger the entropy value, and the more regular the system is (less random), the smaller the entropy value.

All previous chemical reactions and physical transformations that take place spontaneously are always accompanied by an increase in irregularity (i.e., an increase in the entropy value).

The processes that take place in solution always lead to an increase in entropy. When sugar crystals dissolve in water, the regular structural system of the sugar (the solute) is broken, as is part of the structural regularity of the water (the solvent). Therefore, the solution has more irregularity than the pure solvent combined. When an ionic solid such as sodium chloride (NaCl) is dissolved, the increase in entropy occurs as a result of two factors:

1. The process of forming a solution (mixing the solute with the solvent).
2. Breaking down a solid compound into ions.

Heating also increases the entropy of the system. Heating, in addition to the translational movements of the molecules, increases the rotational and vibrational movements. In addition, increasing the temperature increases the types of energies that are all related to the movement of molecules, and therefore the two copies increase the randomness of the system, so the entropy of the system increases.

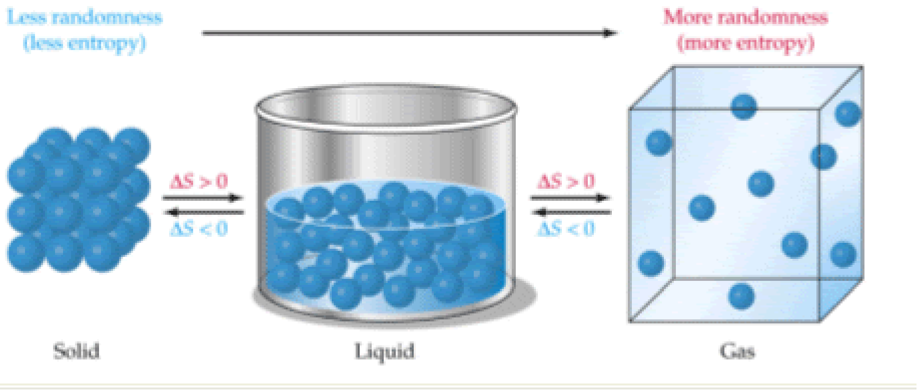
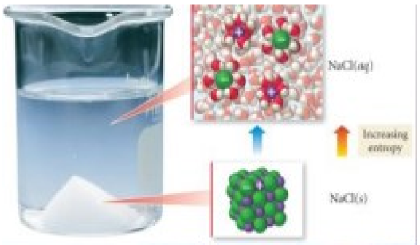


Fig.IV.1:The entropy of gases is greater than the entropy of liquids, and this in turn is greater than the entropy of solids.

1. Various examples to illustrate the increase in the entropy of a system

- Mixing the ink drop with water is easy and occurs naturally. However, if we want to separate the ink drop from the water again so that we have pure water and pure ink, that is a difficult process and can only be accomplished by putting in work. We say that the state of the mixture has a high entropy, while the state of pure water and pure ink is a state in which the entropy is low.

- It is easy to dissolve salt in water, but to re-separate the salt through evaporation, i.e., expending energy, and here we say that the entropy of the salt solution is higher than the entropy of pure salt and pure water.



- Crystals that form from a salt solution when water evaporates. Crystals are more ordered than salt molecules in solution, but the evaporation of water is more random than in an aqueous solution. When we talk about the entire process, the entropy, or randomness, of the system increases.

Entropy is a state function like enthalpy, so its absolute value cannot be measured, but rather the change in entropy is measured. $\mathbf{\Delta S_{syst} = S_f - S_i}$

$$\oint dS = \oint \frac{\partial Q}{T}$$

Where: S_f is the final entropy and S_f is the initial entropy.

dQ: The amount of elemental (infinitesimal) heat exchanged at temperature T, between a system and the external medium during transformation.

Caution: Depending on these two previous relationships, the change can be calculated regardless of the type of system and the nature of the transformation. But if we want to express the relationship between the three entropies: "System/Surroundings/Universe"

During the transformation, we can write:

$$\Delta S_{total} = \Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \geq 0$$

Important note:

- ✓ If $\Delta S_{sys} < 0$ (i.e., a decrease in the entropy of the system), this is necessarily matched by an increase in the entropy of the external medium (i.e., $\Delta S_{surr} > 0$).
- ✓ On the other hand, if the transformation is reversible, then: $\Delta S_{total} = 0$.
- ✓ If the transformation is irreversible, then: $\Delta S_{total} > 0$.

2. Text of the Second Law of Thermodynamics:

Entropy (randomness) is a quantity that describes and determines the energy that is not available to do work in a thermal process, meaning that as energy is transformed or transferred from another place, more of it is lost. The second law of thermodynamics states that there is a natural tendency for isolated systems to change and automatically shift towards a distributed state and automatically into a more random state.

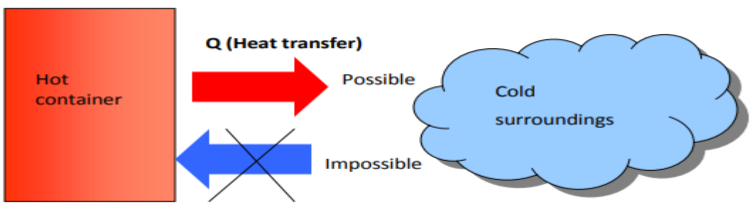


Fig.IV.2:The spontaneous transformation of an isolated system is irreversible

IV.3. Entropy changes

1. State of change of physical state:

The entropic change during the transformation from one physical state to another physical state under a constant temperature is equal to:

$$dS = \frac{\partial Q_{rev}}{T} \Rightarrow \Delta S = \frac{Q_{rev}}{T}$$

Illustrative example: Calculate the change in entropy of 2 moles of distilled water under a pressure of 1 atm, given Lvap = 540 Cal. g-1

$$dS = \frac{\partial Q_{rev}}{T} \Rightarrow \Delta S = \frac{Q_{rev}}{T} = \frac{m \times L_{Vap}}{T_{Vap}} = \frac{m \times M \times L_{Vap}}{T_{Vap}}$$

$$\Delta S = \frac{2 \times 18 \times 540}{370} = 52{,}22\ Cal.K^{-1}$$

2. Condition of mixing two liquids:

When a mass (m_1) of temperature (T_1) is mixed with a mass (m_2) of a liquid at temperature (T_2) in an insulated container without a change in the physical state, the change in entropy is:

$$\mathbf{\Delta S = \Delta S_1 + \Delta S_2}$$

Where the entropic change of mass (m_1): ΔS_1

$$\Delta S_1 = \int_{T_1}^{T_{éq}} \frac{\partial Q_{rev}}{T} = \int_{T_1}^{T_{éq}} \frac{m_1.c.dT}{T} = m_1.c.ln.\frac{T_{éq}}{T_1}$$

The entropic change of mass (m_2): ΔS_2

$$\Delta S_2 = \int_{T_2}^{T_{éq}} \frac{\partial Q_{rev}}{T} = \int_{T_2}^{T_{éq}} \frac{m_2.c.dT}{T} = m_2.c.ln.\frac{T_{éq}}{T_2}$$

$$\Delta S = m_1.c.ln.\frac{T_{éq}}{T_1} + m_2.c.ln.\frac{T_{éq}}{T_2}$$

$$\Delta S = c.ln.T_{eq}^{\,m_1+m_2} - c.(ln.T_1^{\,m_1} + ln.T_2^{\,m_2})$$

Among them:

$$\boxed{\Delta S = c.ln.\frac{T_{éq}^{\,m_1+m_2}}{T_1^{\,m_1} \times T_2^{\,m_2}}}$$

Where $T_{éq}$ in the case of the same fluid is $T_{eq} = \frac{T_1.m_1 + T_2.m_2}{m_1 + m_2}$

In the case of two different liquids: $T_{eq} = \frac{T_1.c_1.m_1 + T_2.c_2.m_2}{c_1.m_1 + c_2.m_2}$

Let the change in entropy sound

$$\boxed{\Delta S = ln.\frac{T_{éq}{}^{c_1.m_1+c_2.m_2}}{T_1{}^{c_1.\ m_1}\times T_2{}^{c_2.\ m_2}}}$$

Illustrative example: Calculate the change in entropy when mixing 500 g of ethyl alcohol (C_2H_5OH), temperature 60°C, with 1000 g of the same alcohol, temperature 20°C, in an insulated vessel, noting that: c_p= 1 Cal. K^{-1}.$mole^{-1}$

Solution: Since the system is isolated $Q_1 + Q_2 = 0$

Calculating $T_{éq}$ Equilibrium Heat

$$T_{eq} = \frac{T_1.m_1+T_2.m_2}{m_1+m_2} = \frac{500\ (60+273{,}15)+1000\ (20+273{,}15}{50+1000}$$

$$T_{eq} = 306{,}33\ K$$

Since $\Delta S = c.ln.\frac{T_{éq}{}^{m_1+m_2}}{T_1{}^{m_1}\times T_2{}^{m_2}} = 1.ln.\frac{306{,}33^{\frac{1}{46}(500+1000)}}{333{,}15^{\frac{500}{46}}\times 293{,}15^{\frac{1000}{46}}}$

$$\boldsymbol{\Delta S = 0{,}06\ Cal.K^{-1}}$$

IV.4. Entropy in terms of the variables T, V and P:

1. Entropy in terms of variables T and V for an inverse transformation:

From our first principle

$$\Delta U = \delta W + \delta Q \Rightarrow \delta Q = \Delta U - \delta W$$

$$\Delta U = n.c_V.dT \text{ ، } \delta W = -n.R.T.\frac{dV}{V}$$

Therefore, $dS = \frac{\delta Q_{rev}}{T} = n.c_V.dT + n.R.T.\frac{dV}{V}$

Integrally, we find that:

$$\boxed{\Delta S = n.c_V.\ln\frac{T_2}{T_1} + n.R.\ln\frac{V_2}{V_1}}$$

And some other cases:

Shift T= $C_o{}^{nst}$

$$\boxed{\Delta S = n.R.\ln\frac{V_2}{V_1}}$$

Shift V= $C_o{}^{nst}$

$$\boxed{\Delta S = n.c_V.\ln\frac{T_2}{T_1}}$$

2. Entropy in terms of variables P and V for an inverse transformation:

From the ideal gas equation: P.V =n.R.T ⇒ d(P.V)= d(n.R.T)

$$\Rightarrow P.dV+V.dP= n.R.d\,T$$

Dividing by P.V we find:

$$\frac{V.dP}{P.V}+\frac{P.dV}{P.V}=\frac{n.R.dT}{P.V}$$

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

we've got

$$dS = n.c_V.\frac{dT}{T}+n.R.\frac{dV}{V}=n.c_V.\left(\frac{dP}{P}+\frac{dV}{V}\right)+n.R.\frac{dV}{V}=n.c_V.\left(\frac{dP}{P}\right)+n.c_P.\frac{dV}{V}$$

Through integration, we find

$$\boxed{\Delta S = n.c_V.\ln\frac{P_2}{P_1}+n.c_P.\ln\frac{V_2}{V_1}}$$

And some other cases:

Shift P= C_o^{nst}

$$\boxed{\Delta S= n.c_P.\ln\frac{V_2}{V_1}}$$

Shift V= C_o^{nst}

$$\boxed{\Delta S = n.c_V.\ln\frac{P_2}{P_1}}$$

3. Entropy in terms of variables P and T for an inverse transformation:

From the general law for ideal gases, we have: $\frac{dP}{P}+\frac{dV}{V}=\frac{dT}{T}$

Through substitution and integration, we find

$$\boxed{\Delta S = n.c_P.\ln\frac{T_2}{T_1}+n.R.\ln\frac{P_1}{P_2}} \qquad \boxed{\Delta S = n.c_P.\ln\frac{T_2}{T_1}-n.R.\ln\frac{P_2}{P_1}}$$

And some other cases:

Shift P= C_o^{nst}

$$\boxed{\Delta S = n.c_P.\ln\frac{T_2}{T_1}}$$

Shift T= C_o^{nst}

$$\boxed{\Delta S = n.R.\ln\frac{P_2}{P_1}}$$

4. Entropy of adiabatic transformation:

Since Q=O then $\boxed{\Delta S=0}$

Illustrative example:

Calculate the change in entropy during the reversible transformation of two moles of gas (H_2) from the initial state to the final state:

- Initial state: P_1 = 202.7 Pa, V_1 = 30 L
- Final state: P_1 = 102.3 Pa, V_1 = 100 L

Note that: c_p= 30.96 $J.K^{-1}.mole^{-1}$

The solution:

We have $dS = \frac{\partial Q}{T} = \frac{dU}{T} - \frac{\partial W}{T}$

From the above, we have that $\Delta S = n.c_V.\ln\frac{P_2}{P_1} + n.c_P.\ln\frac{V_2}{V_1}$

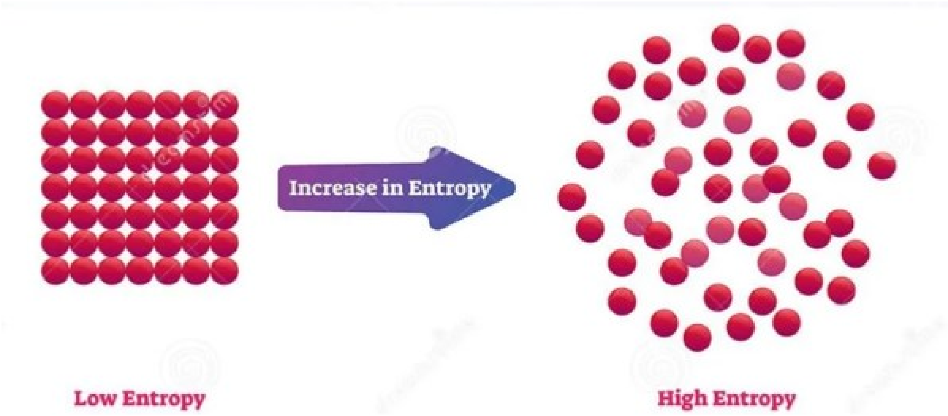
$$\Delta S = n.(c_P - R).\ln\frac{P_2}{P_1} + n.c_P.\ln\frac{V_2}{V_1} = 2(30{,}96 - 8{,}314).\ \ln\frac{101{,}3}{201{,}7} + \ 2 \times 30{,}96\ln\frac{100}{30}$$

$$\Delta S=43{,}13\ J.K^{-1}$$

IV.5. 3th Law of Thermodynamics :

1. Statistical interpretation of entropy:

The statistical thermal movement depends mainly on the microscopic description of the system (total) atoms and molecules. It has been experimentally proven during the study of the movement of molecules that the absolute entropy of a pure body changes with the change in molecules. This arrangement is determined by the value of Ω (Omega) and that its value (Ω) decreases as the molecules change. The arrangement of molecules among themselves increased.



NaCl is in the form of small (regular state) Ω crystals

NaCl solution (disorder state) Ω is large

2. Absolute entropy:

Absolute entropy is defined as a measure of the randomness of matter particles in a thermal system (system), that is, it is related to the degree or amount of randomness and chaos.

$$\boxed{S= k \ln \Omega}$$

Where: S: absolute entropy, k: Boltzmann constant (Const Boltzman)

The arrangement of the molecules is ultimately (a very regular arrangement) at zero absolute degrees (0 K), where $\Omega = 1$

3. Text of the third principle

In 1911, the text of Walter Hermann Nernst reads as follows:

"The entropy of a pure, crystalline substance is zero at absolute zero, meaning that $S°_{0\ K} = 0$."

Walther Nernst
1864-1941

4. Entropy of chemical reaction

✍ Standard entropy change for a chemical reaction:

This principle is of great importance in thermodynamics as it helps in calculating the standard entropy of a pure substance at any temperature and calculating the enthalpies of various reactions by applying the Hess relationship.

We know that entropy is a state function, so the entropy of the reaction is only related to the initial state and the final state.

Let the following reaction be: $aA + bB \rightarrow dD + cC$

Application of Hess' law allows the standard entropy of the reaction ($\Delta S°_{298}$)

$$\Delta S°_R = \sum \boldsymbol{n_P}\ (\boldsymbol{S°})\boldsymbol{Products} - \sum \boldsymbol{n_R}\ (\boldsymbol{S°})\boldsymbol{Reactnts}$$

where:

$S°$ $_{(Products)}$: Standard entropy of a product (products).

n_P: Stoichiometric coefficients of products.

$S°$ $_{(Reactnats)}$: the standard entropy of a reactant(s).

n_R: the stochiometric coefficients of the reactants.

Examples of standard entropy values for some substances (solid, liquid and gas) in units (u.e):

$S°_{(g)}$	Gases	$S°_{(l)}$	Solids	S° (s)	Solids
31,23	H_2	16,74	H_2O	1,37	$C_{graphite}$
94,00	O_2	18,17	Hg	0,63	$C_{graphite}$
45,79	N_2	51,20	CCl_4	12,20	Na
46,40	NH_3	70,90	C_6H_{14}	4,51	Si
45,10	H_2O			9,95	Zr
51,10	CO_2	*1 u .e =1 Cal.mol^{-1}.K^{-1}			

Important Alert:

Entropy is always numerically less than enthalpy, and is expressed as Joul or Cal, not KJoul or Kcal.

Special case:

It is not possible to calculate the standard entropy for a reaction at any temperature other than 298 K according to (Kirchhoff's law)

$$\Delta S_T = \Delta S_{298} + \int_{298}^{T_2} \Delta n.c_p\, dT$$

With $\Delta n.c_p = \sum n_i\ (c_p\ )Products - \sum n_i\ (c_p\ )Reactnts$

In the case of constants cp not related to T, one can write

$$C_T = \Delta S_{298} + \Delta n . c_p . ln \frac{T}{298}$$

Absolute entropy of a pure body:

Suppose we have 1 mole of a pure body at a constant pressure P. We heat the body from T_0 to T, to increase the amount of chaos.

$\Delta S = ?$

Pure body at $T_0 = 0$ K (liquid state) → **Pure body at T (gaseous state)**

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

$$\boxed{\Delta S = \int_{T_0}^{T_{Fus}} n . c_{P(s)} \frac{dT}{T} + n . \frac{L_{Fus}}{T_{Fus}} + \int_{T_{Fus}}^{T_{Vap}} n . c_{P(l)} \frac{dT}{T} + n . \frac{L_{Vap}}{T_{Vap}} + \int_{T_{Vap}}^{T} n . c_{P(g)} \frac{dT}{T}}$$

The various transformations are represented as follows:

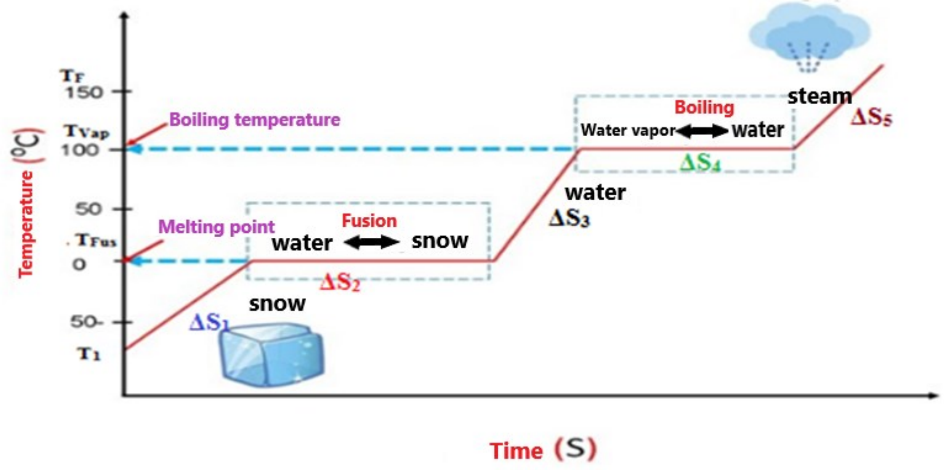


Fig.IV.3: Phase Transition of Water diagram

IV.6. Gibbs Free Energy

It is clear from the above that although increasing the randomness of the system (ΔS = positive value) and heat emission (ΔS = negative value) are among the preferred properties that accompany spontaneous changes, there are a number of spontaneous variables that are accompanied by either a decrease in the amount of randomness (ΔS = value Negative) or energy absorption (ΔH = positive value), so the change in entropy (positive or negative) alone - that is, in isolation from enthalpy - or knowing the enthalpy change alone - that is, in isolation from the change in entropy - does not help to accurately determine the possibility of the change occurring. Automatically or vice versa.

In the year 1800, Professor of Mathematics and Physics J.Willard Gibbs was able to formulate a relationship that combines enthalpy (H) and entropy (S), which allows us to predict the spontaneity of a reaction in a simpler way than relying on using the values of enthalpy and entropy separately, so enter The scientist Gibbs developed a new thermodynamic function named after him: Gibbs Free Energy, or free enthalpy, which is symbolized by the symbol (G).

(with constant temperature and pressure) $G = H-TS$

Since free energy depends on the two functions of entropy and enthalpy, free energy is also a state function, and therefore free energy does not depend on the path of change or transformation, but rather depends on the initial state (reactants, G_R) and the final state (products, G_P) of the system $\Delta G = G_P - G_R$

Since the spontaneous reaction is accompanied by a decrease in energy or enthalpy, which is part of the free energy relationship, the spontaneity of the reaction requires that (G_P) be less than (G_R), or in other words, ΔG is a negative quantity.

The Gibbs free energy (ΔG) is a real indicator of the spontaneity of physical changes and chemical reactions or not. In any case, the relationship between the quantitative signal ΔG and the type of chemical reaction or physical change can be summarized as follows:

Type of reaction (pressure and temperature constant)	ΔG value
The reaction or physical change is non-spontaneous (it occurs spontaneously in the opposite direction)	Positive ($\Delta G>0$)
Reaction or physical change in equilibrium	Zero ($\Delta G=0$)
The reaction or physical change takes place spontaneously	Negative ($\Delta G<0$)

In addition to the above, the Gibbs-Helmholtz equation can be used to calculate the change in free energy of the system when the temperature and pressure are constant.

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

Forming strong bonds means: $\Delta H<0$

Greater randomness or chaos means: $\Delta S>0$

Hence, the transformation is likely if $\Delta G < 0$, that is, the smaller it is, the greater the probability of the transformation occurring.

Illustrative example:

Carbon combustion at 298 K. What is the most inevitable interaction?

Reaction	**$\Delta H°_{298}$ (Kcal.mol^{-1})**	**$\Delta S°_{298}$ (Kcal.mol^{-1}.K^{-1})**	**$\Delta G°_{298}$ (Kcal.mol^{-1})**
$C+\frac{1}{2}O_2 \rightarrow CO$	-26,4	47,3	-32,8
$C+O_2 \rightarrow CO_2$	-14,1	51,1	-94,3

Therefore, the formation of CO_2 is the most likely reaction because its free enthalpy is the smallest.

We therefore have a criterion for evolution that is a function of system variables, valid for application regardless of whether a system is isolated or not. Therefore, the following can be stated:

“The condition for spontaneous evolution of a system at constant temperature and pressure is a decrease in free enthalpy.”

If standard values are used for both the change in enthalpy ($\Delta H°$) and the change in entropy ($\Delta S°$), then the measured change in free energy is called the change in standard free energy ($\Delta G°$). Accordingly, the above equation is reformulated as follows: $\Delta G° = \Delta H° - T\,\Delta S°$

1. Standard Gibbs Free Energy of Reaction

The standard Gibbs free energy of the reaction, which is symbolized by the symbol ($\Delta G°_R$), is defined as the change in the value of the free energy of the reaction when it takes place under the standard conditions for the reaction (25 °C and 1 atm). To calculate ($\Delta G°_R$) for any reaction, the Kiss energy values can be used. Standard Gibbs free energy of formation (which is symbolized by the symbol ($\Delta G°_f$). The standard Gibbs free energy of formation is defined as the amount of change in free energy when forming one mole of any compound from its basic elements by proving its forms at standard conditions of 25°C and 1atm.

The change in the standard free energy of any chemical reaction can be found by using the values of the standard free energies of formation for the reactants $(\Delta G°_f)_R$ and the products $(\Delta G°_f)_P$, in the same way we used to calculate the standard enthalpy change (Hess's law).

$$\boxed{\Delta G°_R = \sum n_P\ (\Delta G°_f)\mathit{Products} - \sum n_R\ (\Delta G°_f)\mathit{Reactnts}}$$

Important note:

- The values of $\Delta G°_f$ for simple bodies are taken from the thermodynamics table (at 298K, 1atm)
- The values of $\Delta G°_f$ for any element in its standard state are zero.
- For a reaction to be spontaneous, the temperature must be: $\Delta G°_R = \Delta H°_R - T\ \Delta S°_R \leq 0$

So:

$$\boxed{T \geq \frac{\Delta H°}{\Delta S°}}$$

It is called the minimum temperature

- One of the important applications of free enthalpy is its use in calculating the equilibrium constant of a chemical system (K) through the following relationship:

  $\Delta G°R + RT.\ \mathrm{Ln}\ K = 0 \Rightarrow$ $\boxed{K = exp^{(-\frac{\Delta G°_R}{R.T})}}$

Exercise series
(Second and third principles of thermodynamics)

Exercise - 1-:

Predict whether the change in entropy ΔS is greater or less than zero for the following processes:

A. Ethyl alcohol freezes
B. Evaporation of bromine liquid
C. Dissolution of glucose in water
D. Nitrogen gas cooling from 80°C to 20°C.

Answer: A - D: $\Delta S<0$, B - C: $\Delta S>0$

Exercise - 2-:

We want to evaporate 1 mole of solid iodine (I_2) taken at a temperature of 25°C. Then calculate the change that will occur in entropy ($\Delta S°$) between the temperature of 25°C and the point of evaporation of 184°C, and this is under constant pressure. Note that:

$Cp(I_2,s) = 54.6\ J.mol^{-1}.\ K^{-1}$, $Cp\ (I_2,\ l) = 81{,}5\ J.mol^{-1}.K^{-1}$, $T_{Fus} = 113.6\ °C$, $T_{Vap}=184°C$, $\Delta H°_{\ Fus}\ (I_2,s) = 15{,}64\ kJ.mol^{-1}$, $\Delta H°_{\ Vap}\ (I_2,\ l) = 25{,}5\ kJ.\ mol^{-1}$.

The answer $\Delta°S_R = 124.06\ J.K^{-1}$

Exercise - 3-:

We consider the following reaction: $H_2O_{(g)} + CO_{(g)} \rightarrow H_{2(g)} + CO_{2(g)}$

Given:

Compound	$\Delta H°_f$ ($KJ.mol^{-1}$)	$\Delta G°_f$ ($KJ.mol^{-1}$)	$S°$ ($J.mol^{-1}.K^{-1}$)
$CO_{2(g)}$	-393. 50	-394.38	213.60
$H_2O_{(g)}$	-241.80	-228.61	-
$CO_{(g)}$	-110.50	-137.28	197.90
$H_{2(g)}$	-	-	130.60

- Calculate $\Delta°H$, $\Delta°G$, $\Delta°S$ for this reaction.

- Calculate the S° of water $H_2O(g)$ at 25°C.

Answer: $\Delta°H_R$=-41,2 KJ, $\Delta°G_R$=-28,49 KJ, $\Delta°S_R$=-42,6 $J.K^{-1}$, $S°(H_2O,g)$ =188,7 $J.K^{-1}$

Exercise 4:

H_2O_2 melts at a temperature of (-17°C) and its latent heat of fusion at this temperature is 10.53 KJ/mol

- Calculate ΔS° for the reaction $H_2O_{2(l)} \overset{\Delta S°}{\leftrightarrow} H_2O_{2\,(s)}$

Answer: ΔS° = 38.79 $J.K^{-1}$

Exercise - 5-:

We take a thermally insulated container (so that we can neglect the heat capacity), containing 20 cm3 of water at 1.9 °C, and immerse a piece of copper with a mass of 200 g at a temperature of 100 °C. We assume that the heat capacities of water and copper are not related to temperature. The heat capacity of copper is: C=0.09 $Cal.g^{-1}.K^{-1}$

- Calculate the temperature of the bulk at equilibrium.
- Calculate the change in entropy of the sentence. Does the obtained result appear correct?

Answer: T_{eq} = 283 K, ΔS=3,50 $J.K^{-1}$

Additional exercises

Exercise - 1-:

Which of the following statements is true and which is false?

1. Exothermic reactions are spontaneous reactions.
2. A reaction that has ΔS equal to a positive quantity is a spontaneous reaction.
3. If ΔH and ΔS have positive values, the value of ΔG will decrease when the temperature increases.

Exercise - 2-:

If the reaction for the preparation of an acrylonitrile compound by combining propene with ammonia in the presence of oxygen at 24.4°C is represented by the equation:

$$C_3H_{6(g)} + NH_{3(g)} + \frac{3}{2}O_{2(g)} \rightarrow CH_2-CHCN_{(l)} + 3\,H_2O_{(l)}$$

If you know that the values $\Delta H°_f$, $\Delta G°_f$, and S° for the reactants are as in the following table:

$H_2O_{(l)}$	CH_2-CHCN	O_2	NH_3	C_3H_6	
-285,82	172.9	0	-46,11	20,41	$\Delta H°_f$ (J.mol^{-1})
69,91	188	205,14	192,45	226,9	$S°$ (J.mol^{-1}.K^{-1})
-237,12	208,6	0	-16,45	74,62	$\Delta G°_f$ (J.mol^{-1})

- Calculate Δ°H, Δ°G, and Δ°S for this reaction.

Exercise - 3-:

- Calculate the change in enthalpy, entropy, and free energy at standard conditions for the two reactions:

$$CaCO_{3\,(g)} \rightarrow CaO_{(s)} + CO_{2\,(g)}$$

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

$\Delta H°_f$ ($CaCO_3$,g) = -1206,9 kJ.mol^{-1} ; $\Delta H°_f$ (CaO , s) = -6351 kJ.mol^{-1} ,

$\Delta H°_{f,}$ (CO_2 ,g)= -393,5 kJ.mol^{-1} ; $\Delta H°_f$ (NH_3 ,g) = -45,9 kJ.mol^{-1}

$\Delta H°_f$ (N_2 ,g) = 0 ; $\Delta H°_f$ (H_2 ,g) =0

$\Delta S°$ ($CaCO_3$,g) = 92,9 J.mol^{-1} .K^{-1}; $\Delta S°$ (CaO ,s) = 38,2 J.mol^{-1} .K^{-1}

$\Delta S°_,$ $CO_{2\,(g)}$= -213,7 kJ.mol^{-1} ; $\Delta S°$ (NH_3 ,g) = 193 J.mol^{-1} .K^{-1}

$\Delta S°$ (N_2 ,g) = 191,5 J.mol^{-1} .K^{-1} ; $\Delta S°$ (H_2 ,g) =130,6 J.mol^{-1} .K^{-1}

- Calculate the value of the standard free energy change ΔG°. Are these reactions spontaneous at 398 K?

Exercise -4-:

The following reactions occur inside the mammalian liver at a temperature of 37°C and a pH = 7.5

Asparate + Citrulline → Arginosuccinate + H_2O $\Delta G°_1$ = 34,32 kJ.mol^{-1}

Arginosuccinate → Arginine + Fumarte $\Delta G°_2$ = 11,71 kJ.mol^{-1}

- Calculate ΔG° at 37°C and pH = 7.5 for the hydrolysis of arginine to become citrulline according to the reaction:

Arginine + H_2O → Citrulline + NH_4^+

Exercise - 5-:

- Calculate the entropy changes during the transformation of 9g from ice at (-10°C) to water vapor at (120°C) and under atmospheric pressure, noting that:

cp (H_2O, s) = 9 Cal. mol^{-1}. K^{-1}, cp (H_2O $_,l$) = 18 Cal mol^{-1}.K^{-1},

cp (H_2O, g)= 7,2 Cal mol^{-1}.K^{-1}, ΔH_{fus} (H_2O, s) = 1300 Cal .mol^{-1}

$\Delta^{\circ} H_{vap}$ (H_2O $_,l$) = 9700 Cal.mol^{-1}

Chapter Five

V.1. Introduction

When a chemical reaction occurs spontaneously, the concentrations of the reactants and products change while the free energy of the system decreases. Eventually, the free energy reaches a minimum, and the system reaches equilibrium. If we track the concentrations while this is happening, we notice that they reach stable values, as you can see from the figure: reaching equilibrium for the reaction: $A + B \rightleftharpoons C + D$.

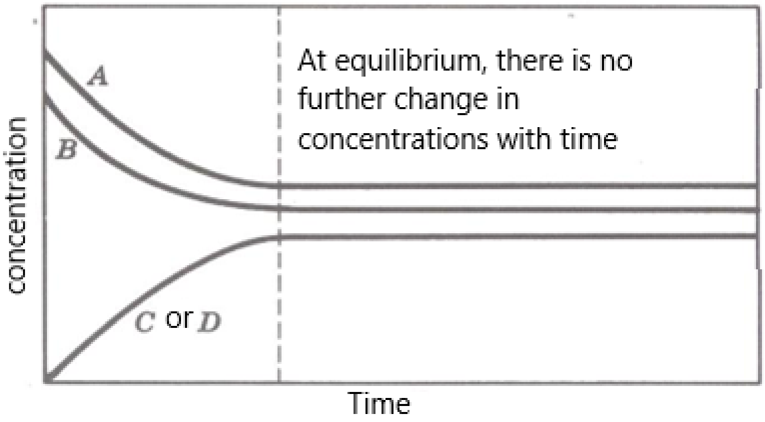


Fig.V.1 : Equilibre in reaction

We find that the rate at which products are formed from reactants is close to the rate at which reactants are formed from products. When equilibrium is finally reached, both the forward and reverse reactions occur at the same speeds, and the concentrations do not change after that. That is, the equilibrium is dynamic in the sense that the forward and reverse reactions continue without a noticeable change in concentrations. All chemical systems tend towards equilibrium.

V.2. Static equilibrium and dynamic equilibrium

It is said to be in a state of equilibrium when it does not notice any changes over time

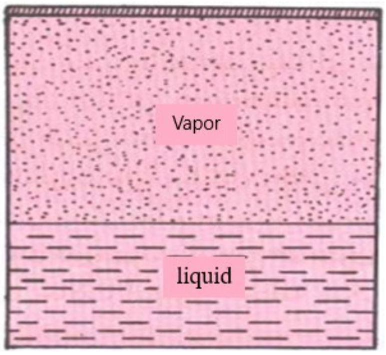
✍ Static Equilibrium

It is characterized by the absence of changes either at the macroscopic level or at the microscopic level.

✍ Dynamic Equilibrium

It is characterized by the absence of changes at the macroscopic level of the dynamically balanced system, but it is characterized by the occurrence of active changes at the molecular level.

Illustrative example:



A state of dynamic equilibrium for a system consisting of liquid water and water vapor in which the rates of evaporation and condensation are equal. It can be noted that the number of water molecules in the gaseous and in this means that no physical changes occur in the system.

Chemical equilibria are dynamic equilibria.

V.3. Irreversible and reversible reactions

Chemists are interested in studying many chemical reactions that serve many application fields, especially industrial ones. The chemical reaction occurs between substances that mix the reacting substances with each other, and when certain conditions are available, these substances disappear, and new substances are formed, called the resulting substances. Chemical reactions are divided - according to the direction of the reaction - into two parts:

- Irreversible reactions (one-way) (→)
- Reversible reactions (two-way) (⇌)

Irreversible reactions, which are called complete reactions, are defined as: chemical reactions in which, under certain conditions, one or all of the reacting substances are completely consumed, and the resulting substances do not have the same reaction conditions, as they occur in only one direction, which is the direction of the resulting substances. These reactions are symbolized by an arrow. One-way (→) whose head points to the resulting materials. For example, when automobile fuel (gasoline) is completely burned, it results in the formation of carbon dioxide and water vapor. This process is irreversible. It is very difficult, if not impossible, to be able to convert the carbon dioxide and water vapor resulting from this process into gasoline. Once again, we say that such changes occurred in one direction and that they are complete, irreversible interactions.

Examples include: $H_2SO_{4\,(aq)} + 2NaOH_{(aq)} \rightarrow Na_2SO_{4\,(aq)} + 2H_2O_{(l)}$

$$Na_2CO_{3\,(s)} + 2HCl_{(aq)} \rightarrow NaCl_{(aq)} + CO_{2\,(g)} + H_2O_{(l)}$$

As for the other type of reactions, they are non-general reactions and are called reversible reactions. These are reactions in which the reactants are not completely consumed because the resulting materials begin to form the reactants, and this situation continues no matter how long the reaction time, meaning the reactants are not completely consumed. This is indicated in the equation by placing two arrows. They have two opposite sides (⇌) to indicate this, meaning that the reaction goes in two directions, forward and backward. For example, the process of respiration takes place by the gas exchange method, as the blood coming to the pulmonary alveoli is loaded with water vapor and CO_2 gas, so the blood excretes these substances and takes in oxygen gas, so it becomes oxygenated blood that did not give oxygen in the process of internal respiration and takes in water vapor and CO_2, and so the breathing process continues, and there are many Examples that express chemical reactions and reversible physical changes include: $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

$$Fe_3O_{4\,(s)} + 4H_{2\,(g)} \rightleftharpoons 3Fe_{(s)} + 4H_2O_{(l)}$$

$$N_2O_{4\,(g)} \rightleftharpoons 2NO_{2\,(g)}$$

The most important differences between reversible and irreversible reactions can be summarized in the following table:

The most important differences between reversible and irreversible reactions are irreversible reactions

Reversible reactions	Irreversible reactions
Occurs in opposite directions (⇌)	Occurs in one direction (→)
The products react with each other to give the reactants	The reactants react almost completely.
Part of the reactants react	The resulting substances do not

	react with each other

V.4. Properties of chemical equilibrium

- ✍ The chemical system moves towards a state of equilibrium automatically, meaning that it continues at a rate that may be large or small, and it does not move away from the state of equilibrium automatically, but by an external influence, such as: a change in pressure or temperature. Once a chemical system is left to itself, it begins to return to a state of chemical equilibrium. The reason for all known systems to reach a state of equilibrium is the difference in the speed of the reverse reactions in them, and that the state of chemical equilibrium is a state where the speeds of the forward and reverse reactions in a chemical system are equal.
- ✍ The state of chemical equilibrium can be reached from both sides, i.e. the reactants side or the products side. In the example of thermal cracking of calcium carbonate, we find at each specific temperature a specific amount of carbon dioxide in equilibrium with... $CaCO_{3(s)}$, $CaO_{(s)}$
- ✍ Chemical equilibrium is dynamic, however, the concentration of substances is constant and does not change with the passage of time because the speed of the forward reaction is equal to the speed of the backward reaction, and therefore the visible and tangible properties are constant.

V.5. Reflexive homogeneous and heterogeneous reactions

Reversible homogenous reactions

Examples of these are reactions in which the reactants and products are all in the same phase (note that all reactions take place in a closed system).

$$N_2O_{4\,(g)} \rightleftharpoons 2NO_{2\,(g)}$$

$$Zn_{(s)} + S_{(s)} \rightleftharpoons ZnS_{(s)}$$

$$HCOOH_{(l)} + CH_3OH_{(l)} \rightleftharpoons HCOOCH_{3\,(l)} + H_2O_{(l)}$$

Irreversible homogenous reactions

Examples of these are reactions in which the reactants and products are present in more than one phase (note that all reactions take place in a closed system).

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$

$$2\,NaHCO_{3\,(s)} \rightleftharpoons Na_2CO_{3\,(s)} + CO_{2\,(g)} + 4H_2O_{\,(g)}$$

$$2Hg_{(l)} + O_{2(g)} \rightleftharpoons 2HgO_{(s)}$$

V.6. The Law of Mass Action and Chemical Equilibrium

Experimentally, it was found that each independent reaction has its own specific equilibrium state, which exists in a specific relationship between the concentrations of the reactants and the products.

To clarify this relationship, we will consider the reaction between hydrogen and iodine. In 1941, the two scientists Taylor and Crist conducted several important experiments for the following reaction:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

When one mole of hydrogen gas is mixed with one mole of iodine gas in the reaction vessel to form hydrogen iodide gas at 445°C, 2 moles of hydrogen iodide should be formed.

However, it was found practically by analyzing the mixture when this reaction reaches a state of dynamic chemical equilibrium that it contains 78% of HI gas and 11% of both iodine and hydrogen gases in their molecular states. Likewise, if pure HI gas is heated at

At the same temperature, it disintegrates into hydrogen and iodine gases, and the mixture always contains 78% of HI gas at equilibrium and 11% each of iodine and hydrogen gases.

The relationship between the speed of a chemical reaction and the concentrations of substances is called the law of mass action, which states: “When the temperature is constant, the speed of the chemical reaction in any direction is directly proportional to the molar concentrations of the reacting substances, each of which is raised to an exponent representing the number of moles placed in front of each substance in a balanced chemical equation.

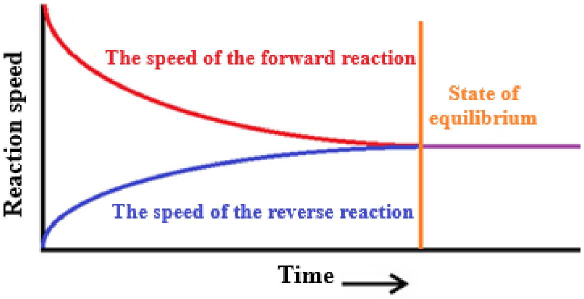
When applying the law of mass action to the reaction referred to above

$$H_{2\,(g)} + I_{2\,(g)} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} 2HI_{\,(g)}$$

The speed of the forward reaction (R_f) and the speed of the backward reaction (R_b) can be expressed mathematically and according to the law of mass action as follows:

$$R_f = k_f [H_2] [I_2] , \quad R_b = - k_b [H_2]^2$$

V.7. Equilibrium Constant



Suppose we have the following balanced, reversible reaction:

$$aA + bB \rightleftharpoons cC + dD$$

Where A, B, C, and D represent the reactants and products, while a, b, c, and d represent the numbers of their moles in the balanced reaction equation. When applying the law of mass action to the forward reaction, we find that:

$$R_f = k_f [A]^a [B]^b$$

When we apply the law of mass action to the back reaction, we get the following relationship:

$$R_b = k_b [C]^c [D]^d$$

Where: K_b, K_f and represent constants proportional to the speed of the forward and backward reactions, respectively.

When equilibrium is achieved, the speed of the forward reaction equals the speed of the backward reaction ($R_f = R_b$), so we get: $k_b [C]^c [D]^d = k_f [A]^a [B]^b$

So:

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

Dividing a fixed value k_f by another fixed value k_b is another fixed quantity known as the equilibrium constant (K_{eq}), so equation (4) becomes as follows:

$$\boxed{K_{eq} = \frac{[D]^d[C]^c}{[A]^a[B]^b}}$$

The equilibrium constant (K_{eq}) is defined as the ratio between the constant proportional to the speed of the forward reaction k_f and the constant proportional to the speed of the backward reaction k_b. It is also known as the product of the molar concentrations of the resulting substances at equilibrium divided by the product of the molar concentrations of the reactants at equilibrium, each raised to the power of the number of moles in the balanced reaction equation, which is a constant value when the temperature is constant.

Confirming notes for the above:

② The state of chemical equilibrium does not mean that the reaction has stopped, it is a (dynamic state)

② When equilibrium is reached, the concentrations of the reactants and products are stabilized.

☞ Conditions for maintaining equilibrium:

In order for chemical equilibrium to remain, it must be:

1. All reactants and products are present in the reaction space (no gas or precipitate is released or a fully ionized substance is formed).
2. Reaction conditions such as: (concentration - pressure - temperature) are constant, meaning they do not change
    - Do not add or remove any of the substances, whether they are reactants or products.
    - No heating or cooling.
    - Do not increase or decrease the volume of the reaction vessel in order to change the pressure.

Illustrative example:

Let the equilibrium reaction be the following:

$$N_{2\,(g)} + 3H_{2\,(g)} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} 2NH_{3\,(g)}$$

It was found that the forward reaction speed constant k_f equals 0.11 and the backward reaction speed constant kb equals 0.05. Calculate the equilibrium constant (K_{eq}) for the reaction.

Solution: $\mathbf{K_{eq}} = \frac{k_f}{k_b} = \frac{0,11}{0,05} = \mathbf{2,2}$

V.8. Methods of Expressing the Equilibrium Constant

The equilibrium constant is a fixed quantity that expresses the state of equilibrium reached by a group of reversibly reacting chemicals when the speeds of the two reversible reactions are equal. The value of the equilibrium constant is constant at a certain temperature and is obtained experimentally. From the law of mass action, this constant has a value that is a fraction whose numerator is the product of the concentrations of the resulting substances and whose denominator is the product of the concentrations of the reactants, raising the concentration of each substance to a power equal to its coefficient in the balanced equation.

✍ Equilibrium Constant in Terms of Molar Concentrations

When measuring the concentrations of reactants and products when equilibrium is achieved in molarity [M], the equilibrium constant is symbolized by the symbol (K_c). The equilibrium constant is in terms of molar concentrations, so it is its equilibrium constant and is written in the following form:

$$\boxed{K_c = \frac{[D]^d \times [C]^c}{[A]^a \times [B]^b}}$$

Important note:

The equilibrium constant is sometimes written in units and other times without units, and this depends on the number of products produced and the number of reactants. If the number of products is equal to the number of reactants, K_c is without a unit.

- ✓ If (a=b=c=d) is equal, then K_c has no units
- ✓ For example, if (a=b=1, c=d=2), then K_c $(mol.L^{-1})^2$

✍ Equilibrium Constant in Terms of Partial Pressure

Many chemical equilibria occur between gaseous substances or involve gaseous substances, and it is often appropriate to identify the quantity of a gas in terms of its pressure, as the gas pressure (P) is related to its quantity (number of moles) (n) through the general gas law: $PV = n\,R\,T \Rightarrow P = \frac{n}{V} R.T$

So
$$\frac{n}{V} = \frac{P}{R.T} = P\,(R.T)^{-1}$$
$$\frac{n}{V} = C = P\,(R.T)^{-1}$$

Where C represents the molar concentration, which is represented by parentheses: [ ]

We denote the equilibrium constant by the symbol Kp when expressed in terms of molecular pressures. If the substances in the following reaction are in the gaseous state: $aA_{(g)} + bB_{(g)} \leftrightharpoons cC_{(g)} + dD_{(g)}$

The equilibrium constant in terms of molecular pressures is written:

$$\boxed{K_p = \frac{P_{(D)}{}^{d} \times P_{(C)}{}^{c}}{P_{(A)}{}^{a} \times P_{(B)}{}^{b}}}$$

Important note:

The K_p law is used only if substances are in a gaseous state, because pressure only acts on a gas. Substances that are in a solid (S) or liquid (L) state (such as a solvent) do not have their concentrations recorded in the equilibrium constant law because their concentration remains constant during the chemical reaction (its value is considered equal to unity), regardless of how much their quantity varies at a certain temperature.

✍ The relationship between K_p and K_c

There is a relationship between the equilibrium constant expressed in terms of partial pressures Kp and the equilibrium constant expressed in terms of molar concentrations Kc according to the following two relationships:

$$\boxed{K_p = K_c\,(RT)^{\Delta n_g}}$$

Or in other form:

$$\boxed{K_c = K_p\,(RT)^{-\Delta n_g}}$$

The symbol Δn is defined according to the following relationship:

$$\Delta n_{(g)} = \Sigma\,\Delta n_{(g)\ \text{(Products)}} - \Sigma\,\Delta n_{(g)\ \text{(Reactants)}}$$

Where $\Delta n_{(g)}$: the difference between the number of moles of product gases and the number of moles of reactant gases

The relationship between K_P and K_c depends on the value of Δn and my agencies:

- Δn equals zero, then the value of $K_P = K_c$
- If Δn is positive, the value of K_P is greater than the value of K_c
- If Δn is negative, the value of K_P is smaller than the value of K_c

Illustrative example:

Assume that equilibrium occurs for the following reaction at a temperature of 300 K

$$NH_4HS_{(s)} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NH_{3\,(g)} + H_2S_{(g)}$$

It was found that the values of the molecular pressures for both product gases at equilibrium equal 0.3 atm. Calculate K_p and K_C for the reaction.

Solution: $K_p = P_{NH3}\, P_{H2S} = (0{,}3)\,(0{,}3) = 0{,}9 \;\Rightarrow\; \mathbf{K_p = 0{,}9}$

$$\Delta n_{(g)} = \Sigma\, \Delta n_{(g)\ (Products)} - \Sigma\, \Delta n_{(g)\ (Reactants)}$$

$$\Delta n_{(g)} = 2-0 = 2$$

$$K_c = K_p\ (RT)^{-\Delta n_g}$$

$$K_c = 0{,}09\times\ (0{,}082 \times 300)^{-2} = 1{,}5 \times 10^{-4} \;\Rightarrow\; \mathbf{K_c = 1,5 \times 10^{-4}}$$

- Notes that must be taken into account when writing the equilibrium constant formula:

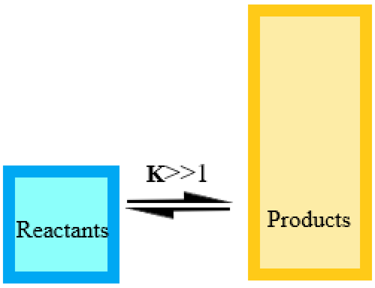
1. Make sure the reaction equation is balanced before you think about writing the equilibrium constant formula.
2. The exponents on the concentrations in the equilibrium law are exactly the same as the coefficients for these gases in the balanced equation.
3. Pure solids and liquids that react or produce their concentrations do not appear in the equilibrium constant formula as a function of pressure, because their concentrations remain constant.
4. The solvent concentration does not appear in the equilibrium constant formula, because it remains constant.

✍ The importance of the equilibrium constant:

Knowing the value of the equilibrium constant is of great importance, as its numerical value can:

- Determine the direction of the reaction
- Explaining the relationship between the equilibrium constant and the method of writing the equation.

✍ The direction of the reaction depends on knowing the value of the equilibrium constant

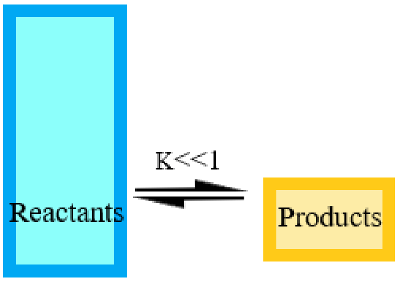


1. If the value of the reaction equilibrium constant is positive ($K_c > 1$), this means that:
   - The concentration of products is greater than the concentration of reactants
   - The repulsive (forward) reaction is dominant

Example: The following reaction is progressing toward completion because Kc>1

$$H_{2\,(g)} + Cl_{2\,(g)} \rightleftharpoons 2HCl_{\,(g)} \quad Kc = 10^{32}$$

2. If the value of the reaction equilibrium constant is negative (Kc < 1), this means that:
   - The concentration of the products is less than the concentration of the reactants
   - The reverse (back) reaction is dominant



Example: The following reaction does not proceed to completion because Kc < 1

$$AgCl_{\,(s)} \rightleftharpoons Ag^{+}_{\,(aq)} + Cl^{-}_{\,(aq)} \quad Kc = 1{,}7\,.10^{-10}$$

3. If the value of the equilibrium constant (Kc = 1), this means that: concentration of products = concentration of reactants
4. The numerical value of the equilibrium constant K_C changes only with the temperature of the system.

Very important note:

Substances that are not written in the equation for the equilibrium constant Kc are solids (S) and pure water if it is a solvent (because their concentrations are constant, regardless of their quantity). Otherwise, they are written in the equation for the equilibrium constant, such as (liquids, solutions, gases).

[Products] >[Reactants]   [Products] =[Reactants]   [Products]< [Reactants]

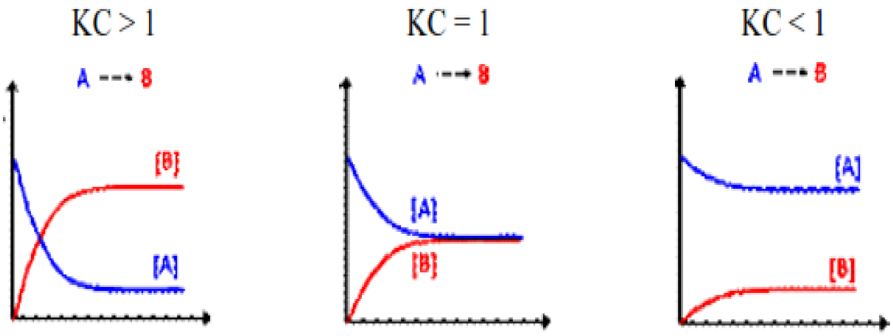


Fig.V.1: Expression graphically of concentration, time, and the value of the reaction equilibrium constant K_C

V.9. Reaction Quotient

At any moment of the reaction, we can know the direction of the reaction or the state of equilibrium if we can know the concentrations of the resulting and reacting materials at that moment, through which we can determine a value called the reaction quotient, which is symbolized by the symbol (Q) - where Q is from Quotient, which means the quotient, which is A hypothetical value for the equilibrium constant that is calculated at a certain moment during the reaction to predict its arrival at equilibrium. Q is expressed in the same relationship used to express Kc. The main difference between them is that the concentrations used in the Q relationship are not necessarily the values when the reaction reaches equilibrium, and the relationship between Kc and Q can be By predicting the state of equilibrium or the direction of the reaction, according to the following:

1. If Kc = Q, then the system is in equilibrium, and the concentrations of the products and reactants are equilibrium concentrations, that is, they will remain constant.

2. When Q is greater than (Q>Kc) Kc, the reaction is not in a state of equilibrium, and the concentrations of the products are higher than their concentrations at equilibrium, so they decrease to reach a state of equilibrium. For this to happen, the reaction moves from the right (the products) to the left (the reactants).
3. When Q is smaller than (Q < Kc) Kc, the reaction is also not in a state of equilibrium, as the concentrations of the products are less than their concentrations at the equilibrium state, so their value increases to reach the equilibrium state, and to do this, the reaction moves from the left (the reactants) to the right (the products).

Summary of the relationship between Q and Kc

The equilibrium	Quantities of reactants and products	Comparison
The balance does not shift in any direction	The amounts of reactants and products do not change	Kc= Q
The equilibrium shifts to the left	The amounts of reactants increase and the products decrease	Q>Kc
The equilibrium shifts to the right	The amounts of products increase and the amounts of reactants decrease	Q<Kc

Illustrative example:

The equilibrium constant for the reaction $3H_2 + N_2 \rightleftharpoons 2NH_3$

At 500°C it is 0.06. Study the following cases and decide the direction of the reaction (note that all concentrations are expressed in mol/L)

$[H_2]$	$[N_2]$	$[NH_3]$	
2×10^{-3}	10^{-5}	10^{-3}	(1)
0,354	$1{,}5\times 10^{-5}$	2×10^{-4}	(2)
10^{-2}	5,00	10^{-4}	(3)

The solution:

We must determine the value of Q for each case and compare it with the value of Kc to predict the direction of the reaction:

For case (1)

$$\mathbf{Q_{(1)}} = \frac{[NH_3]^2}{[H_2]^3 \times [N_2]} = \frac{(10^{-3})^2}{(2\times10^{-3})^3 \times (10^{-5})} = \mathbf{12.5 \times 10^5}$$

- ✓ Since the value of Q is greater than the value of Kc, the reaction proceeds in the backward direction, that is: the system shifts to the left (toward the reactants) until the reaction reaches a new equilibrium state.

In the same way, the remaining cases are calculated:

we find: $Q_{(2)} = 0{,}06$

- ✓ The value of Q is equal to the value of Kc, so the reactor is in equilibrium and the concentrations are fixed equilibrium concentrations.

$$Q_{(3)} = 0.002$$

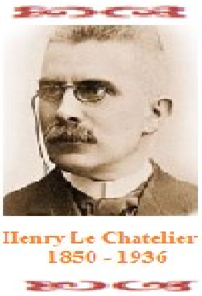
- ✓ The value of Q is smaller than the value of Kc. So the reaction is unbalanced and moves in a forward direction. That is: the system shifts to the right, towards the products, until the reaction reaches a new equilibrium.

V.10. Factors affecting the chemical equilibrium constant:

The value of the chemical equilibrium constant does not change except by changing the temperature.

Le Chatelier's Principle

It is a principle attributed to the French scientist Henri Louis Le Chatelier, who arrived at it in 1883 and states that “when the balance of a certain chemical system is disturbed by the action of an external stimulus, this system’s position of equilibrium will shift towards the direction opposite to the action of the external stimulus.” This is an attempt to nullify the effect of this external influence and then restore balance again.



Henry Le Chatelier
1850 - 1936

That is: everything that is added is reacted to, and everything that is removed is replaced.

Additional information:

The scientist Le Chatelier developed what is known as the Le Chatelier principle, rule, or law of mobile equilibrium. Le Chatelier's principle is considered the chemical version of Newton's third law. Le Chatelier's principle says that: whatever the change in a system in equilibrium, the system responds to the opposite of this change. The external influences that may lead to an imbalance are limited to the following:

1. The effect of adding a catalyst to any reaction:

The catalyst increases the speed of the reaction as a result of lowering the activation energy of the reaction. In a chemically balanced reaction, adding the catalyst will increase the speeds of the direct and reverse reactions.

Important note:

A catalyst (catalyst) is a substance that does not participate in a chemical reaction, but only helps to increase its speed.

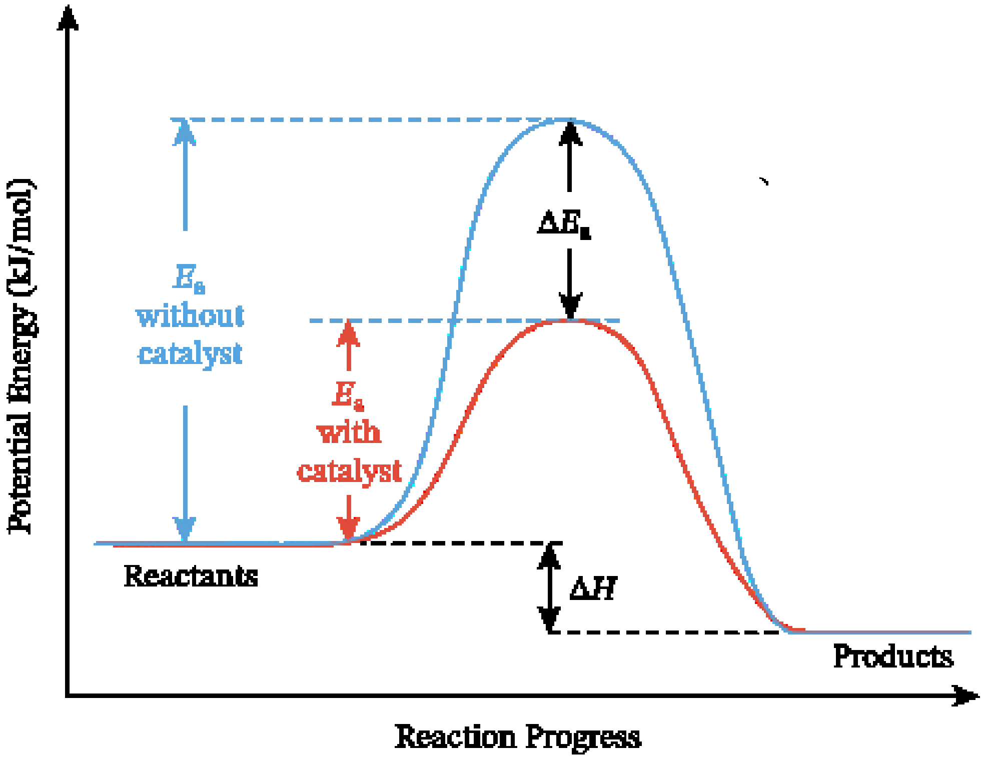


Fig.V.3 : Energy diagram for a reversible chemical reaction in the presence and absence of a catalyst, as they differ in activation

2. Effect of changing temperatures on equilibrium:

Raising the temperature increases the speed of the chemical reaction, and the Hoff t'Van equation has been determined the relationship between the reaction temperature and the reaction rate constant at constant pressure and constant volume is as follows:

$$\ln K_p = \frac{-\Delta H^\circ}{R.T} + Constant$$

The effect of increasing or decreasing temperature on the equilibrium position and the equilibrium constant can be summarized in the following table:

Influencing factor	Type of interaction	State of equilibrium	The value of the equilibrium constant
Increased temperature	Exothermic ($\Delta \boldsymbol{H} < 0$)	It shifts to the left	It decrease
Temperature decrease		It shifts to the right	It increases
Increased temperature	Endothermic ($\Delta \boldsymbol{H} > 0$)	It shifts to the right	It increases
Temperature decrease		It shifts to the left	It decrease
Increased temperature	Neither Endothermic nor exothermic ($\Delta \boldsymbol{H} = 0$)	Does not affect	Does not affect
Temperature decrease			

3. The effect of changing the concentration of reactants or products on the equilibrium

The effect of increasing or decreasing the concentration of each of the reactants or products on the chemical equilibrium when the temperature is constant can be summarized in the following table:

Influencing factor	State of equilibrium	The value of the equilibrium constant
Increasing the concentration of reactants	It shifts to the left	do not change
Increasing the concentration of products	It shifts to the right	
Decreasing the concentration of reactants	It shifts to the right	
Decreasing the concentration of products	It shifts to the left	

4. The effect of changing pressure on equilibrium:

A change in volume leads to a change in pressure when the temperature remains constant. We therefore logically expect that an increase in external pressure on a system should favor any change that results in a smaller volume (Boyle's Law). We do not expect changes in pressure to have any clear effect on the position of equilibrium in reactions in which all reactants or products are solids or liquids, because these aspects (solid and liquid) are virtually incompressible. However, pressure changes can have significant effects on equilibria involving reactions that produce or consume gases.

The effect of increasing or decreasing pressure for each of the reactants or products on the chemical equilibrium when the temperature is constant can be summarized in the following table:

Influencing factor	Type of interaction	State of equilibrium	The equilibrium constant
Increased pressure	$(\Delta\boldsymbol{n} > 0)$	It shifts to the left	The value of the equilibrium constant does not change

Increased pressure	$(\Delta\boldsymbol{n} < 0)$	It shifts to the right	
Decreased pressure	$(\Delta\boldsymbol{n} > 0)$	It shifts to the right	
Decreased pressure	$(\Delta\boldsymbol{n} < 0)$	It shifts to the left	
Increased pressure	$(\Delta\boldsymbol{n} = 0)$	Does not affect	
Decreased pressure	$(\Delta\boldsymbol{n} = 0)$	Does not affect	

The summary of this table is:

- When the pressure increases, the equilibrium shifts to the side (right or left - products first reactants) in which the number of gaseous moles is lower.
- When the pressure decreases, the equilibrium shifts to the direction where the number of gaseous moles is greater.
- When the number of gaseous moles in the products and the number of gaseous moles in the reactants are equal, the pressure does not affect the position of equilibrium, whether it increases or decreases.

V.11. The relationship between free energy and the equilibrium constant:

There is a relationship between the change in the standard free energy °ΔG of the reaction and the location of equilibrium, or, in other words, it determines the number of moles of reaction and products that are present when the chemical system reaches equilibrium.

Suppose we have the following balanced, reversible reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$\mathbf{\Delta G = \Delta G^\circ + RT\ ln}\ \frac{[\mathbf{D}]^{\mathbf{d}} \times [\mathbf{C}]^{\mathbf{c}}}{[\mathbf{A}]^{\mathbf{a}} \times [\mathbf{B}]^{\mathbf{b}}}$$

$$\mathbf{\Delta G = \Delta G^\circ + RT\ lnQ}$$

At equilibrium: ($\Delta G = 0, Q = K_{eq}$)

$$\Delta G = \Delta G° + RT \ln Q \Leftrightarrow 0 = \Delta G° + RT \ln K_{eq}$$

$$\Delta G° = - RT \ln K \Leftrightarrow \Delta G° = - 2.303\ RT \log K_{eq}$$

K_{eq} is called the thermodynamic equilibrium constant and may be expressed in molar concentrations, so the law becomes:

$$\Delta G° = - RT \ln Kc$$

It may be expressed in partial pressures, as in the case of gases:

$$\Delta G° = - RT \ln K_p$$

This equation is one of the most important in thermodynamics because it enables us to know the change in standard free energy ΔG° from knowing the value of the equilibrium constant K_{eq} and vice versa. This relationship can be explained in the following table:

ΔG°	**ln K_{eq}**	**K_{eq}**	**Notes**
Negative	Positive	>1	The reaction proceeds automatically from reactions to products
0	0	-1	The reaction is in equilibrium (the ratio between products and reactants is constant)
Negative	Positive	<1	The reaction does not occur automatically, but rather the reverse reaction occurs - that is, the products are transformed into the reactants automatically

Exercise series
(Second and third principles of thermodynamics)

Exercise - 1-:

The following chemical reaction was studied at a certain temperature:

$$SO_{2(g)} + NO_{2(g)} \rightleftharpoons SO_{3(g)} + NO_{(g)}$$

It turns out that it contains the following when balanced: 0.6 mol of SO_2, 0.3 mol of NO_2,1.1 mol of SO_3, and 0.8 mol of NO in a 1L container.

1. Write the reaction equilibrium constant.
2. Calculate the reaction equilibrium constant.
3. If the above quantities are placed in a 2l container, will this affect the equilibrium constant?

Answer: Kc=4.89. Increasing the volume has no effect on the value of the equilibrium constant.

Exercise - 2-:

Let the following reaction be:

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

When mixing N_2 and H_2 in a molar ratio of (1:3) and at a pressure of 100 atm and a temperature of 300°C, the volume percentage of ammonia was 52% at equilibrium.

1. What are the partial pressures of H_2, N_2, and NH_3 at equilibrium?
2. Calculate Kc, Kp for this system.

Answer: $K_C = 10{,}66$ ، $K_P = 4{,}83 \times 10^{-3}$

Exercise - 3-:

Let the following equilibrium be in the gas phase at 500° K:

$$PCl_{5\,(g)} \rightleftharpoons PCl_{3\,(g)} + Cl_{2\,(g)}$$

It has an equilibrium constant of Kc = 0.04. In a 5 liter container, we add 0.2 mol of $PCl_{5(g)}$ and 0.1 mol of PCl_3.

Calculate:

1. Composition of the mixture when balanced.
2. The total pressure in the vessel is at equilibrium.
3. Partial pressure of compounds at equilibrium.
4. Kp value at 500K°

Answer: Kp = 1.64

Exercise -4-:

What is the effect of the following factors on the amount of chlorine (Cl_2) produced in the following reaction:

$$4HCl_{(g)} + O_{2\,(g)} \rightleftharpoons 2H_2O_{(g)} + 2Cl_{2\,(g)} \quad \Delta H = +27 \text{ kcal}$$

A- Raise the temperature.

B- Reduce the temperature.

C- Increased oxygen concentration.

D- Increase the size of the vessel

Answer: A-D: Equilibrium shifts to the left (reactants), B-C: Equilibrium shifts to the right (products).

Exercise - 5-:

Let the chemical equilibrium be at 418 K

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

We put 1 mol of $C_2H_5OH_{(g)}$ in a container. When the reaction stops, the pressure value is equal to 10 atm, and the dissociation coefficient of $C_2H_5OH_{(g)}$ is equal to 0.62.

1. Write the expression for the equilibrium constant Kp (T) in terms of the dissociation coefficient.
2. Calculate the equilibrium constant Kp at 418 K.
3. Determine the moles of each gas at equilibrium
4. Calculate the change in standard free enthalpy for equilibrium at 418 K.

a. Is the reaction in the forward direction (1) spontaneous? 418 Reasons.

b. What is the effect resulting from high pressure? Explain.

c. In which direction does the equilibrium shift when 0.5 mol of $C_2H_{4\,(g)}$ is added? Give reasons.

Answer: Kp = 6.24 atm, $\Delta G° = 399.64$ Cal

Additional exercises

Exercise - 1-:

Explain the following:

1. Increasing the volume of the reaction vessel for a gaseous reaction $\Sigma\ \Delta n_{(g)\ (Products)} < \Sigma\ \Delta n_{(g)\ (Reactants)}$ leads to a decrease in the product.
2. In a hypothetical balanced reaction: energy + $A_{(g)} \rightleftharpoons B_{(g)}$ The temperature of the reaction vessel does not change when the total pressure increases.
3. The value of the equilibrium constant for irreversible reactions is very large.
4. The temperature of an endothermic reaction rises when $Kc= 0.3$ and $Q=1$
5. A reaction is considered exothermic if the Kc value of the reaction decreases when the reaction temperature is increased.
6. The value of K increases when the reaction temperature is raised in the case of endothermic reactions.
7. Increasing the pressure on an equilibrium mixture ($\Delta n_{(g)} = +1$), the equilibrium shifts towards the reactants.
8. Some reactions stop completely, while others appear to be stopped.
9. In the following balanced reaction:

$$SO_2Cl_{2\,(g)} + \text{energy} \rightleftharpoons SO_{2\,(g)} + Cl_{2\,(g)}$$

The temperature of the reaction increases when SO_2 is added to the equilibrium mixture.

Exercise - 2-:

Explain the following in light of the Hess relationship ($\Delta G=\Delta H-T\Delta S$)

1. The ice melting process is automatic under normal conditions.
2. Water does not decompose into its primary elements under normal conditions.
3. Sulfur dioxide gas dissolves in water automatically and emits heat during its dissolution.
4. Calcium carbonate does not decompose at normal temperatures.
5. The decomposition of mercury oxide II is always spontaneous at high temperatures and not under normal conditions.

6. Water does not freeze automatically under normal conditions.

Exercise -3-:

Let the following reaction be:

$$SO_{2\,(g)} + 1/2\ O_{2\,(g)} \rightleftharpoons SO_{2\,(g)}$$

The equilibrium constant for this reaction is 9.2 at 700 K and ΔH_R= -10.3 Kcal

1. Give the expression Kp.
2. Calculate Kp at 530 K.
3. Give the equilibrium conditions.
4. Calculate the standard free enthalpy ΔG° for equilibrium at 530 K.
5. Calculate the standard free entropy ΔS° (taking ΔS° for the reaction as a constant between 700 K and 530 K).

Exercise - 4-:

The pressure constants (Kp) for the following equilibria are given by the relations:

(I) $2\,C_{(s)} + O_{2\,(g)} \rightarrow 2CO_{(g)}$ $\quad \ln Kp\,(1) = \frac{26860}{T} + 21$

(II) $C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$ $\quad \ln Kp\,(2) = \frac{47380}{T} + 0{,}1$

(III) $CO_{2\,(g)} + C_{(s)} \rightarrow 2CO_{(g)}$ $\quad \ln Kp\,(3) = ?$

1. a. Write the expression for the equilibrium constant ln Kp (3) for the equilibrium equation (III) in terms of T.

   b. Calculate Kp (3) at 500°C.
2. Calculate ΔH° for reactions (I), (II) and (III) if performed at constant pressure.
3. Let the previous reaction (III) proceed with 1 mol of $CO_{2\,(g)}$ and 1 amount of $C_{(s)}$ under a total pressure of 1 atm.
4. Calculate the temperature that must be maintained for a mixture consisting of 50% CO_2 and 50% CO.

Exercise - 5-:

Nitric oxide was prepared at 500 K and 1 atm according to the following reaction:

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

1. If the number of initial moles of O_2 and N_2 is equal to 1 mol. Calculate the equilibrium constant Kp in terms of the dissociation coefficient α.
2. What is the direction of equilibrium at?

   A- High pressure.

   B- Decrease in the amount of oxygen.
3. The reaction occurs at 800 K followed by a decrease in the nitrogen concentration. Does this preparation reaction give off heat? Reasons.
4. At 500 K, Kc = 4. Find the value of Kp at this temperature.

Exercise - 6-:

To reduce air pollution, they are considering using methanol as a car fuel. Methanol is produced according to the reaction:

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$$

They conducted three experiments:

The first experiment:

Conducted at 210°C.

Into an empty 1L container, add 1 mol $CO_{(g)}$ and 2.6 mol $H_{2(g)}$. The group reached a state of equilibrium. In this case, there was 0.9 mol $CH_3OH_{(g)}$ in the container.

1. i. Write an expression for the equilibrium constant.

   ii. Calculate the value of the equilibrium constant at 210°C. Separate your accounts.

   iii. Until equilibrium was reached, did the pressure in the vessel increase, decrease, or not change? Explain.
2. After some time, they increased the temperature in the pot. When the group again reached equilibrium, there was less than 0.9 mol $CH_3OH_{(g)}$ in the container.

   - Is methanol production an endothermic or exothermic reaction? Explain.

Second experience:

Conducted at 210°C.

Into an empty container with a volume of 10 L, enter the mixture of two gases, $CO_{(g)}$ and $H_{2(g)}$. When the group reached equilibrium, there were 2 mol $CO_{(g)}$ and 4 mol $H_{2(g)}$ in the container.

- Find the concentration of $CH_3OH_{(g)}$ at equilibrium. Separate your accounts.

Third experiment:

Conducted at 210°C. In an empty 1 liter container.

They checked the composition of the gases in the vessel, when the group did not reach equilibrium. At the moment of examination, there were 0.4 mol $CO_{(g)}$, 0.3 mol $H_{2(g)}$, and 0.6 mol $CH_3OH_{(g)}$ in the container. The group reached a state of equilibrium.

- What is the concentration of $CH_3OH_{(g)}$ at equilibrium: greater than 0.6 mol per liter, less than 0.6 mol per liter, or equal to 0.6 mol per liter? Explain and detail your calculations.

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