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كلية التكنولوجيا
FACULTY OF TECHNOLOGY

Faculty of Technology

Vice Deanship of Post-Graduation, Scientific Research and External Relations

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شهادة ادارية

المصادقة على تقارير خبرة للموافقة على مطبوعة بيداغوجية

بعد الإطلاع على تقارير لجنة الخبراء للموافقة على المطبوعة البيداغوجية للأستاذة : **شنة مليكة – أستاذ محاضر قسم أ** بالقاعدة المشتركة بكلية التكنولوجيا بجامعة محمد بوضياف بالمسيلة والتي كانت كلها ايجابية.

تمّ تقرير التّالي:

1-المصادقة على تقارير لجنة الخبراء للموافقة المطبوعة البيداغوجية والمعنونة بـــ:

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2- حيث تمّ تشكيل هذه اللجنة بناء على اجتماع المجلس العلمي للكلية المنعقد بتاريخ **2026/02/17** المكونة من السّادة الآتية أسماؤهم:

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وتمت الموافقة بالاجماع على هذه المطبوعة.

رئيس المجلس العلمي للكلية

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People's Democratic Republic Of Algeria

Ministry Of Higher Education And Scientific Rfesfrearch

Mohamed Boudiaf M'sila University

Faculty of Science and Technology

Course booklet Course Chemistry II

Directed by: Dr CHENNA Malika

Academic Year : 2025/2026

PREFACE

Le présent polycopié que je présente est un support pédagogique destiné essentiellement aux étudiants de la première année technologie . Ce polycopié sert à mieux saisir la chimie générale.

Les objectifs de ce polycopié sont :

- D'approfondir les concepts de chimie générale et organique de base et se familiariser avec le calcul des différents paramètres.
- Compléter sa connaissance des concepts de base de chimie générale et organique par des applications numériques qui touchent plusieurs exemples.

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Foreword

This document is intended for first-year undergraduate students in the new LMD (Bachelor's, Master's, Doctorate) technology program. Chemical Thermodynamics (Chemistry II) is a 3-credit course. with the following content: Equations of state for gases, intermolecular forces, laws of thermodynamics, internal energy and entropy; equilibrium criteria, free energy; partial molar quantities, chemical potential; chemical equilibrium in ideal and non-ideal systems; thermodynamics of mixtures; statistical mechanics: microstates and randomness, probability and distribution functions; Boltzmann distribution; statistical thermodynamics of gases.

OBJECTIVES

• To introduce the students to the various terms in thermodynamics, including thermodynamic system, boundary, surroundings, state functions, processes, etc.

• To introduce the various equations of state and their consequences in thermodynamics.

• To help students understand the nature of intermolecular forces in gases and liquids, as well as their consequences.

• To introduce and explain the first law of thermodynamics, its implications, applications, and consequences.

• To explain the concept of thermochemistry, the laws of thermochemistry, enthalpy changes associated with various reactions, and the related theory.

• To introduce and explain the concept of entropy and the second law of thermodynamics and its associated thermochemical consequences.

• To explain the concept of the third law of thermodynamics.

Ce n'est pas dans la science qu'est le bonheur, mais dans l'acquisition de la science. »

EDGAR POE (1809/1849), LE POUVOIR DES MOTS

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Thermodunamics

1. Introduction

Thermodynamics is the study of how heat moves around in ‘macroscopic’ objects. Throughout these lectures, we will talk a lot about laws and models. Models are simplified, empirical description of a real system, which generally develops overtime as our knowledge progresses. In contrast, laws derive from fundamental principles of Physics and thus apply universally. Examples of laws are the energy conservation law, Newton’s laws of motion, but also quantum mechanics, special and general relativity, etc…. Examples of models include the ideal gas, the Bohr atom etc…

The Journey to the study of thermodynamics dates back to 1865, when a German Chemist, Rudolf Clausius suggested that the principles of thermochemistry could be applied to the principles of thermodynamics. This laid a foundation for an American mathematical physicist, Willard Gibbs to publish a work on the equilibrium of heterogeneous substances in which a graphical approach to the measurement of thermodynamic equilibrium of a chemical reaction was first revealed. The work of Gibbs was strongly supported and improved upon by Clausius and Sadi Carnot.

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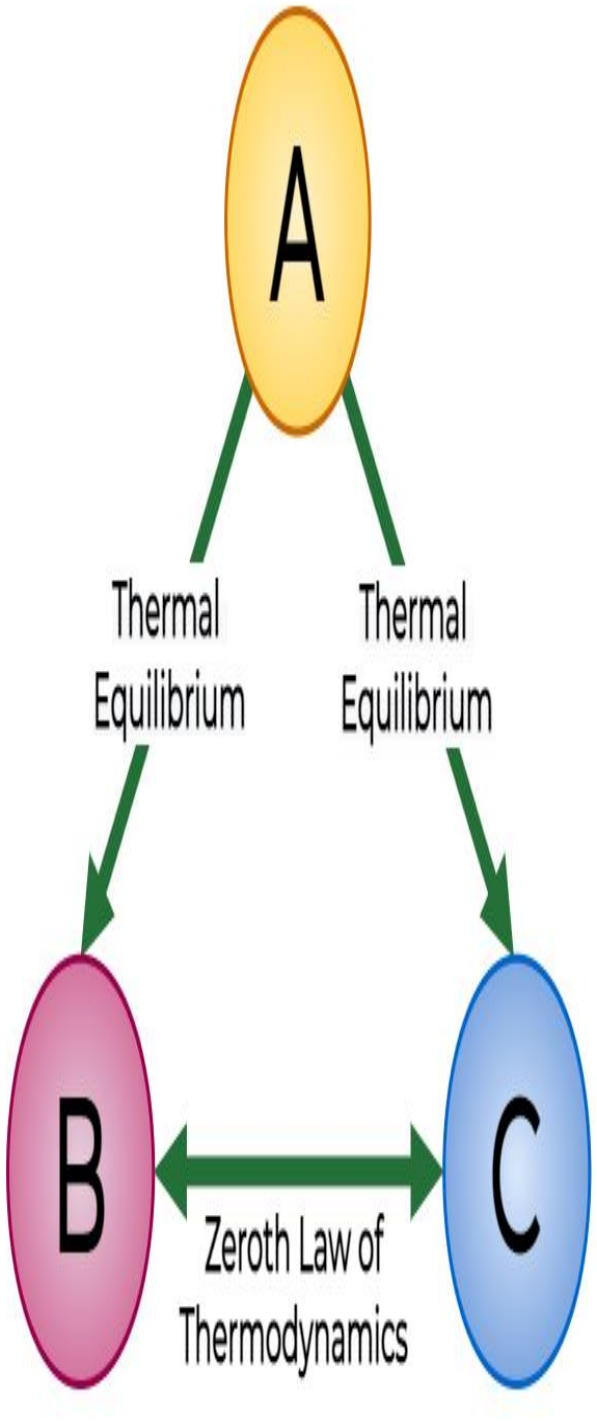
2. The Zeroth Law of Thermodynamics



Course contents

- Thermodynamical system
- Equilibrium of system
- Extensive, intensive, and specific quantities
- Quasi-static, reversible and irreversible processes
- Development of equation of state
- Development of equation of state
- Mathematical condition of a state function (D.T.E)

2. The Zeroth Law of Thermodynamics

The zeroth law states that if two thermodynamic systems are both in thermal equilibrium with a third system, then the two systems are in thermal equilibrium with each other. Two systems are said to be in thermal equilibrium if a wall permeable only to heat links them, and they do not change over time.

2.1-Thermodynamical systems

Before we embark on deriving the laws of thermodynamics, it is necessary to define the main vocabulary we will be using throughout these lectures.

2.1.1- Thermodynamical system

Whatever "macroscopic" part of the Universe we select for study."Macroscopic" here means made of a large number of particles, N, i.e. $N \geq N_A \approx 6.02\ 10^{23}$, with $_A$ the Avogadro number. This is very important, as some properties (eg. temperature) do not apply for single particles. As an isolated system is not a very realistic concept (apart if one studies the Universe as a whole!), one is led to define the

2.1.2 Surroundings of a system

This is simply the vicinity of a system. Generally, the surroundings will be much larger than the system itself, so will not be treated in the same way. The system and its surroundings are separated from one another by a *boundary*. Together, system and surroundings form what is called the

2.1.3 Total system

This is a thermodynamical system which can be con- sidered as *isolated* to a good approximation.

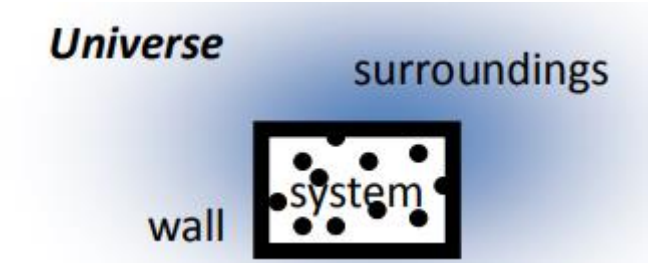


Figure 2.1: Schematic Diagram Of A System

2.1.4 Open, close, adiabatic, and isolated systems

Systems can be *open*, *closed*, *adiabatic*, and *isolated*.

- **Open system** can exchange mass and energy with the environment.

A **closed system** cannot exchange the mass but it can receive or lose energy in the form of heat due to the thermal contact with the bath or through the work done on the system.

- **Adiabatic system** is thermally isolated so that it cannot receive or lose heat, although work can be done on this system. The corresponding processes (such as compression/expansion) are called *adiabatic processes*. Fast processes are adiabatic, too, because the heat exchange through the surface requires a too long time and becomes inefficient during the time of the process.
- **Isolated system** cannot exchange neither mass nor energy, there is no contact between the system and the environment.

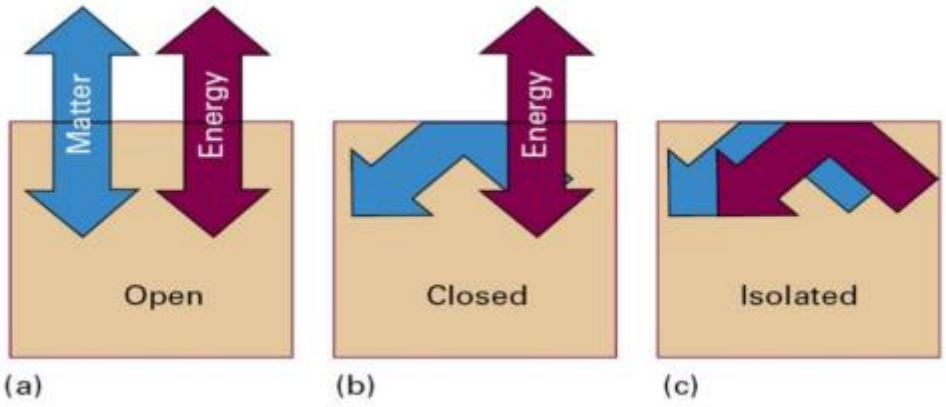


Figure 2.2: Schematic diagram of a thermodynamical

- **Homogeneous system**

A homogeneous system is defined as a system of linear equations where all of the constant terms are zero, leading to a solution space characterized by the linear combinations of its variables.

- **Heterogeneous system**

Heterogeneous computing refers to *systems that use more than one kind of processor or core*. These systems gain performance or energy efficiency

2. The Zeroth Law of Thermodynamics

2.2 Equilibrium of system

A thermodynamic system is said to exist in thermodynamic equilibrium when no change in any macroscopic property is registered if the system is isolated from its surrounding. A thermodynamic system will be in a state of thermodynamic equilibrium if the system is the state of Thermal equilibrium, Mechanical equilibrium and Chemical equilibrium

2.2.1 Mechanical equilibrium

A physical system made up of many parts is in mechanical equilibrium if the net force on each of its individual parts is zero.

2.2.2 Thermal equilibrium

is reached when there is no change in temperature of system with respect to time.

2.2.3 Chemical equilibrium

Condition in the course of a reversible chemical reaction in which no net change in the amounts of reactants and products occurs. A reversible chemical reaction is one in which the products, as soon as they are formed, react to produce the original reactants.

- Stable equilibrium - System is at its lowest possible energy level.
- Metastable equilibrium - System satisfies above two criteria, but is not at lowest possible energy.

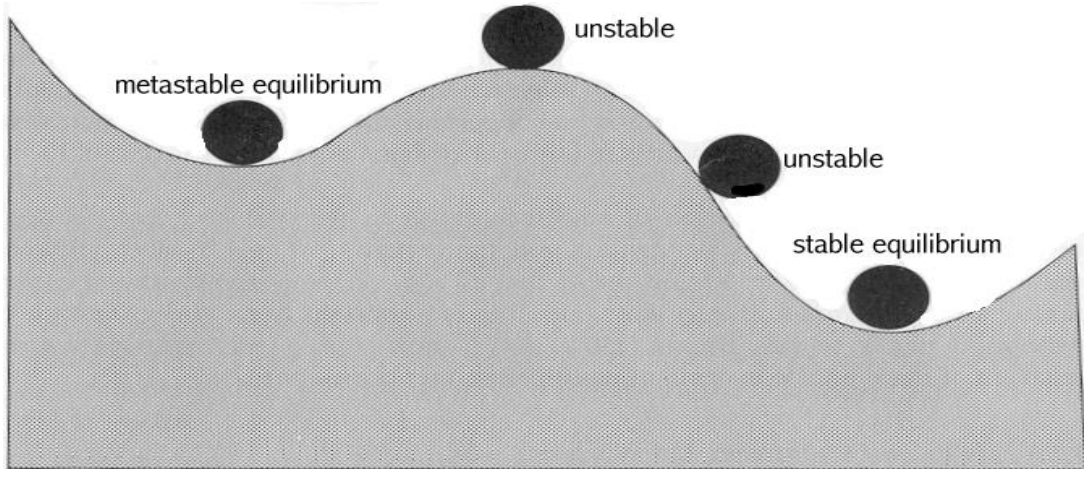


Figure 2.3: Schematic diagram of a thermodynamical

2.3 Extensive, intensive, and specific quantities

Macroscopic physical quantities can be *intensive* and *extensive*. Intensive quantities (pressure P, temperature T) do not depend on the size (mass) of the system, while the extensive quantities (mass M, volume V, energy E or U) scale with the system size. To make this definition more precise, one can split the system into two equal parts by an imaginary membrane. The intensive quantities of the two resulting systems will remain the same while the extensive quantities of each subsystem will be half of that for the whole system.

Specific quantities is the third type of quantities that can be obtained from an extensive quantity by division by another extensive quantity. By this definition, specific quantities do not depend on the system size. An example of specific quantity is the mass density

$$\rho = \frac{M}{V}$$

2.4 Quasi-static, reversible and irreversible processes

In the preface, it is ritten that thermodynamics studies macroscopic systems at equilibrium, while equilibrium is a time-independent state reached because of relaxation under time-independent conditions. On the other hand, thermodynamic considers processes such as compression/expansion or heating that evolve in time. Isn't here a contra- diction with the equilibrium nature of thermodynamics? The solution of this paradox is that, "good" thermodynamic processes must be *quasi-static* or *quasi-equilibrium*. This means that the external parameters that control the system change with time so slowly that the system at any moment of time is very close to the equilibrium, corresponding to the instantaneous values of the control parameters. These external parameters define the macroscopic quantities of the system at any stage of the process that can be represented as a continuous line in the space of these quantities, such as (P, V). Such space can be called *configurational space*. If the external parameters change fast, the system deviates from the equilibrium and, in most cases, its macroscopic quantities become undefined. In this case the process cannot be represented as a line in the (P, V) or other diagram. For instance, fast compression of a gas creates sound waves or even shock waves that travel through the system making density, pressure, and temperature non-uniform, so that there are no unique values of these quantities. In this case, only the initial and final states of the system are equilibrium states but there is no line connecting them.

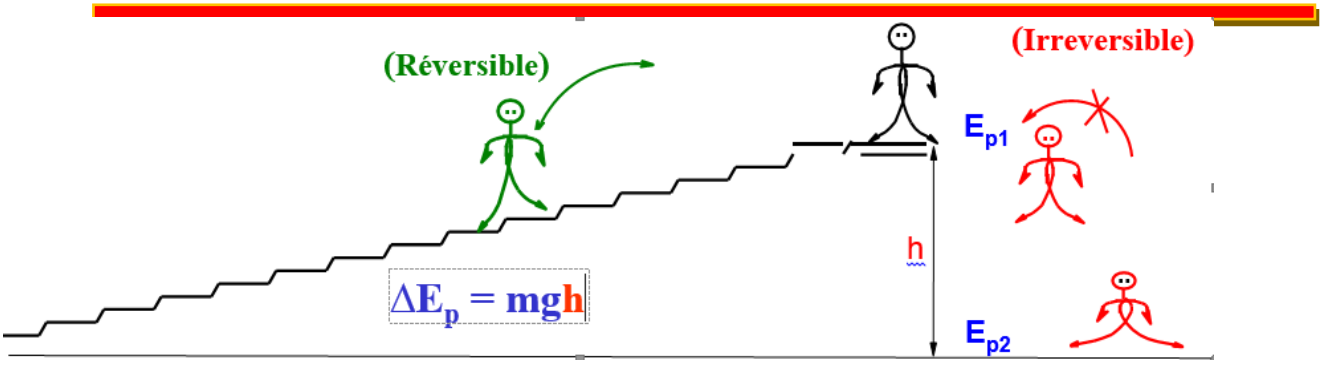


Figure 2.4: Schematic diagram of Reversible and irreversible process

2.5 Temperature

On the intuitive level, temperature is associated with notions "hot" and "cold". The experience shows that if hot and cold bodies are brought in contact, their temperatures would eventually equilibrate. Consider a system in a thermal contact with the bath and make a quasi-static compression or expansion of the system plotting its states in the (P, V) diagram. As the bath is large, its temperature remains unchanged and as the process is slow, the temperature of the system will have the same unchanged value. In this way one obtains the isothermal curve, or *isotherm*, in the (P, V) plot. Repeating this with different temperatures of the bath, one obtains many isotherms. For most of substances (except water near 4° C) isotherms corresponding to different temperatures do not cross. This allows to define the *empirical temperature* T as a parameter labeling isotherms:

$$\varphi(P, V) = T. \quad (2)$$

Indeed, if $T = \text{const}$, P and V are related and belong to a particular isotherm. Note that any monotonic function of the empirical temperature (e.g., T or T^2) can serve as empirical temperature as well, so that the choice of the latter is not unique. Eq. (2) is the basis of thermometers using different substances such as alcohol, mercury, ideal gas, etc. One can, say, fix P to the athmospheric pressure and measure V (or the hight of the alcohol or mercury column) that changes with temperature.

It is convenient to choose the empirical temperature using the experimental fact of thermal expansion and define the change of the temperature as proportional to the change of the volume: $\Delta T \propto \Delta V$. Here it is important that upon warming or cooling the volumes of different substances change proportionally to each other in a wide range of the to be defined temperature: $\Delta V_1 \quad \Delta V_2 \quad \Delta V_3 \quad \ldots$ Thus, there is no contradiction in the definition of the temperature using different substances, The only thing is to choose the proportionality coefficients in the above formula for different substances and the additive

constant (offset) in T. This has been done historically in a number of different ways, resulting in the Fahrenheit, Celsius, Kelvin, and many other defunct temperature scales.

The advantage of the Celsius scale is using very natural events, melting of ice and boiling of water (at normal conditions), to define the basic temperature points $0^{\circ}C$ and $100^{\circ}C$. Physicists use the Kelvin scale in which the temperature, corresponding to the extrapolated point, where the volume (or pressure) of the ideal gas vanishes, is set to zero and one degree of temperature difference is the same as in the Celsius scale. The relation between the two scales is

$$T(^{\circ}\mathrm{C}) = T(^{\circ}\mathrm{K}) - 273.15. \qquad (3)$$

Existence of the temperature as the new (non-mechanical) quantity that equilibrates in the case of systems in thermal contact, is called the *zeroth law of thermodynamics*.

2.6 Pressure (P)

It is defined as the force per unit area exerted by a body/matter/system on its surface in a direction normal to the surface.

&	Pascal	bar	Atm. normale	Torr	livre par pouce carré
	1 Pa	1 bar	1 atm	1 Torr	1 psi
1 Pa	≡ 1 N/m^2	10^{-5}	$9{,}8692\times10^{-6}$	$7{,}5006\times10^{-3}$	$1{,}450377\times10^{-4}$
1 bar	10^5	≡ 10^6 dyn/cm^2	0,98692	750,06	14,50377
1 atm	$1{,}01325\times10^5$	1,01325	≡ p_0	≡ 760	14,69595
1 Torr	133,3224	$1{,}333224\times10^{-3}$	$1{,}315789\times10^{-3}$	≈ 1 mm Hg	$1{,}933678\times10^{-2}$
1 psi	$6{,}8948\times10^3$	$6{,}8948\times10^{-2}$	$6{,}8046\times10^{-2}$	51,71493	≡ 1 lb/po^2

psi: pound-force per square inch, c.-à-d., livre par pouce carré.

- **Absolute volume (V)**

It is defined as three-dimensional space occupied by matter i.e. gas or liquid. It is measured in m^3.

- **Specific volume (v)**

It is defined as the volume occupied per unit mass of a gas/ fluid. It is reciprocal of the density. Unit of sp. vol. in S.I. system of units is m^3/kg.

2. The Zeroth Law of Thermodynamics

R = **universal gas constant** = 8,32 $J.K^{-1}.mol^{-1}$
N = Avogadro's number (NA)= 6,023 x 10^{23} mol^{-1}
T = temperature (K) (zero absolu = 0 K = - 273°C)
V = volume (m^3) (1 m^3 = 10^3 L)
m = Mass (kg)
P = pressure (Pa) (1 atm = 101,325 x 10^3 Pa = 1,01 bar)n_i = **number of moles** i (mol)
$x_i = n_i/n_t$ = **mole fraction**
partial pressure $P_i = x_i.P_t \Rightarrow P_iV = n_iRT$
concentration $c_i = [\,i\,] = n_i/V$ (mol.L^{-1})
Energy (J) (1 cal = 4,18 J)

systeme Composition

2.7 States of matter

Matter can change states when energy is added or removed from the system. Usually, this energy results from changes in pressure or temperature. When matter changes states it undergoes a a phase transition or phase change. The six most common phase changes are shown in Figure 1. 3.

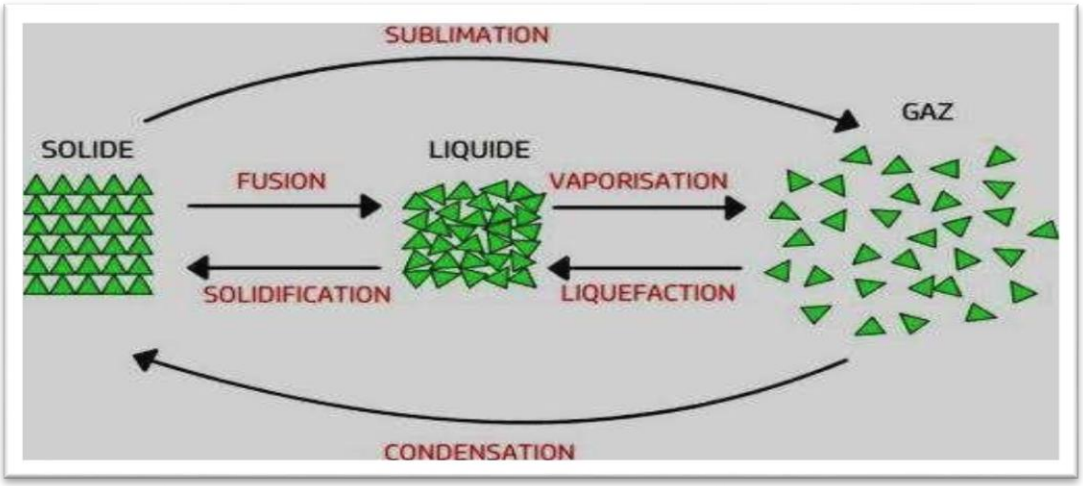
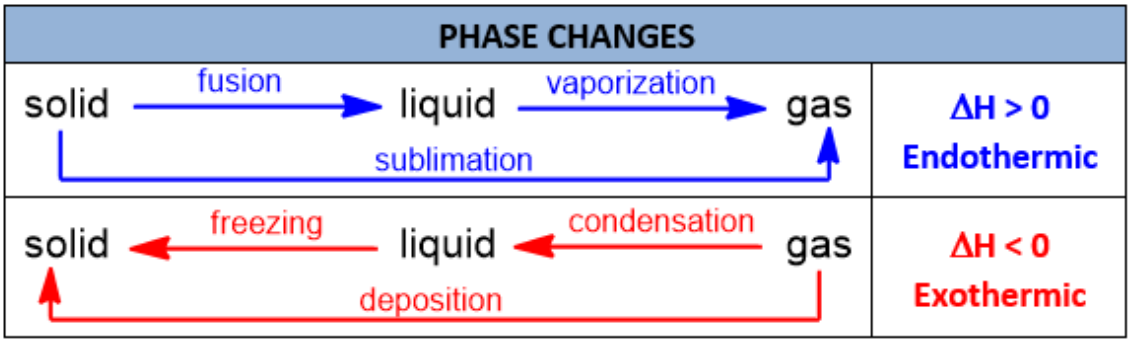


Fig. 1. 3. Phase changes between states of matter.

2. The Zeroth Law of Thermodynamics



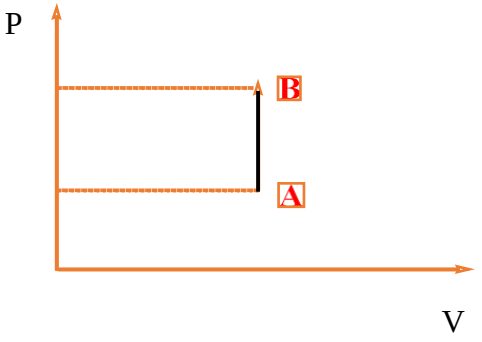
Deposition - changing from gas to a solid;

- **Sublimation** - changing from a solid to gas.
- Phase changes are *always* accompanied by a change in the energy of a system
- The heat required to change the phase of a sample of mass is called **the latent heat**. For example: The latent heat of vaporization (L_v) is the amount of heat needed to cause a phase change between liquid and gas.

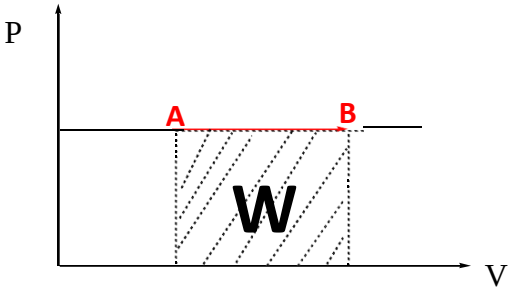
2.8 Thermodynamic Processes

A thermodynamic process refers to series of changes that occur in a thermodynamic system. There are four types:

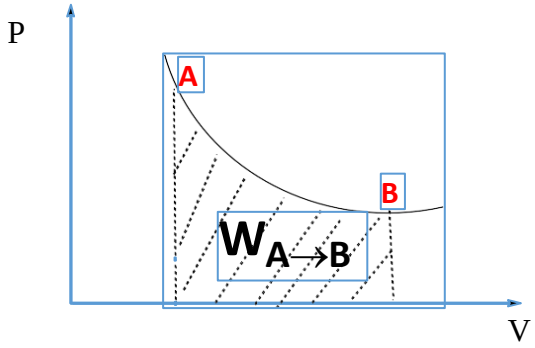
- Isochoric process: during which the system's volume does not change; V=Constant ΔV=0



- **Isobaric process**: during which the system's pressure does not change; P=Constant ΔP=0



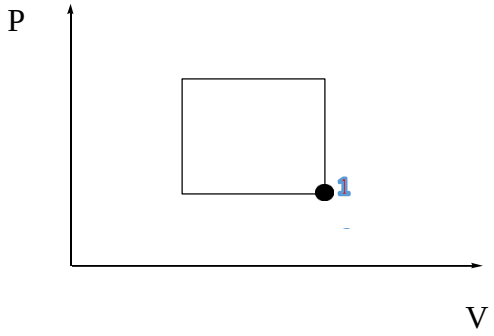
- **Isothermal process***:* during which the system's temperature remains constant; T=Constant ΔT=0.



- **Adiabatic process :**

  An adiabatic process is a thermodynamic process in which there is no exchange of heat between the system and surrounding, that is, the heat remains constant.

- **Cyclic process:** if the system returns back to its initial state after doing some work then the process is said to be a cyclic process. (**figure bellow**).



2.8 Development of equation of state

2.8.1 Boyle's law

Robert Boyle (1662) was the first to develop a documented equation of state, which he obtained through series of experiments using J-shaped glass tube to study the variation of the volume of afixed mass of a gas with pressure (at constant temperature). In support of Robert Boyle work, Edme Mariotte (1676) also confirmed the relationship between pressure and volume of a fixed mass of a gas at constant temperature. Boyle's law states that at constant temperature, the volume of a fixed mass of a gas is inversely proportional to its pressure. Mathematically, Boyle'slaw can be expressed as follows,

$$V \alpha \frac{1}{P}$$

$$PV = K$$

Therefore, according to Boyle's law, the product of the pressure and volume for a given mass ofa gas will always be constant provided the temperature is constant. It also implies that a plot of volume (V) against the inverse of pressure (1/P) and also a plot of pressure against volume will follow predicted patterns as shown in the figures below,

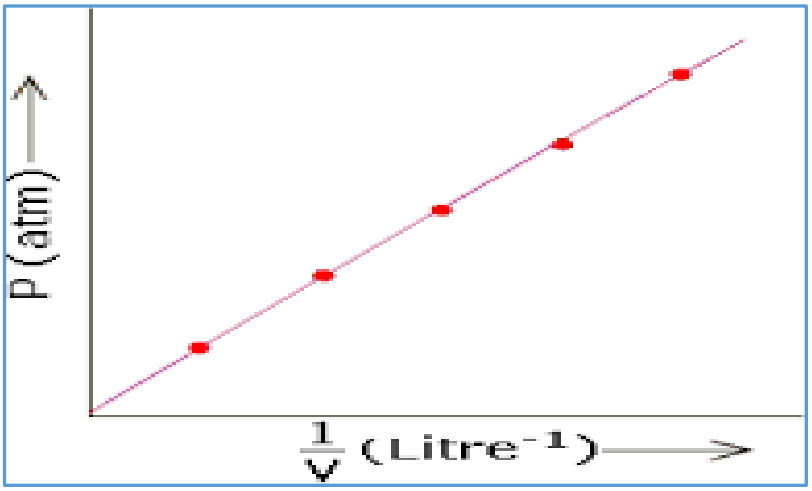


Fig. 1: Variation of pressure of ideal gas with the inverse of its volume according to Boyle's law

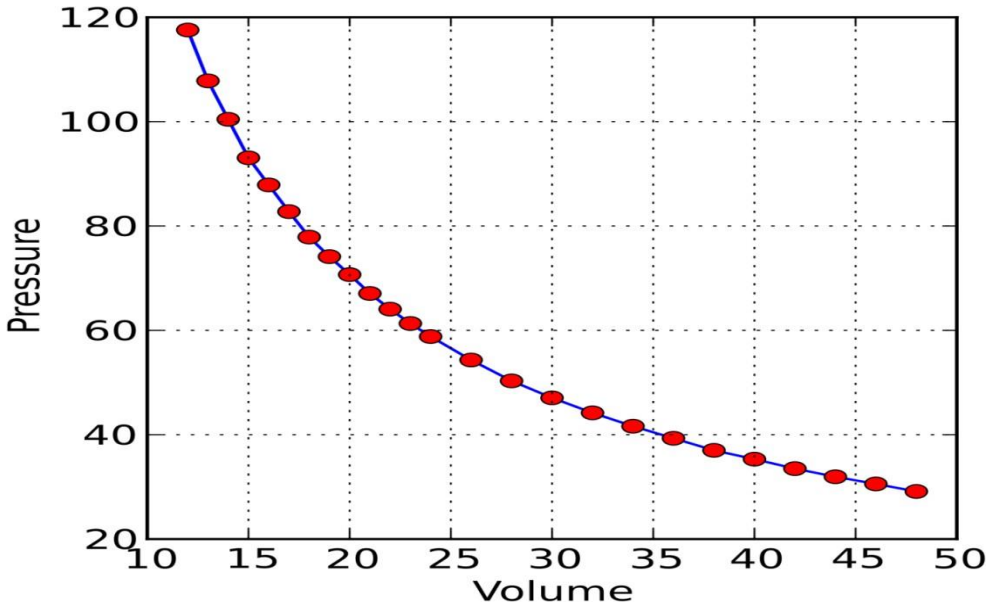


Fig. 2 Variation of pressure with volume according to Boyle's law

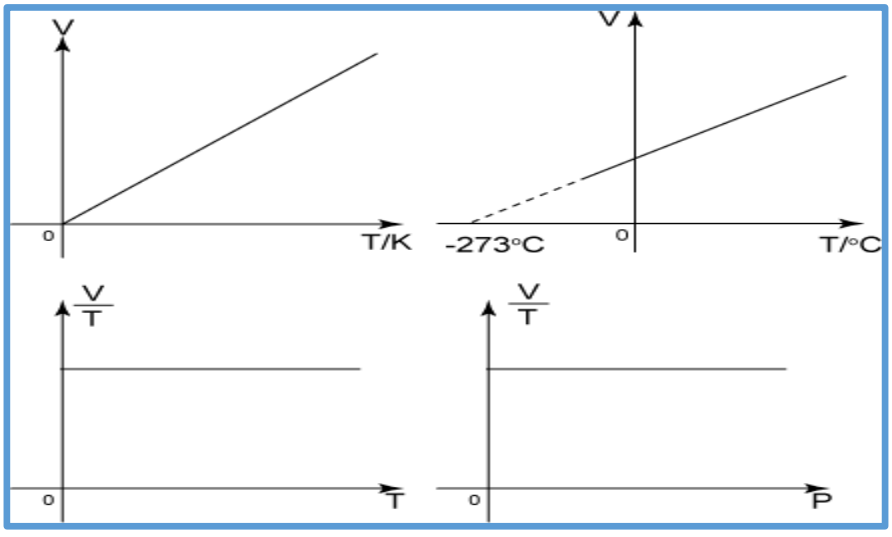
2.8.2 Charles law

The next level of development of equation of state for gases was pioneered by Jacques Charles (1787) and Jospeh Louis Gay-Lussac (1802). Charles found that the expansive be haviour of air and some gases over a range of temperature, followed a similar pattern. In repeating similar experiments, Gay-Lussac found that there was a linear relationship between volume and temperature. Charles law states that at constant pressure, the volume of a given mass of a gas is directly proportional to its absolute temperature. Mathematically, Charles'law can be expressed as follows.

$$V \alpha T$$

$$\frac{V}{T} = K$$

Hence, according to Charles' law, the ratio of the volume of a fixed mass of a gas to its temperature, will always be a constant provided the pressure is held constant. This also translate to interprets a plot of V against T as linear with zero intercept and slope, equal to K. Graphical representation of Charles' law in various forms are presented in Fig. 3 below



Fig, 3: Various plots representing Charles' law

2.8.3Dalton law

Dalton law (1801) is concerned about the partial pressure exerted by gases in a mixture. The law states that for a mixture of gases which do not react chemically, the total pressure of the gas is the sum of the partial pressures exerted by the individual gases in the mixture. This implies that if a components of a gas mixture are labeled as A, B, C, D .....N, then the total pressure of the gas will be expressed as

$$P_T = P_A + P_B + P_C + P_D \ldots\ldots\ldots + P_N = \sum_{i=A}^{N} P_i$$

2.8.4 The ideal gas equation

The ideal gas equation was developed by Emile Clapeyron, who combined Boyle and Charleslaws in 1834. The equation can be written as,

$$PV = nRT$$

where n is the number of moles of the gas and R is the universal gas constant, which is numerically equal to 8.314 J/mol/K

2.8.5 Van der Waal equation of state

In 1974, J. D. Van der Waals derived an equation of state that can be used to interpret the behaviour of real gases. This was necessary because real gases do not obey the ideal gas equationand at high pressures or low temperatures. Therefore, van der Waal equation is a modification ofthe real gas equation and can be written as,

$$(PV)_{cor} = \left(P + \frac{a}{V^2}\right)(V - b) = RT \text{ (for 1 mole of a gas)}$$

$$(PV)_{cor} = \left(P + \frac{a}{V^2}\right)(V - b) = nRT \text{ (for n moles of a gas)}$$

2.9 Mathematical condition of a state function (D.T.E)

The differential of a state function, a function of several independent variables, is an exact total differential (ETD). This means it is equal to the sum of its partial differentials with respect to each variable. For a function of two variables *F(x,y) :*

$$dF = \left(\frac{\partial F}{\partial X}\right) dx + \left(\frac{\partial F}{\partial Y}\right) dy$$

$\left(\frac{\partial F}{\partial X}\right)$ is the partial derivative of Fwith respect to x and the same for y.

The order of variation of the independent variables x and y has no effect on the result. This translates mathematically into the fact that the crossed second derivatives of the function F with respect to x and y are equal.

$$\frac{\partial^2 F}{\partial x \partial y} = \frac{\partial^2 F}{\partial y \partial x}$$

Application example: *(case of a perfect gas)*

Consider a perfect gas whose state is given by its temperature ***T*** and pressure ***P.*** To carryout a transformation, the pressure or temperature of the gas is varied from initial values ***Ti*** and ***Pi*** to final values $\boldsymbol{T_f}$ and $\boldsymbol{P_f}$ **.**

The quantity of matter is considered constant

Volume case

The equation of state for the perfect gas gives us an explicit expression for the volume as a function of these two parameters:

Volume therefore appears as a state function. From this expression, we can calculate the change in volume of the gas during the transformation from the initial to the final state:

$$\mathrm{V(T,P)} = \frac{nRT}{P}$$

$$\Delta V = V_f - V_I = nR\left[\frac{T_f}{P_f} - \frac{T_i}{P_i}\right]$$

2. The Zeroth Law of Thermodynamics

The same variation can be verified by following two different transformation paths. For the first path, we vary the pressure from P_i to P_f, keeping the temperature constant and equal to Ti , then we vary the temperature from T_i to T_f, keeping the pressure constant and equal to P_f , then vice versa.

In the second path, we proceed in the same way, but vary the temperature before the pressure.

For a small infinitesimal variation in pressure and temperature, we can write :

$$dV = \left(\frac{\partial V}{\partial T}\right) dT + \left(\frac{\partial V}{\partial P}\right) dP$$

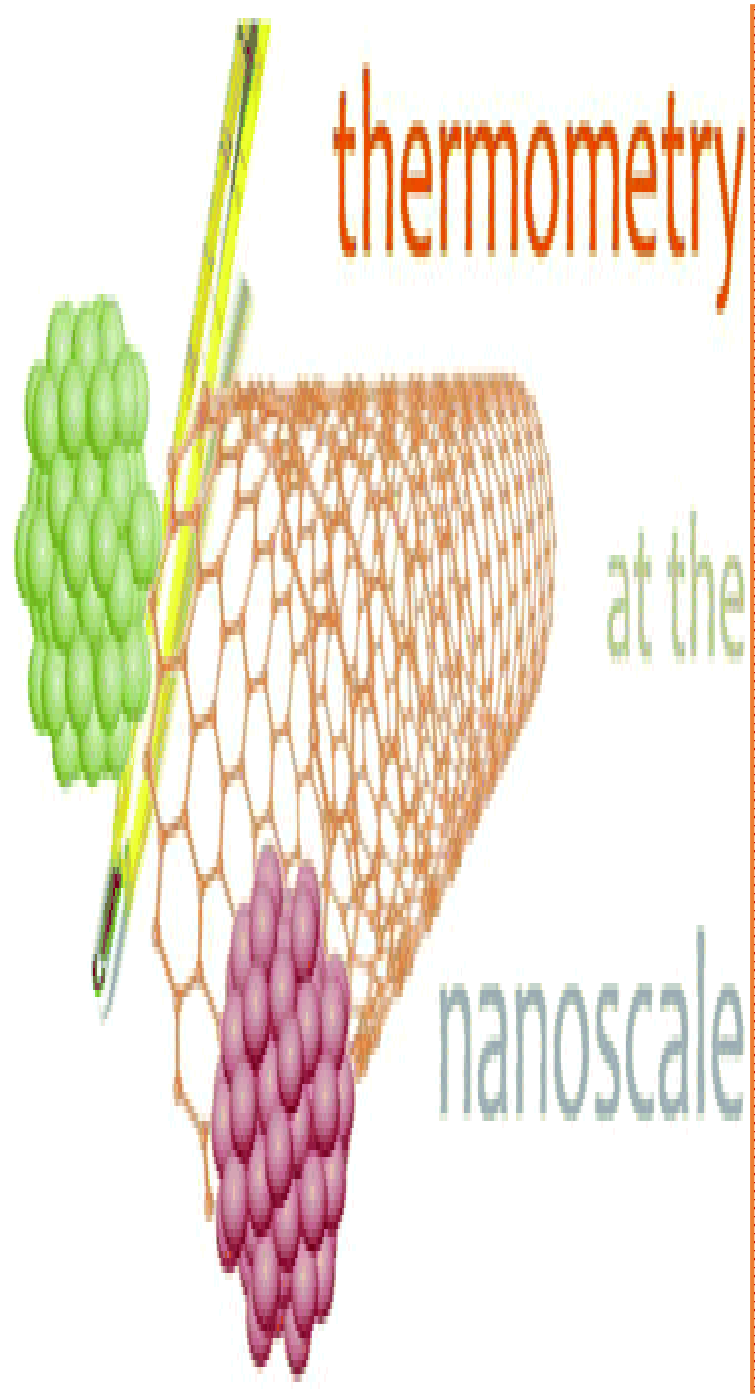
Using the equation of state :

$$dV = \left(\frac{nR}{P}\right) dT + \left(\frac{nRT}{P^2}\right) dP$$

Law 1 — The zeroth law of Thermodynamics. If A, B and C are different thermodynamical systems and A is in thermodynamical equilibrium with B and B is in thermodynamical equilibrium with C, then A is in thermodynamical equilibrium with C.

2. The Zeroth Law of Thermodynamics

3.Thermometry



Course contents

- Temperature
- Scale of temperature
- Temperature measurement
- Liquid Thermometer
- Gas Thermometers
- Electrical Resistance Thermometer
- Platinum Resistance Thermometer
- Construction Of Platinum Resistance Thermometer

3.Thermometry

Thermometry is the science and practice of temperature measurement. Any measurable change in a thermometric probe (e.g. the dilatation of a liquid in a capillary tube, variation of the electrical resistance of a conductor, of the refractive index in a transparent material, and so on). Can be used to mark temperature levels that should later be calibrated against an internationally agreed unit if the measure is to be related to other thermodynamic variables (if the measure is only needed to establish an ordering in thermal levels, no calibration is required).

Thermometry is sometimes split in metrological studies in two subfields: contact thermometry and non- contact thermometry. Thermometers measure their own temperature, not that of the surroundings except if in thermal equilibrium. As there can never be complete thermal uniformity at large, thermometry is always associated to a heat transfer problem with some space-time coordinates of measurement, given rise to time-series plots and temperature maps (profiles, if one-dimensional).

3.1 Temperature

Measure of hotness or coldness expressed in terms of any of several arbitrary scales and indicating the direction in which heat energy will spontaneously flow, from a hotter body (one at a higher temperature) to a colder body (one at a lower temperature). Temperature is not the equivalent of the energy of a thermodynamic system; a burning match is at a much higher temperature than an iceberg, but the total heat energy contained in an iceberg is much greater than the energy contained in a match. Temperature, similar to pressure or density, is called an intensive property—one that is independent of the quantity of matter being considered—as distinguished from extensive properties, such as mass or volume.

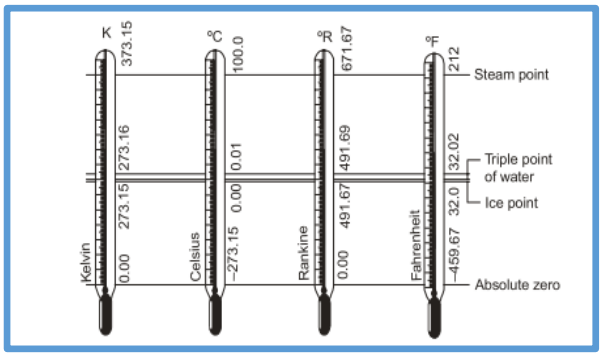


Fig.3.1 Different temperature scales

3.Thermometry

3.2 Scale of temperature

Is a methodology of calibrating the physical quantity temperature in metrology. Empirical scales measure temperature in relation to convenient and stable parameters or **reference points**, such as the freezing and boiling point of water. Absolute temperature is based on thermodynamic principles: using the lowest possible temperature as the zero point, and selecting a convenient incremental unit.Celsius, Kelvin, and Fahrenheit are common **temperature scales**. Other scales used throughout history include Rankine, Rømer, Newton, Delisle, Réaumur, Gas mark, Leiden, and Wedgwood.

3.2.1 Temperature Scales

❖ Celsius Scale (°C)

Defined by Anders Celsius in 1742.

0°C corresponds to the melting point of ice, and 100°C to the boiling point of water at atmospheric pressure.

- On the Celsius scale, the lower fixed point is the temperature of melting pure ice, also known as the ice point. The ice point is fixed at 0^0C.
- The upper fixed point is the temperature of the steam just above boiling water and is known as the steam point.

* The steam points is 100^0C. We can then divide the temperature range between the two fixed points into number of equal parts called degrees.

Absolute zero is the lowest temperature possible, it -273^0C or 0 K (Kelvin).

* On the kelvin scale or the absolute scale, one division is called the kelvin and is exaxtly equal to one division or degree on the Celsius scale.

*To convert degree celcius to kelvin, use the following equation

3.Thermometry

❖ **Kelvin scale (K):**

Absolute temperature scale where **θ K = -273.15°C. T(K) = t(°C) +273.15**

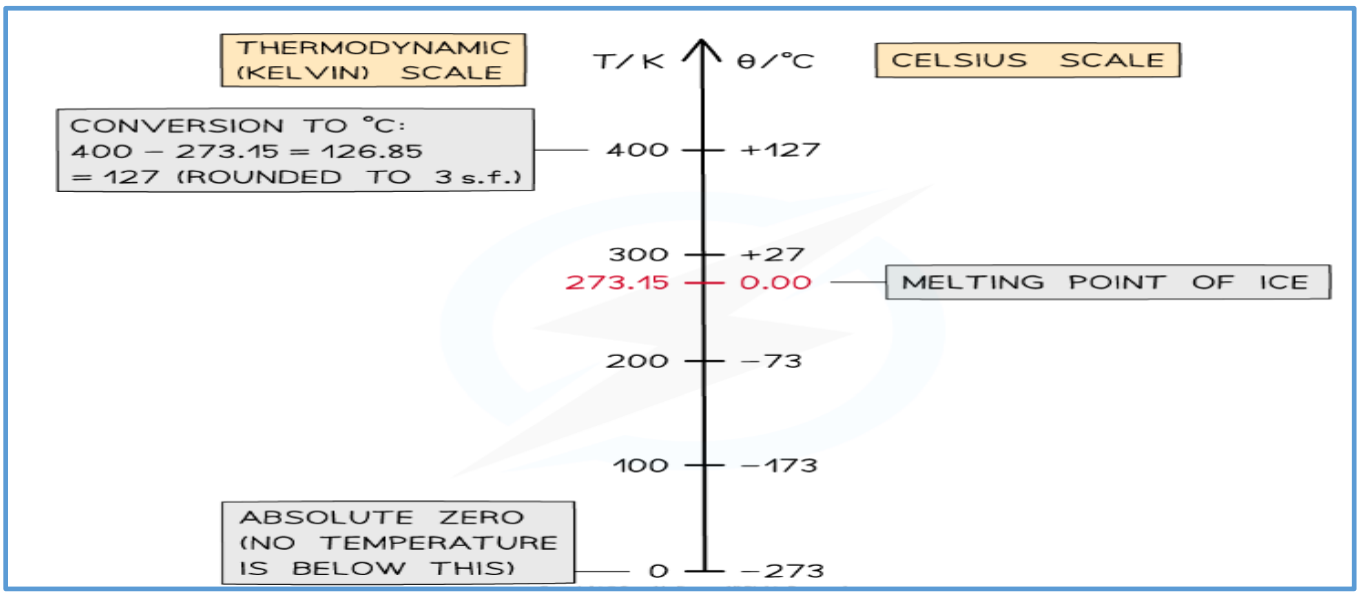


Fig 3.2 Conversion chart relating the temperature on the Kelvin and Celsius scales

❖ **Fahrenheit Scale (°F)**

The Fahrenheit scale sets 32°F as the freezing point of water and 212°F as the boiling point, creating a span of 180°F between the two. This means that each degree Celsius equals 1.8 degrees Fahrenheit. There are several stories about how Daniel Fahrenheit developed the scale.

Here's a breakdown of key reference points on the Fahrenheit scale:

- 32°F: The freezing point of pure water.
- 212°F: The boiling point of pure water under standard atmospheric pressure.
- 98.6°F: The approximate average human body temperature.
- 0°F: Originally based on the freezing point of a specific saltwater solution, a mixture of ice, water, and ammonium chloride, which Fahrenheit considered the lowest attainable temperature at the time. Fahrenheit chose these reference points and divisions for his scale based on early temperature measurement techniques and his desire for a scale with finer divisions than existing ones.

3.Thermometry

- The salt water solution provided a reliable low point, and he initially aimed for 100 degrees as the human body temperature, which was later refined.

  Defined by Gabriel Fahrenheit in 1724. 32°F corresponds to ice melting, and 212°F to water boiling.

  Conversion: **θ°F = 1.8 × t(°C) + 32**

Échelle	°C	°F	K
Zéro absolu	-273,15	-459,67	0
Fusion	0	+32	+273,15
Ébullition	+100	+212	+373.15

  $$T(K) = t(°C) + 273{,}15$$

  $$T(K) = \frac{5}{9}\left(t(°F) + 459{,}67\right)$$

À partir de :	Kelvin	Celsius	Fahrenheit	Rankine	Réaumur
$T_{Kelvin} =$	T_K	$T_C + 273{,}15$	$\frac{5}{9}(T_F + 459{,}67)$	$\frac{5}{9}T_{Ra}$	$\frac{5}{4}T_{Re} + 273{,}15$
$T_{Celsius} =$	$T_K - 273{,}15$	T_C	$\frac{5}{9}(T_F - 32)$.	$\frac{5}{9}(T_{Ra} - 491{,}67)$	$\frac{5}{4}T_{Re}$
$T_{Fahrenheit} =$	$\frac{9}{5}T_K - 459{,}67$	$\frac{9}{5}T_C + 32$	T_F	$T_{Ra} - 459{,}67$	$\frac{9}{4}T_{Re} + 32$
$T_{Rankine} =$	$\frac{9}{5}T_K$	$\frac{9}{5}T_C + 491{,}67$	$T_F + 459{,}67$	T_{Ra}	$\frac{9}{4}T_{Re} + 491{,}67$
$T_{Reaumur} =$	$\frac{4}{5}(T_K - 273{,}15)$	$\frac{4}{5}T_C$	$\frac{4}{9}(T_F - 32)$	$\frac{4}{9}(T_{Ra} - 491{,}67)$	T_{Re}

Table 3.1 of temperature conversions between different scales

3.3. Temperature measurement

For measurement of temperature number of thermometers are available using different thermometric properties of the thermometric substances. Length, volume, pressure, resistance, e.m.f. etc. are the commonly used thermometric properties for thermometers. Different thermometers developed using these thermometric properties are given below.

3.3.1 Liquid Thermometer

Liquid thermometers are those thermometers that employ liquids as the thermometric substance and the change in volume of liquid with heat interaction is the characteristics used for temperature measurement. Commonly used liquids in such thermometers are Mercury and Alcohol. Fig. 2.3 shows the mercury in glass thermometer. In this the change in volume of the mercury results in the rise or fall in the level of mercury column in the glass tube. Out of the two liquids mercury is preferred over alcohol as it has low

specific heat and hence absorbs little heat from body. Mercury is comparatively a good conductor of heat. Mercury can be seen in a fine capillary tube conveniently. Mercury does not wet the wall of the tube. Mercury has a uniform coefficient of expansion over a wide range of temperature and remains liquid over a large range as its freezing and boiling points are –39ºC and 357°C respectively.

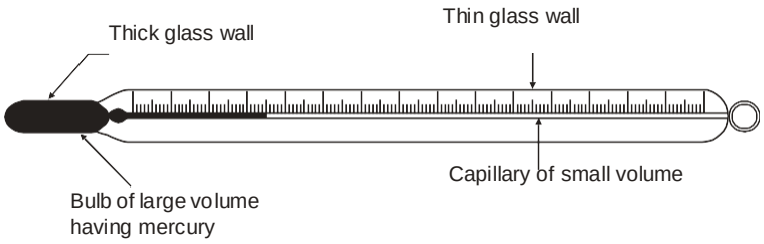


Fig. 3.3 Mercury in glass thermometer

3.3.2 Gas Thermometers

Thermometers using gaseous thermometric substance are called gas thermometers. Gas thermometers are advantageous over the liquid thermometers as the coefficient of expansion of gases is more compared to liquids therefore these are more sensitive. Also thermal capacity of a gas is low compared to liquid so even a small change can also be recorded accurately. Gas thermometers are not suitable for routine work as they are large, cumbersome and can be used only in certain fixed conditions. These are used mainly for calibration and standardization purpose. Main types of gas thermometers are discussed ahead.

3.3.3. Electrical resistance thermometer

Electrical resistance thermometer first eveloped by Siemen in 1871, also known as 'Platinum Resistance Thermometer' works on the principle of change in resistance of the thermometric substance (platinum) with temperature. Thus resistance is the thermometric property used in these thermometers. It consists of a pure platinum wire wound in a double spiral on a mica plate. Two ends of the platinum wire are connected to the copper leads (for low temperatures) or platinum leads (for high temperatures). Principle of Wheatston bridge is employed in these thermometers, as shown in Fig. 2.6. It has a set of compensating leads having exactly similar resistance as leads used. Platinum wire and the compensating leads are enclosed in a sealed glazed porcelain tube having binding terminals at the top. The resistance of wire can be mathematically related as

$$R_t = R_0 \cdot (1 + a \cdot t + b \cdot t^2)$$

where *a* and *b* are the constants having their values depending upon the nature of material used.

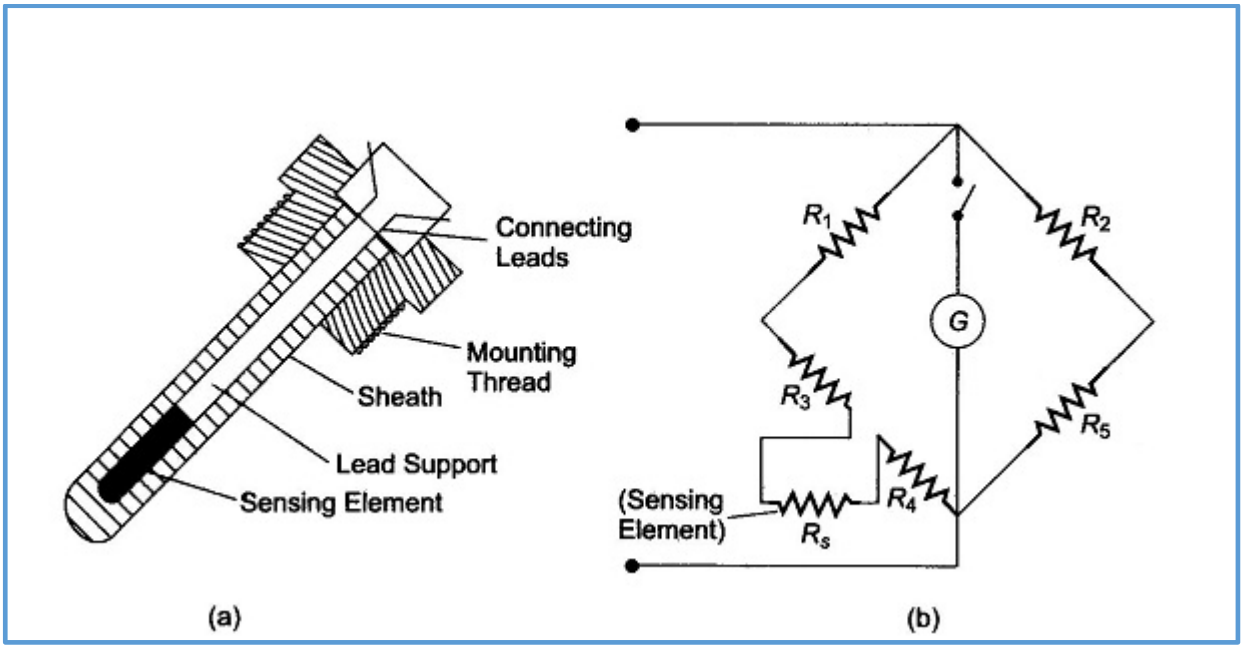


Fig 3.4. *Electrical resistance thermometer*(principle of wheatstone bridge)

3.3.4 Platinum Resistance Thermometer

Definition: The platinum thermal resistance (PTR) uses platinum for determining the temperature. It works on the principle that the resistance of platinum changes with the change of temperature. The thermometer measures the temperature over the range of 200℃ to1200°C. The platinum is an unreactive metal and can easily be drawn into fine wires. Because of these properties of platinum, it is used as a sensing element in thermometer.

How Platinum Resistance Thermometer Works?

The resistance of platinum increases linearly with the temperature, and this property of the metal is used for measuring the temperature. The resistance of the platinum is measured by passing the alternating or direct current through it. Because of the current, the voltage induces across the metal which measures through the voltmeter. The reading of voltage is converted into the temperature with the help of the calibration equation.

3.3.5 Construction of Platinum Resistance Thermometer

The figure 4 below shows the platinum resistance thermometer. The platinum sensing coil is enclosed inside a bulb which is either made of glass or Pyrex. The insulator deposit on the surface of the glass tube is also used for sensing the temperature.

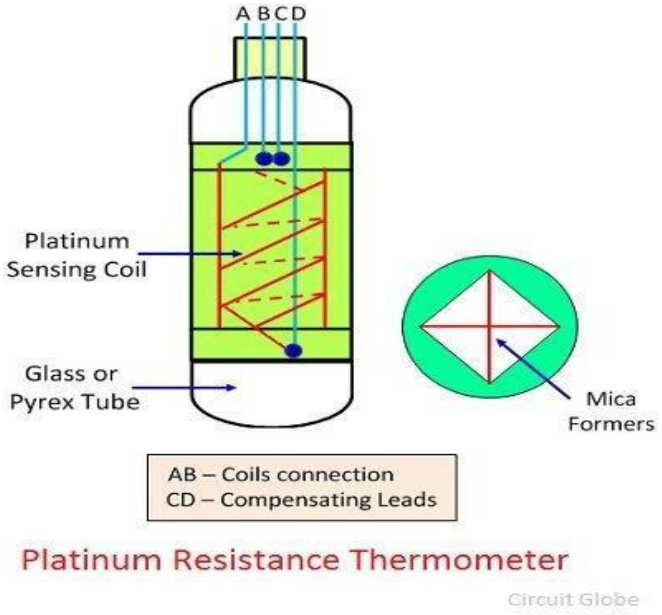


Fig. 3.5. Platinum resistance Thermometer

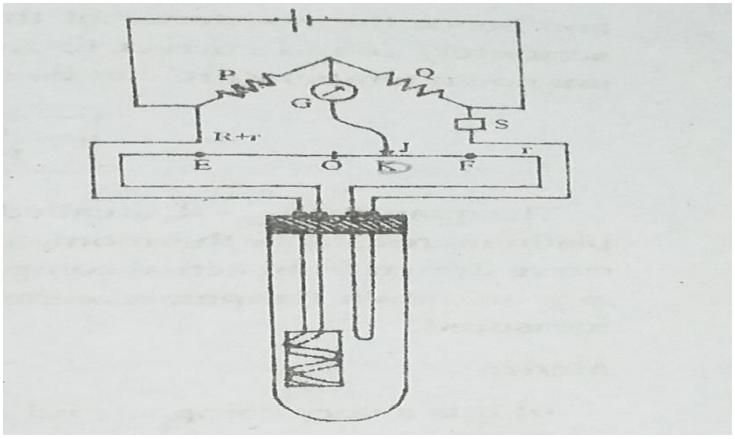


Fig. 3.6. Circuit diagram of PRT

In this PTR, the double wire of the platinum is wound on the strip of the mica. Here the double wires are used for reducing the inductive effect. The mica is used as an insulator, and it is placed at the ends of the tube.

The Ebonite cap is placed at the open end of the tube. The terminals of the copper wire are joined together with the help of the thick copper lead. The other ends of the copper leads are joined to the terminal AB fitted in the Ebonite cap. For reducing the effect of copper wire resistance on the thermometer, the two similar copper wires are connected to the upper- end terminals called CD. These wires are called the compensating lead.

The industrial type thermometer is shown in the figure 6 below. The platinum wire is protected by the stainless steel tube or by the glass coating. Glass or ceramic seal are the sensing elements. The sealing has two advantages. They provide the strength to the thermometer and protect the sensing element against the chemical reaction.

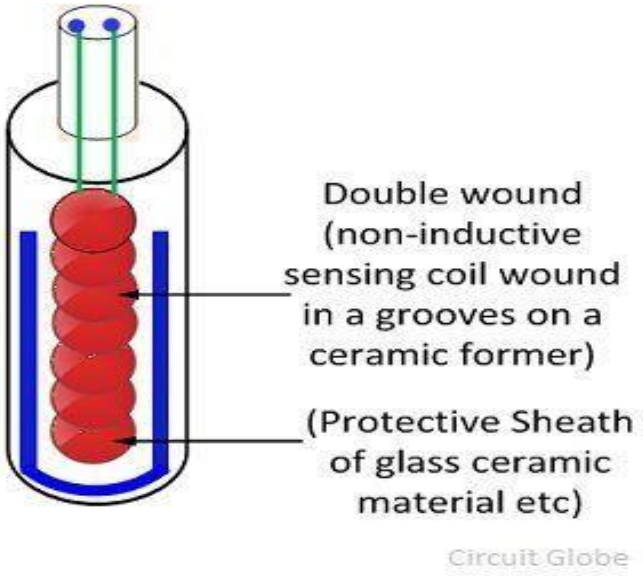


Fig3. 6. Industrial type thermometer

5.4.Advantages of Platinum Resistance Thermometer

The temperature measurement through platinum resistance thermometer is easier as compared to the gas thermometer.

The meter gives the precise reading of temperature.

The thermometer has a wide range from 200 to 1200° Celsius.

The thermometer is quite sensitive.

The platinum has same resistance at the same temperature.

5.4.1Disadvantages of Platinum Resistance Thermometer

The following are the disadvantages of platinum thermal resistance.

The thermometer gives the slow response. The melting point of the thermometer is 1800° Celcius. But when platinum measures the temperature higher than 1200°C they start evaporating. When the thermometer constructed carefully, it provides the excellent sensitivity and high range of measurement.

Expression for R_t

P=Q (P, Q -Equal resistance in the ratio arms)

Resistance of the arm AD = Resistance of the arm CD

Balancing point D is to the right of O

$$\mathbf{Rt} + r + (l+x)\,\rho = S + r + (l-x)\,\rho$$

$$\mathbf{Rt} = S - 2x\rho$$

$\mathbf{R_t}$–resistance of the platinum wire

r – resistance of the compensating leads

2I – length of the wire EF

ρ - resistivity of the compensating leads.

Knowing $\mathbf{R_t}$, the temperature can be determined.

5.4.2 Expression for temperature of PRT

If we neglect the term βt^2

$$R_t = R_o(1+\alpha t)$$

If the resistance of platinum wire is R_0 at the ice-point, R_{100} at the steam-point and R_t at an unknown temperature t, then

$$R_{100} = R_o\,(1+\alpha 100),\quad R_t = R_o(1+\alpha t)$$

$$R_t - R_o = R_o \text{ and } R_{100} - R_o = 100R_o\alpha$$

$$or\ \frac{R_t - R_0}{R_{100} - R_0} = \frac{t}{100}$$

$$t = \left(\frac{R_t - R_0}{R_{100} - R_0}\right)100$$

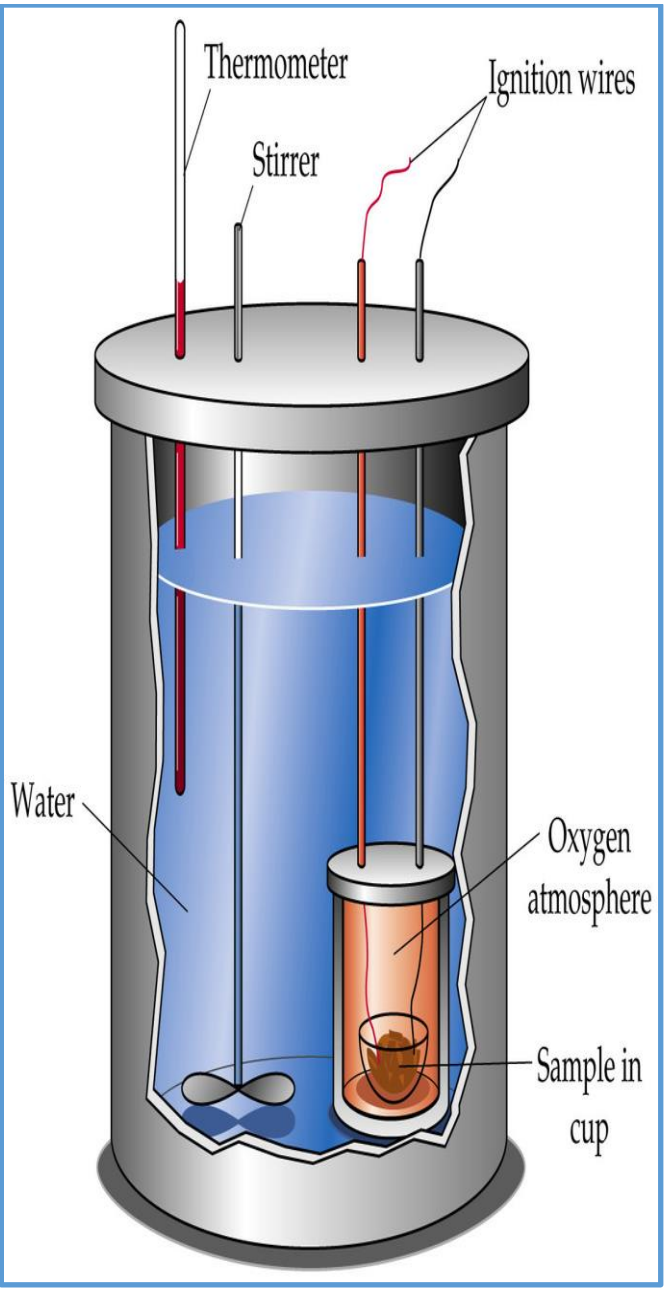
Knowing the values of R_0, R_{100} and R_t can be calculated.

The temperature on the platinum scale differs from the corresponding the temperature on the gas scale. Callendar showed that the difference between the temperature θ on the gas scale and the corresponding temperature t on the platinum scale is given by

$$\theta - t = \delta\theta - t = \delta\left(\left(\frac{\theta}{100}\right)^2 - \left(\frac{\theta}{100}\right)\right)$$

Here δ is a constant for platinum

4. Calorimetry



Course contents

- Calorimeter
- Heat Capacity
- Specific Heat Capacity
- Method Of Mixtures (Or) Law Of Heat Exchange
- Heat Capacity For Ideal Gases
- Latent Heat Of Change Of State (Lf, Lv,)
- phase Changes To A Less Energetic State Are As Follows

CALORIMETRY

4. Definition

Heat One technique we can use to measure the amount of heat involved in a chemical or physical process is known as Calorimetry.Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter).The measurement of heat transfer using this approach requires the definition of A system (the substance or substances undergoing the chemical or physical change) **Surroundings** (the region or spaces that either provides heat to the system or absorb heat from the system).

Knowledge of the **heat capacity of the systems**, and careful measurements of the masses of the system and surroundings and their temperatures before and after the process allows one to calculate the heat transferred as described in this section.

4.1Calorimeter

A **calorimeter** is a device used to measure the amount of heat involved in a chemical or physical process.

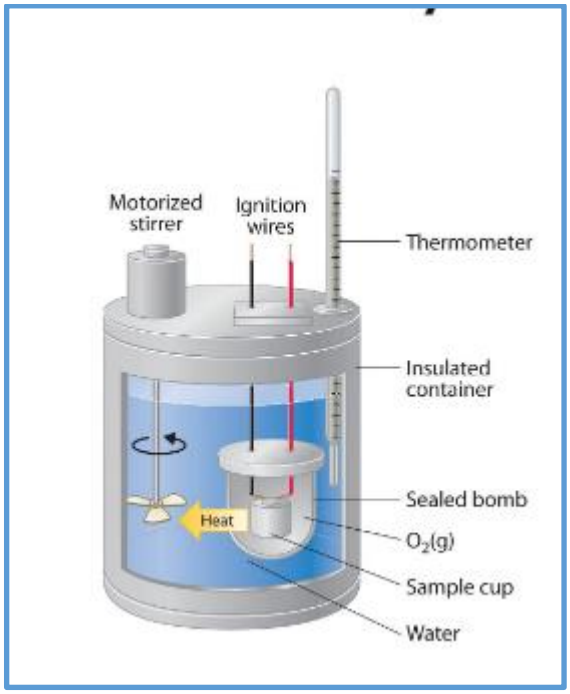


Fig. 4.1. Calorimeter

For example,

- When an **exothermic reaction** occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature.
- When an **endothermic reaction** occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature (Figure 1). The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.

In a calorimetric determination, either

- (a) an **exothermic** process occurs and heat, *Q*, is **negative**, indicating that thermal energy is transferred from the system to its surroundings, or
- (b) an **endothermic** process occurs and heat, *Q*, is **positive**, indicating that thermal energy is transferred from the surroundings to the system.

4.2 Heat Capacity

- It is actually the heat needed for a substance's temperature to change by one degree. This, therefore, shows that it is applicable to any type of matter. "Heat capacity" is the ratio of heat transfer "Q" to change in temperature "ΔT."
- In formulaic expression, it is **C = Q / ΔT.**
- In its SI unit notation, it uses units of energy / degree (energy per degree). C = **J / K.**

4.3 Specific Heat Capacity

- The specific heat is the amount of heat per unit mass required to raise the temperature by one degree Celsius.
- So, if the mass of the object whose specific heat capacity is calculated is m, the specific heat capacity is c, then the heat needed to raise the temperature of the system by θ is

$$Q = mc\theta$$

m = mass	(kg)
c = specific heat capacity	(J kg^{-1} $°C^{-1}$)
θ = temperature change	(°C)

4.4 Method of Mixtures (or) Law of Heat Exchange

- The Principle of Heat Exchange states that when two substances at different

temperatures are mixed,

The amount of heat lost by the HOT substance equals the amount of heat gained by the COOLER substance, assuming no heat is lost to the environment.

Example

The heat loss from the 100g of 80°C water is gained by the 100g of 20°C water resulting in a final temperature of 50°C.

Experiment to find Specific heat capacity-Solid

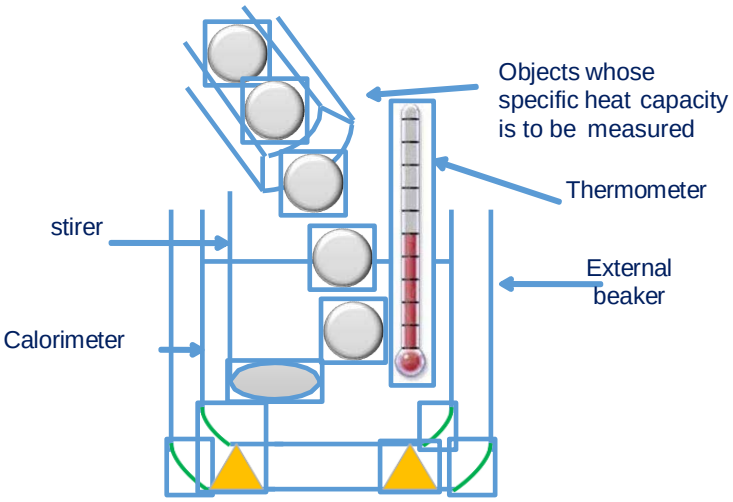


Fig. 4.2. Experimental setup

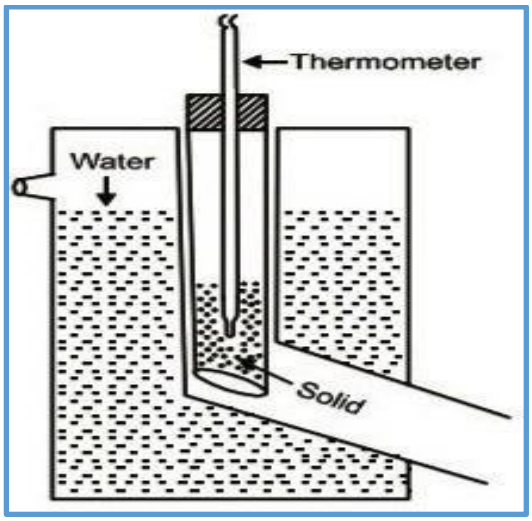


Fig. 4.3 . Heating arrangement

4. Calorimetry

•

At equilibrium, Heat lost Q is (m c θ) = Heat gained Q is (m c θ)

The specific heat of the substance is calculated with the help of the law of heat exchange

Procedure

- Measure the weight of the calorimeter and the stirrer (m_1).
- Pour water to the calorimeter so that water fills about ⅓ of the calorimeter's volume.
- Measure the weight of the calorimeter, the stirrer and water (m_2). So the weight of the water is (m_2-m_1).
- Measure the initial temperature of calorimeter stirrer and water (**θ_1**)
- Measure the total weight of the objects to be about thrice the weight of the total volume of water(m_3)
    - Heat the objects using a **Nicholson's heater** and record their initial temperature(**θ_2**).
- Introduce the objects to the calorimeter + water system and stir the objects.

Record the final temperature of the system (**θ**)

Theory

Let the mass of calorimeter + stirrer = m_1,

Mass of calorimeter + stirrer + water = m_2

Total mass of the objects = m_3

Initial temperature of the calorimeter + stirrer +water = θ_1

Initial temperature of the objects = θ_2 and

Final temperature of the system = θ

The specific heat capacity of the calorimeter = C,

The specific heat capacity of the water = C_W

The specific heat capacity of the objects = C_s.

According to the Principle of method of Mixtures,

Heat gained (Q) = Heat lost (Q)

Heat gained by calorimeter& stirrer = $m_1 C (\theta - \theta_1)$

Heat gained by water = $(m_2 - m_1) C_w (\theta - \theta_1)$

Heat lost by the hot object = $m_3 C_s (\theta_2 - \theta)$

Assuming that the heat loss to the environment as negligible,

Heat emitted by the objects = Heat gained by (water + calorimeter)

Therefore,

Thus, $m_3C_s(\theta_2 - \theta) = \{ m_1C(\theta - \theta_1) + (m_2 - m_1)C_W(\theta - \theta_1) \}$

$m_3C_s(\theta_2 - \theta) = \{ m_1C + (m_2 - m_1)C_W \}\{\theta - \theta_1\}$

$C_s = [\{ m_1C + (m_2 - m_1)C_W\}\{\theta - \theta_1\}] / [m_3(\theta_2 - \theta)]$ fixed so that te volume of the gas is constant.

Quantity of heat given to the gas =1*C_VdT=C_VdT

This quantity of heat is used in increasing the internal energy of the gas

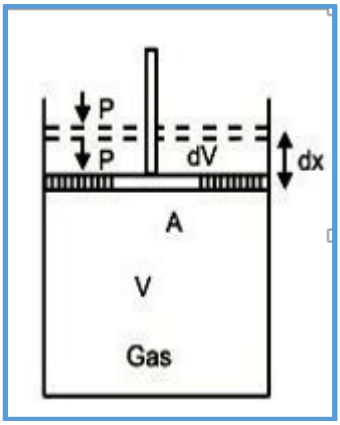


Fig. 4.4. Cylinder with piston

Let us suppose that the same gas is now given a certain amount of heat at constant pressure P so that the temperature increases by Dt. Since the gas is heated at constant pressure, the volume increases, the gas expands, Hence the piston moves up through a distance dx. Let dV be the increase in volume of the gas. Quantity of heat supplied to the gas= 1 * C_P dT = C_P dT

This quantity of heat supplied to the gas at constant pressure is used in two ways,

(i) In raising of heat supplied to the gas corresponding to a raise of temperature of dT.i.e., by C_v dt.

(ii) In doing the work of expanding the gas against the external pressure.

External work done by the gas in expansion

= Force * distance

=P_A * dx = PdV

Hence $Cp\ dT = C_V \cdot dT + R \cdot dT$

$$C_P = C_V + R$$

This formula is known as Mayer's formula.

R=8.31 J $mol^{-1}K^{-1}$. In SI units, R=8.314J $(kgmol)^{-1}$ K^{-1}

R is the universal gas constant.

4.5Heat capacity for ideal gases

- **Monoatomic ideal gases**

Examples **:** He, Ar, Ne...

$C_p=5/2nR$

$C_v=3/2$ nR

With:

n: number of moles.
R: ideal gas constant.

- **Diatomic ideal gases:**

Examples **:** O_2, N_2, H_2...

- C_P =7/2nR
- C_V =5/2 nR

4.6. Latent heat of change of state (Lf, Lv,)

The heat required to produce a phase *change* without causing temperature change in the system, is called *latent heat.*

Phase changes to a more energetic state include the following:

- Melting—Solid to liquid
- Vaporization—Liquid to gas (included boiling and evaporation)
- Sublimation—Solid to gas
- IonizationGas to plasma

4.6 Phase changes to a less energetic state are as follows

- Condensation—Gas to liquid
- Freezing—Liquid to solid
- Recombination—Plasma to gas
- DepositionGas to solid

The heat, Q, required to change the phase of a sample of mass m is

- $Q=mL_f$ (for melting/freezing),
- $Q=mL_v$ (for vaporization/condensation),

where L_f is the latent heat of fusion, and L_v is the latent heat of vaporization.

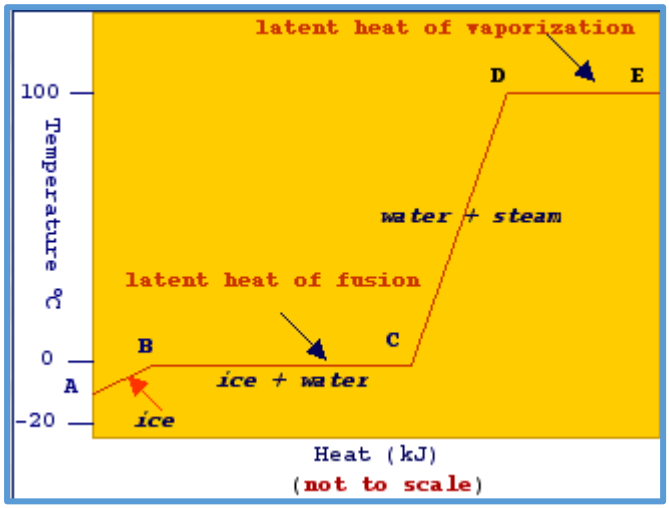
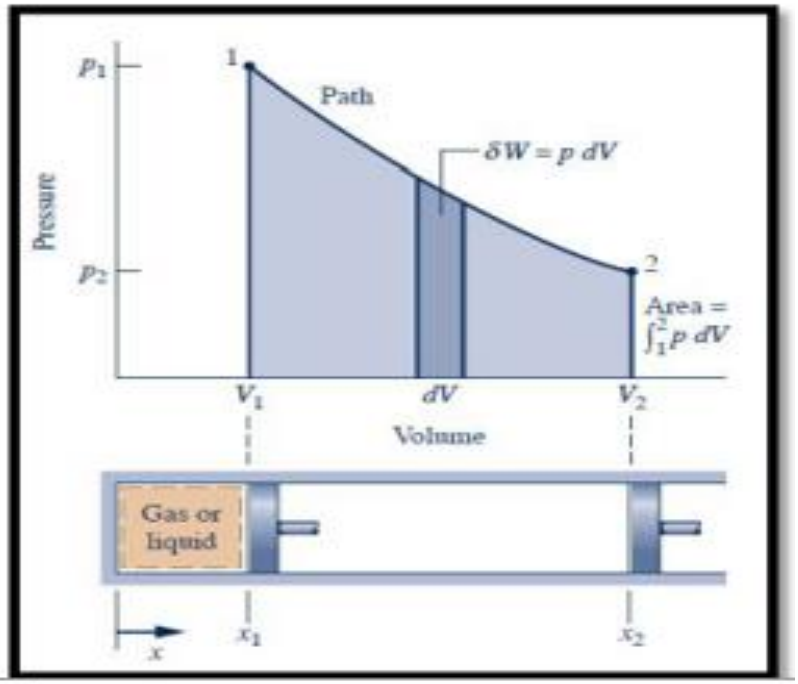


Fig 4.6 Phase changes to a less energetic state

4. Calorimetry

5. The first law of Thermodynamics



Course contents

- First Law of Thermodynamics
- Definition of work & heat
- Thermodynamic Processes And Calculation Of Work
- Constant pressure process or isobaric process
- Constant volume process or isochoric process
- Constant temperature process or isothermal process
- Adiabatic process
- Internal energy
- Thermochemical equations
- Pecific heats and their relation with internal energy and enthalpy
- Thermochemical equations

5.thermodynamics:conservation of energy

Benjamin Thompson (Count Runsford) 1753-1814 discovered the equivalence of work and heat in the course of manufacturing canon (1797) by boring solid metal submerged in the water. He was intrigued by the water boiling because of mechanical work of boring, as no heat had been added to the water. In his words, "is it possible that such a quantity of heat as would have caused five pounds of ice cold water to boil could have been furnished by so inconsiderable a quantity of metallic dust merely in consequence of a change in its capacity for heat. Other experiments later discovered more evidence until some fifty years after the above experiment.

James Prescott Joule (1818-1889) an English scientist and one time student assistant to John Dalton (1766-1844) with assistance from Lord Kelvin showed conclusively that mechanical work and heat are equivalent.

5.1 First Law of Thermodynamics

The first law of Thermodynamics The internal energy of an isolated system is conserved under any thermodynamical change. This is the macroscopic version of the familiar energy conservation law of physics. This law applies to an isolated system, i.e. according to our previous definitions to the total system constituted by the system plus its surroundings. In other words, whatever internal energy is gained by the system itself must be lost by its surroundings and vice-versa.We saw from the zeroth law that there are two kinds of energy that can be transferred between a thermodynamical system and its surroundings:

1. work, W , by mechanical contact
2. heat, Q, by thermal contact

This leads us to rewrite the first law for any thermodynamical system (i.e. not necessarily isolated), as:

The first law of Thermodynamics (differential form). Under an infinitesimally small thermodynamical change,

$$dU = dQ + dW$$

5.2 Definition of work & heat

According to the laws of mechanics, the infinitesimal amount of work one, when moving a macroscopic object against an opposing force, $\vec{F}$, is given by $\vec{dW} = \vec{F} * \vec{d}$, with $\vec{dh}$

the infinitesimal displacement of the object. In Thermodynamics, $\vec{F}$ is imparted by the system's surroundings and the macroscopic object is the separating wall (which can be set in motion if mechanical equilibrium is to be achieved). As pressure is force divided by surface area of the mobile wall, and displacement becomes volume when multiplied by this surface area, we obtain that

$$w_{1\to 2} = \int_{v1}^{v2} -pdV$$

As for heat, its preferred definition is from the first law of Thermodynamics and the definition of work:

Q = ΔU- W, i.e. whatever is left over when work is subtracted from the internal energy change of the system. It is always well defined, since ΔU and W are always well defined. It is also a practical definition: this is how you will calculate Q in thermodynamical problems!

Q and W are path dependent, U is not it depends only on the state of the system, not how the system got to that state. the change in state is accomplished by the energy interactions. If we assume the system to have the heat interaction ΔQ and work interaction ΔW, then from the basic principles it can be said that Energy lost = Energy gained

5.3.Thermodynamic Processes And Calculation Of Work

Thermodynamic processes can be precisely categorized as cyclic process and non-cyclic process. The cyclic process is the one in which the initial and final states are identical i.e. system returns to its initial states after occurrence of process. The non cyclic process is the one in which the initial and final states are different i.e. the occurrence of process is accompanied by the state change.

Let us consider a system consisting of a tank filled with water and fitted with a stirrer at room temperature, Fig. 3.1. Work can be transferred to the system by the stirrer and the temperature of water shall rise. When stirring stops, the system shall cool down till it reaches to the room temperature. Thus, the process is cyclic as the initial and final states are identical.

Let us now take a cylinder having piston and gas filled inside. If the gas is made to expand due to heating, the piston shall undergo displacement and say the piston displacement is *dx*. If the force exerted by gas on face of piston is *F* and the cross section area of piston is *A*, then the displacement work done may be given by:

$dW = F \cdot dh$

For the gas pressure being *p*, the force may be given by $F = A \cdot \mathrm{d}l$. Substituting for *F*, $dW = \mathrm{P}\, A \cdot \mathrm{d}l$

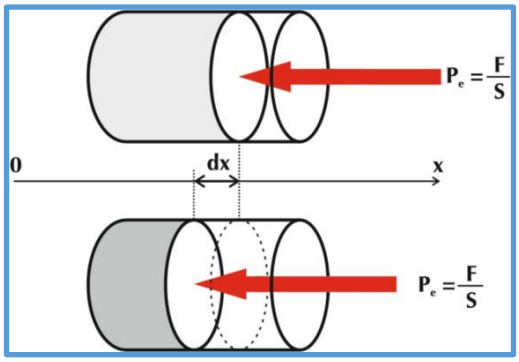


Fig 5.1 Concept of work

or, $dW = p \cdot dV$, where dV is the elemental change in volume or the volumetric displacement. If the total displacement of piston is given by L then the total work can be had by integrating the above dW with respect to x for displacement L, or with respect to volume for volume change.

$$W = \int_{x_1}^{x_2} \overrightarrow{F_{ext}} . \overrightarrow{dx} = \int_{x_1}^{x_2} P_{ext} \overrightarrow{S} . \overrightarrow{dx} = -\int_{V_1}^{V_2} P_{ext}\, dV_{gaz}$$

$$|W_{ext}| = \left| -\int_{V_1}^{V_2} P_{ext}{}^{dV} \right| > \left| -\int_{V_1}^{V_2} P_{int}{}^{dV} \right|$$

$$W_{ext \to syst} = -\int_{V_1}^{V_2} P_{ext}{}^{dV}$$

$$W = \int p \cdot dV = \int P * A dx$$

Now, let us examine whether the work estimated above is in conformity to thermodynamic definition of work or not. If the piston displacement is transferred to a suitable link then the weight can be raised, thus it satisfies thermodynamic definition of work. What about the nature of process? cyclic or non cyclic. It is obvious that the initial and final states are not identical therefore, it is a non-cyclic process. Thus, the work W as defined above refers to thermodynamic work for a non-cyclic process.Thermodynamic processes can be further classified based on the thermodynamic constraints under which they occur. Different types of thermodynamic processes are as detailed below.

5.3.1 Constant pressure process or isobaric process

It refers to the thermodynamic process in which there is no change in pressure during the process. Such type of processes are also known as isobaric processes. To understand let us take a cylindrical vessel having gas in it. It has a piston above it. Piston is free to reciprocate in the cylinder.

To understand let us take a cylindrical vessel having gas in it. It has a piston above it. Piston is free to reciprocate in the cylinder. Under normal situation piston shall be subjected to atmospheric pressure. Now, let heat be added to cylinder from bottom of cylinder. Due to heat addition, presuming energy transfer taking place reversibly and system always remaining in equilibrium, the gas shall try to expand. Expansion of gas results in raising up of the piston and it attains a new state say 2. Process is shown on *p*-*V* diagram in **Fig. 3.2**.

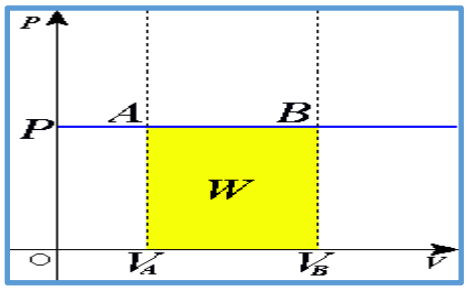


Fig. 5.2 Isobaric process

The work involved in the raising of piston shall be given by,

$$w_{1\to2} = \int_{v1}^{v2} pdV = p(V_2 - V_1)$$

Mathematically from the first law of thermodynamics, it can be given that,

$$\int_1^2 dQ = \int_1^2 dU + \int_1^2 dW$$
$$Q_{1\to2} = mc_P(T_2 - T_1) + p(V_2 - V_1)$$

$$Q_{1-2} = m\,c_v\,(T_2 - T_1) + P(V_2 - V_1)$$
$$= m\,c_v\,(T_2 - T_1) + mR(T_2 - T_1)$$
$$C_V = \frac{R}{(\gamma - 1)}$$
$$Q_{1\to2} = mR(T_2 - T_1)\left(\frac{1}{(\gamma - 1} + 1\right)$$

5.3.2 Constant volume process or isochoric process

When a fluid undergoes a thermodynamic process in a fixed enclosed space such that the process occurs at constant volume, then the process is called constant volume process or isochoric process. Let us consider heating of a gas in fixed enclosure at constant volume. On *p–V* diagram this process is represented by a vertical line as shown in Fig. 3.3. Area under the process line is zero which indicates that there is rise in pressure but there is no work done as there is no change in volume. Work involved shall be,

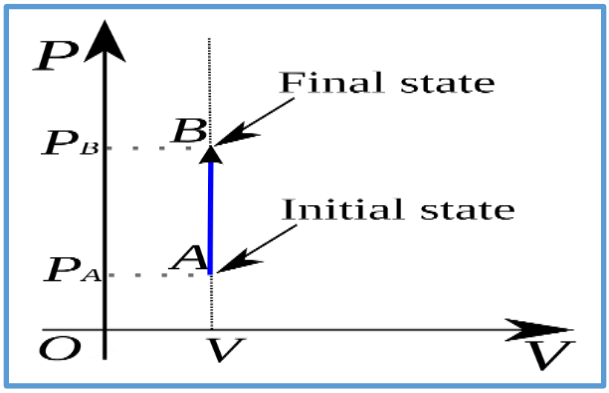


Fig. 5.3 Isochoric process

$$w_{1\to2} = \int_{v1}^{v2} -pdV$$

From first law of thermodynamics,

$$\mathrm{dU} = dQ + dW$$

$$\int_1^2 dQ = \int_1^2 dU - \int_1^2 dW = \int_1^2 dU + 0$$

$$Q_{1\to2} = U_2 - U_1 = mC_V(T_2 - T_1)$$

Thus, it indicates that the effect of heat addition in constant volume process is to increase the temperature and consequently the internal energy of system.

$$\int_1^2 dQ = \int_1^2 dU - \int_1^2 dW = \int_1^2 dU + 0$$

$$Q_{1\to2} = U_2 - U_1 = mC_V(T_2 - T_1)$$

5.3.3 Constant temperature process or isothermal process

Thermodynamic process in which the temperature remains constant is called constant temperature or isothermal process. In this case the gas or vapour may be heated at constant temperature and there shall be no change in internal energy. The work done will be equal to the amount of heat supplied, as shown ahead. For a perfect gas during isothermal process.

$$P_1V_1 = P_2V_2 = Constant, or, p = \frac{P_1V_1}{V}$$

So work involved

$$w_{1\to2} = \int_{v1}^{v2} pdV$$

$$w_{1\to2} = \int_{v1}^{v2} pdV = \int_{V1}^{V2} \frac{P_1V_1}{V} \mathrm{dV} = P_1V_1Ln(\frac{V_2}{V_1})$$

$$w_{1\to2} = P_1V_1Ln\, r$$

Where r= ration of final and initial volumes by first law of thermodynamics

$$\int_1^2 dQ = \int_1^2 dU - \int_1^2 dW = \int_1^2 dU + 0$$

$$\int_1^2 dQ = \int_1^2 dW - \int_1^2 dU$$

$$Q_{1\to2} = w_{1\to2} + (U_2 - U_1) = w_{1\to2} + 0$$

$$(U_2 - U_1) = m_{Cv}(T_2 - T_1)$$

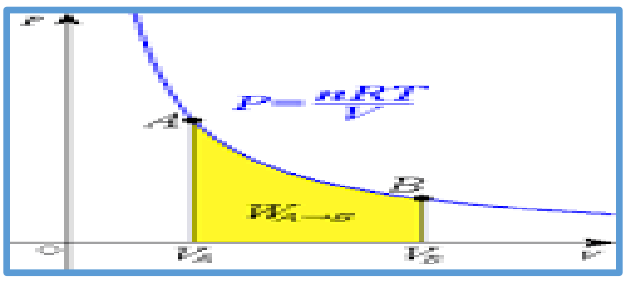


Fig. 5.4 isothermal process

5.3.4 Adiabatic process

An adiabatic process is the thermodynamic process in which there is no heat interaction during the process, i.e. during the process, $Q = 0$. In these processes the work interaction is there at the expense of internal energy. If we talk of adiabatic expansion then it shall mean that work is done at the cost of its own internal energy. The adiabatic process follows the law PV^{γ} = constant where γ is called adiabatic index and is given by the ratio of two specific heats. Thus, it is obvious that adiabatic expansion shall be accompanied by the fall in temperature while temperature will rise during adiabatic compression. The adiabatic expansion process is shown on Fig. 3.5. Work done during expansion shall be,

$$w_{1\to 2} = \int_{v1}^{v2} pdV$$

, where PV^{γ}= constant, therefore solving after substitution. Work shall be

$$W_{1\to 2} = \frac{P_1V_1 - P_2V_2}{(\gamma - 1)}$$

$$\int_1^2 dQ = \int_1^2 dU - \int_1^2 dW = \int_1^2 dU + 0$$

$$\int_1^2 dQ = \int_1^2 dW - \int_1^2 dU$$

$$Q_{1\to 2} = (U_2 - U_1) + \frac{P_1V_1 - P_2V_2}{(\gamma - 1)}$$

$$0 = m_{Cv}(T_2 - T_1) + \frac{P_1V_1 - P_2V_2}{(\gamma - 1)}$$

$$w_{1\to 2} = m_{Cv}(T_1 - T_2)$$

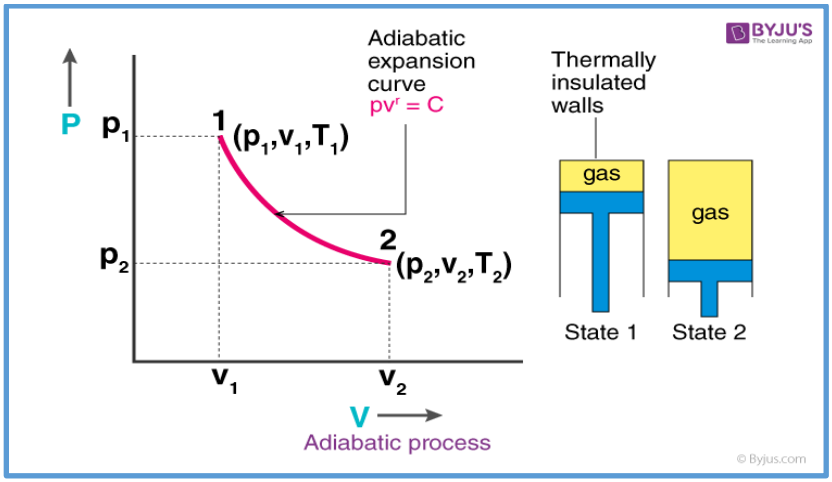


Fig. 5.4 Adiabatic process

5.4. Internal energy and enthalpy

Let us take a mass at certain elevation in earth's gravitational field and make it move with certain velocity. Energy considerations say that the mass shall have the potential energy (P.E = mgz) and kinetic energy (K.E = (1/2) mC^2) stored in it. Similarly, several other forms of energy such as due to magnetic, electrical, solid distortion and surface tension effects can be estimated as the contributory components of stored energy.

Difference of heat and work interactions yield the stored energy as given below; $E = Q + W$. If the energy at macroscopic level as discussed above could be separated from the total stored energy E, then the amount of energy left shall be called internal energy.

Mathematically,

Internal energy, U = (Stored energy) – (Kinetic energy) – (Potential energy) – (Magnetic energy) – (Electrical energy) – (Surface tension energy) – (Solid distortion energy).

Therefore, stored energy is summation of internal energy, potential energy, kinetic energy,

magnetic, electrical, surface tension, solid distortion etc. types of energy.

For the situation when magnetic, electric, surface tension, solid distortion effects are negligible, the stored energy shall be;

$$E = U + \text{KE} + \text{PE}$$

or, $$\text{E} = \text{U} + \frac{mC^2}{2} + \text{mgz}$$

$$e = u + \frac{C^2}{2} + gz$$

or, on unit mass basis; and the change in stored energy relative to some reference state shall be given as,

$$\Delta E = \Delta U + \Delta\text{KE} + \Delta\text{PE}.$$

Enthalpy (H) of a substance at any point is quantification of energy content in it, which could be given by summation of internal energy and flow energy. Enthalpy is very useful thermodynamic property for the analysis of engineering systems.

Mathematically, it is given as, $$\text{H} = \text{U} + \text{PV}$$

On unit mass basis, the specific enthalpy could be given as, $h = u + pv$

A look at expression of enthalpy shows that as we can't have absolute value of internal energy, the absolute value of enthalpy can not be obtained. Therefore only change in enthalpy of substance is considered. For certain frequently used substances such as steam, the enthalpy values of steam are available in tabulated form in Steam Tables at different thermodynamic states.

From the definition of enthalpy;

$$h = u + pv$$

or $$dh = du + p \cdot dv + v \cdot dp.$$

For a constant pressure process, $dp = 0$.

$$dh = du + pdv$$

or, $$dh = dq_p = \text{constt}$$ (From first law of thermodynamics)

5.4 Specific heats and their relation with internal energy and enthalpy

Specific heats of the substance refer to the amount of heat interaction required for causing unit change in temperature of the unit mass of substance. This unit change in temperature may be

realized under constant volume and constant pressure conditions separately. Therefore, the above heat value obtained with heat interaction occurring under constant volume conditions is called specific heat at constant volume, denoted as c_V. Whereas the above heat value obtained with heat interaction occurring under constant pressure conditions is called specific heat at constant pressure, denoted as c_p.

Mathematically, the heat interaction causing ΔT temperature change in m mass of substance can be given as, for isobaric conditions $Q_P = mC_p\Delta T$

$Q_V = mC_V\Delta T$ For isochoric conditions;

$$C_V = \left(\frac{Q_V}{\Delta T}\right)$$

$$C_P = \left(\frac{Q_P}{\Delta T}\right)$$

$$C_p = \left(\frac{dq}{dt}\right)_p = \left(\frac{dH}{dt}\right)_p$$

$$C_v = \left(\frac{dq}{dt}\right)_v = \left(\frac{dU}{dt}\right)_v$$

or,

For getting the specific heat values, substituting $m = 1$, $\Delta T = 1$,

$$Q_P = c_p \; and Q_V = \; c_v$$

The specific heat at constant volume can also be given as the partial derivative of internal energy with respect to temperature at constant volume.

$$C_V = \frac{1}{n}\left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P = \frac{1}{n}\left(\frac{\partial H}{\partial T}\right)_P$$

Thus

Also from first law of thermodynamics, on unit mass basis

$$dq = du + pdv$$

at constant volume, $dv = 0$

$$dq = du$$

or $$dq = c_v \cdot dT = du$$

$$\boxed{c_v = \frac{dq}{dT}}, \text{for } v = \text{constant}$$

Specific heat at constant pressure can be given as the partial derivative of enthalpy with respect to temperature at constant pressure.

From definition of enthalpy, at unit mass basis.

$$h = u + pv$$

or $$dh = du + pdv + vdp$$

at constant pressure, $dp = 0$

$$dh = du + pdv$$

substituting from first law of thermodynamics $dq = du + pdv$

$$dh = dq$$

or $$dq = c_p \cdot dT = dh$$

$$= \boxed{c_p = \frac{dq}{dT}}, \text{for } p = \text{constant}$$

Let us try to establish relationship between c_p and c_v.

From enthalpy definition, at unit mass basis

$$h = u + pv$$

or $$h = u + RT \text{ \{for ideal gas\}}$$

Taking partial derivative,

$$dh = du + RdT$$

Also we know for an ideal gas, c_p

$$dh = c_p \cdot dT;\ du = c_v \cdot dT$$

Substituting *dh* and *du*

$$Cp\ dT = C_v \cdot dT + R \cdot dT$$

or $$c_p = c_v + R$$

$$C_P - C_V = R$$

Difference of specific heats at constant pressure and volume is equal to the gas constant for an ideal gas. Also the ratio of specific heats at constant pressure and volume could be given as γ,

$\gamma = \frac{C_P}{C_V}$ Combining above two relations of c_p and c_v we get,

$$C_p = \frac{\gamma R}{(\gamma - 1)} \quad and\ C_v = \frac{R}{(\gamma - 1)}$$

5.5 Thermochemical equations

In thermochemistry, some features of ordinary chemical reactions are modified. The following examples and highlights differentiate between ordinary chemical equation and thermochemical equations:

i. In thermochemical reactions, the physical state of the reactant and the products must be indicated. For example

Ordinary chemical equation: $2\ H_2 + O_2 \rightarrow 2\ H_2O$

Thermochemical reaction: $2\ H_{2(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(l)}$

ii. The heat change accompanying the reaction must be indicated. For example,

Ordinary Chemical equation: $2\ H_2 + O_2 \rightarrow 2\ H_2O$

Thermochemical equation: $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$ $\Delta H = -572$ kJ

In the above thermochemical equation, the enthalpy change during the reaction is -572 kJ/mol. The negative sign of the enthalpy change indicates that the reaction is exothermic. If the sign of

the enthalpy change is positive (as in the equation below). It means that the reaction is endothermic:

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \quad \Delta H = 40.7 \text{ kJ}$$

In the first example, 572 kJ of heat is given off to the surrounding but in the second example,

40.7 kJ of heat is absorbed from the surrounding. The quantity 40.7 is known as the *enthalpy of vaporization* (often referred to as ‑heat of vaporization‖) of liquid water.

iii. If we multiply or divide the reactant by a factor, the product and the enthalpy change must also be multiplied by the same factor. For example, if we divide equation 4 by a factor of 2,we will have,

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H = -286 \text{ kJ}$$

iv. The standard states as well as properties involved in the reaction must be represented. For example,

$$H_2O(l, 373 \text{ K}, 1 \text{ atm}) \rightarrow H_2O(g, 373 \text{ K}, 1 \text{ atm}) \quad \Delta H^0 = 40.7 \text{ kJ mol}^{-1}$$

The above equation shows that the standard state of water at 1 atm is the solid below 273 K, the liquid between 273 and 373 K and the gas above 373 K. A thermochemical quantity such as ΔH that refers to reactants and products in their standard states is denoted by ΔH^0. The standard state of a substance is the most stable state of that substance. For example, hydrogen gas, oxygen gas and graphite are the most stable states of hydrogen, oxygen and carbon and these are their respective standard states. If the reaction is taking place in solution, the concentration of the dissolved species must be specified. For example, the neutralization of water

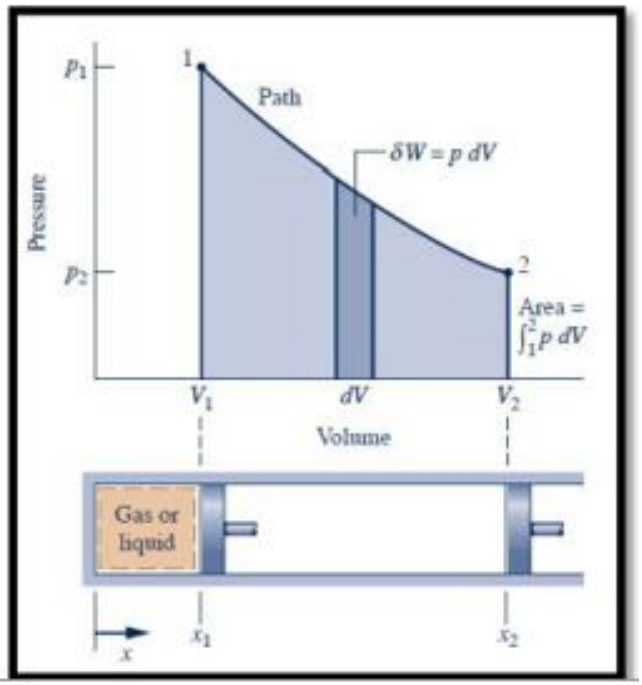
$$H^+(aq, 1M, 298 \text{ K}, 1 \text{ atm}) + OH^-(aq, 1M, 298 \text{ K}, 1 \text{ atm}) \rightarrow H_2O(l, 373 \text{ K}, 1 \text{ atm}) \quad \Delta H = -56.9 \text{ kJ mol}^{-1}$$

Generally, since most thermochemical equations take place at standard conditions. specification of temperature, pressure is not necessary, provided. Thus for the above reaction, we can represent is as,

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} \quad \Delta H^0 = -56.9 \text{ kJ mol}^{-1}$$

5. The first law of Thermodynamics

6. Enthalpies



Course contents

- Standard enthalpies of reactions
- Standard enthalpy of formation
- Laws of thermochemistry
- Bond enthalpy
- The Carnot cycle
- Limitations of first law of thermodynamics

6. Enthalpies

6. 1 Standard enthalpies of reactions

As stated earlier, the enthalpy change for a chemical reaction is the difference between the enthalpy of the product and that of the reactant, thus,

$$\Delta H = Hproducts - Hreactants$$

If the reaction under consideration is for the formation of one mole of the compound from its elements in their standard states, the enthalpies of the elements can be set at zero and the heat of formation will become, $H_f° = \Sigma H_f°_{products} - \Sigma H_f°_{reactants}$.

For example, in the following reaction,

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

$$H_f° = \Sigma H_f°_{products} - \Sigma H_f°_{reactants} = -582 - 0 = -586\ kJ,$$

which defines the *standard enthalpy of formation* of water at 298K.The value $H_f° = -586$ kJ tells us that when hydrogen and oxygen, at a pressure of 1 atm (respectively) and at 298 K react to form 1 mol of liquid water at 25℃ and 1 atm pressure, 586 kJ will be given out to the surrounding. The negative sign indicates that the reaction is exothermic and that the enthalpy of the product is smaller than that of the reactants. Therefore, the standard enthalpy of formation ofa compound is defined as the heat associated with the formation of one mole of the compound from its elements in their standard states. In general, the *standard enthalpy change for a reaction*is given by $\Delta\Sigma H_f°_{products} - \Sigma H_f°_{reactants}$. where $\Delta\Sigma H_f°_{products}$ and $\Sigma H_f°_{reactants}$ are the sum of thestandard enthalpies of formations of all products and reactants reapectively. This definition allows us to predict the enthalpy change of any reaction once the standard enthalpies of formation of the products and reactants are known.

6.2 Standard enthalpy of formation

Standard enthalpy of formation is the enthalpy change associated with the formation of one mole of the substance at standard temperature and pressure. In estimating the enthalpy of formation, the following information must be taken into consideration.

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i. The thermochemical equation defining standard enthalpy of formation must be written in terms of one mole of the substance in question. For example,

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \quad \Delta H° = -92.2$ kJ

The above equation shows that 1 mol of N_2 gas react with 2 mol of H_2 gas to form 2 mol of ammonia in an exothermic reaction, liberating 92.2 kJ of heat. This enthalpy change does not represent the standard enthalpy change since it is not the enthalpy change associated with the formation of 1 mol of ammonia. In order to write the thermochemical equation that shows the standard enthalpy change for the formation of ammonia, we divide the entire equation by a factor of 2, thus

$$\tfrac{1}{2}\, N_2(g) + 3/2\, H_2(g) \rightarrow NH_3(g) \quad \Delta H° = -46.1 \text{ kJ (per mole of } NH_3)$$

ii. The standard heat of formation of a compound should be considered based on the most stable form of the compound at 237 K and at 1 atmospheric pressure. This means for elements that exhibit allotropy, the most stable allotrope should be considered when defining standard enthalpy of formation of a compound involving such elements. For example, carbon can exist as diamond or graphite and the formation of CO_2 from each of these allotropes leads to the release of -393.5 and 395.8 kJ/mol of heat respectively (as shown in the equations below). However, since graphite is the most stable allotrope, the standard heat of formation of CO_2 will refer to the reaction involving graphite and not diamond

$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H° \equiv H_f° = -393.5 \text{ kJ mol}^{-1}$

$C_{(diamond)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H° = -395.8 \text{ kJ mol}^{-1}$

iii. If the product is not the stable one at 273 K, the physical state of the product must be indicated in the thermochemical equation representing standard enthalpy change. For example, water exists in gaseous and liquid states and the enthalpy changes for the two states are as shown in the equations below. However, the one associated with water in the aqueous phase is normally taken for standard enthalpy change.

$H_{2(g)} + \tfrac{1}{2}\, O_{2(g)} \rightarrow H_2O_{(aq)} \quad \Delta H° \equiv H_f° = -285.8 \text{ kJ mol}^{-1}$

$H_{2(g)} + \tfrac{1}{2}\, O_{2(g)} \rightarrow H_2O_{(g)} \quad \Delta H° = -241.8 \text{ kJ mol}^{-1}$

It is significant to note that the differences in enthalpy value between the two states is -44 kJ/mol and this represents the heat of vaporization of water.

iv. The standard enthalpy change for the formation of most compounds are negative (i.e exothermic) but there are cases where the enthalpy change is positive. By convention, such endothermic process is expected to represent instability but there are some endothermic compounds that are stable.

6.3 Laws of thermochemistry

Thermochemistry is based on the framework of two major laws, namely: Hess law and Laplace law. These laws are essential because they aid in thermochemical calculations.

The first thermochemical law was formulated by Hess in 1840. Germain Henri Hess (1802-1850) was a Swiss-born professor of chemistry at St. Petersburg, Russia. This principle, known as *Hess' law of independent heat summation* is a direct consequence of the enthalpy being a state

v. Thermochemical equations representing the enthalpy change of the formation of some compounds may not be feasible. For example, direct reaction of graphite (carbon) with hydrogen gas, does not give methane as simplified in the equation below:

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

vi. The standard enthalpy change associated with the formation of gaseous atom from the element is called heat of atomization. Heats of atomization are always positive and they are very useful in the calculation of bond energies.

vii. The standard enthalpy of formation of ions dissolved in water cannot be measured because this solution has several kinds of ions dissolved in it. Therefore, the general conventionis to adopt a scale in which the enthalpy change of the $H^+_{(aq)}$ is defined as zero. Therefore ionic enthalpies are expressed such that $H_f°$ of the hydrogen ion at *unit activity* (1 M effective concentration) is defined as zero, as shown in the equation below,

$$\tfrac{1}{2}H_{2(g)} \rightarrow H^+_{(aq)} \quad \Delta H° \equiv H_f° = 0 \text{ kJ mol}^{-1}$$

6. Enthalpies

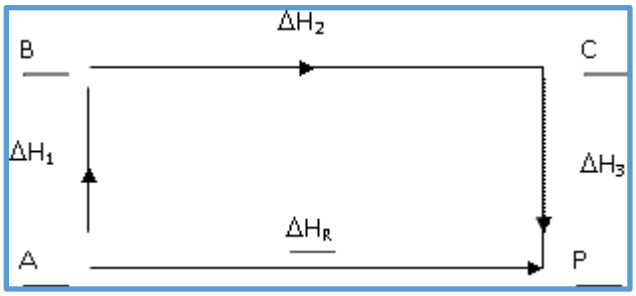
Based on this, the enthalpy of formation of other ionic compounds can be calculated by combining it with the above equation. For example, in the formation of HCl, H_2 gas combine with Cl_2 gas as shown below:

$$\tfrac{1}{2}H_{2(g)} + \tfrac{1}{2}Cl_{2(g)} \rightarrow HCl_{(aq)} \qquad \Delta H^\circ \equiv H_f^\circ = -167 \text{ kJ mol}$$

Since the enthalpy for the formation of $H^+_{(aq)}$ is zero, the enthalpy for the formation of HCl is -167 kJ/mol.

function. Hess' law is one of the most powerful tools of chemistry. It allows the change in the enthalpy (and in other thermodynamic functions) of huge numbers of chemical reactions to be predicted from experimental data. ***Hess law states that the overall enthalpy of a chemical reaction is the sum of the enthalpies of the various steps into which the reaction can be subdivided***.

Let us consider a chemical reaction leading to the formation of a product C and the enthalpy of reaction is ΔH_R. If the different steps that bring about the product are A to B, B to C and C to P, characterised with enthalpies, ΔH_1, ΔH_2 and ΔH_3. Then according to Hess law, $\Delta H_R = \Delta H_1 + \Delta H_2 + \Delta H_3$. This concept is demonstrated in the diagram shown below



6.4 Bond enthalpy

Chemical bonds hold compounds together. This maybe electrovalent or covalent. Most often, the reactants have their individual bonds associated with it. Therefore, before they can react, bonds have to be broken and before products formation, new bonds must be formed Bonds are broken in the reactants while new bonds are formed in the products. Bond enthalpy is the energy needed to break bond in gaseous molecules under standard condition. Due to some complications that may arise in using actual values of bond enthalpy, average bond enthalpies are often used. For example, water consists of two OH bonds and it has been found that the energy needed to break the first O-H bond is significantly higher than the energy needed to break the second O-H bond. Also, the energy needed to break OH bond in molecule such as ethanol is quite different from theenergy needed to break the O-H bond in water and other molecules. Hence the use of average bond enthalpy is justified.

Let us consider the bond enthalpy associated with the breaking of H and O bonds in water and hydroxyl.

$$H_2O_{(g)} \rightarrow H_{(g)} + OH_{(g)} \quad \Delta H^0 + 502\ kJ/mol$$

$$OH_{(g)} \rightarrow H_{(g)} + O_{(g)} \quad \Delta H^0 + 427\ kJ/mol$$

$$H_{2(g)} \rightarrow H_{(g)} + H_{(g)} + O_{(g)} \quad \Delta H^0 \ (502 + 427)\ kJ/mol \qquad = 929\ kJ/mol$$

Therefore, the average bond enthalpy for O-H is 929/2 = 464.50 kJ/mol. The average bond enthalpies and the corresponding bond lengths for some bonds are presented in the Table 2. All bond energies are obtained in the gaseous state so that the enthalpy change associated with the breaking and formation of intermolecular force can be eliminated.

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Bond breaking is an exothermic process while the formation of new bond is an endothermic process. The amount of energy absorbed during the formation of bond is the same as the amount of energy liberated during the breaking of bond. This is the consequence of the second law of thermochemistry (i.e Laplace law), which states that the enthalpy change needed for the formation of a compound is the same as the enthalpy change (but with reverse sign) needed for the decomposition of the compound.

In the course of breaking bonds in the reactants and the formation of new bonds in the products the difference between the bond energies of the reactants and that of the products represents the enthalpy change of the reaction. That is,

$$H = \sum(bond\ breaking\ energies) - \sum(bond\ forming\ energies)$$

Therefore, when $\sum(bond\ breaking\ energies) > \sum(bond\ forming\ energies)$, the reactionis endothermic and when $\sum(bond\ breaking\ energies) < \sum(bond\ frming\ energies)$, the reaction is exothermic. Bond breaking involves separation of atoms that were bonded in a molecule indicating that energy is required (i.e endothermic reaction). However bond forming involves bringing the atoms that are bonded by electrostatic attraction, hence energy is released.

Table 6.1: Average bond enthalpy and bond length for some bonds

Bond	**Average bond enthalpy (kJ/mol)**	**Bond length (10^{-9} m)**
H-H	436	0.074
C-C	347	0.154
C=C	612	0.134
C-H	413	0.108
O=O	498	0.121
O-H	464	0.096
C=O	746	0.120
Cl-Cl	243	0.199

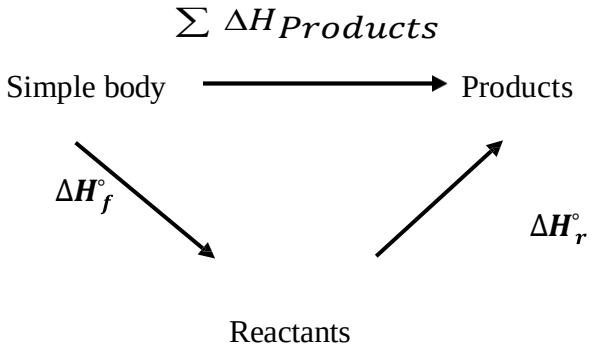
6. Enthalpies

6.4.1Determination of reaction enthalpies (Hess's Law)

6.4.2Determination of reaction enthalpy from formation enthalpies

$$\text{Reactants} \xrightarrow{\Delta H^\circ_r} \text{Products}$$

We can establish another process by constructing the following BORN-HABER cycle:



$\Sigma\Delta H_{cycle}$= 0 => $\Sigma\Delta H_f°(Products)+\Sigma\Delta Hf°(Reactants)+ \Delta H_R°=0$

So, from this equation we notice that the standard enthalpy of a chemical reaction (can also be equal to the sum of the enthalpies of formation of the products minus those of the reactants which can be expressed by the following general relation called the Law from HESS.

$$\Delta HR°= \Sigma vi\Delta Hf°(Products)- \Sigma vi\Delta Hf°(Reactants).$$

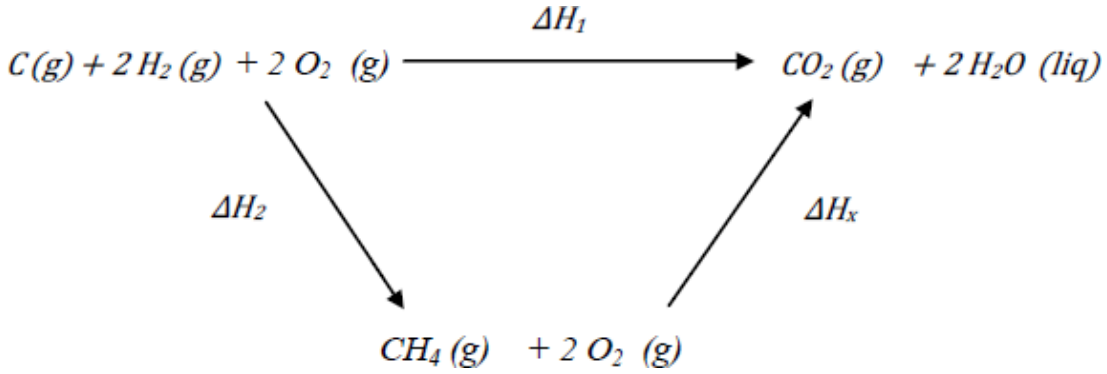
vi: Stoichiometric Coefficients.

Example:

We want to calculate $\Delta HR°$ of the following reaction using other chemical reactions:

$$CH4\ (g) + 2\ O2\ (g) \longrightarrow CO2\ (g) + 2\ H2O\ (liq) \quad \Delta HX\ ° = ?$$

It is possible to construct a Hess cycle involving the previous reaction and transformations involving simple bodies stable under standard conditions at T. This cycle is visualized in the following figure:



ΔH1 = ΔH2 + ΔHx we will therefore have ΔHx = ΔH1-
ΔH2 ΔH1 = 2ΔHf(H2O)+ ΔHf(CO2)

ΔH2 = ΔHf(CH4)

We will finally obtain: ΔHx = ΔHR= 2ΔHf(H2O)+ ΔHf(CO2)-ΔHf(CH4)

We find the general relationship indicated previously:

$$\Delta H_R^\circ = \Sigma\, \nu_i\, \Delta H_f^\circ\,(Products) - \Sigma \nu_i\, \Delta H_f^\circ\,(Reactants)$$

6.4.3Using reaction enthalpies

This type of calculation usually involves the use of **Hess's law**, which states: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps. Hess's law is valid because enthalpy is a state function: Enthalpy changes depend only on where a chemical process starts and ends, but not on the path it takes from start to finish.

Example

$$C(s) + O_2(g) \longrightarrow CO2(g) \qquad \Delta H^\circ_{298} = -394 \text{ kJ}$$

In the two-step process, first carbon monoxide is formed:

$$C(s) + \tfrac{1}{2}\, O_2(g) \longrightarrow CO(g) \quad \Delta H^\circ_{298} = -111 \text{ kJ}$$

Then, carbon monoxide reacts further to form carbon dioxide:

$$CO(g) + \tfrac{1}{2}\, O_2(g) \longrightarrow CO(g) \quad \Delta H°298 = -283 \text{ kJ}$$

The equation describing the overall reaction is the sum of these two chemical changes:

Step 1: $C(s) + ½\ O_2(g) \longrightarrow CO(g)$ **(1)** $\Delta H°_{298} = -111Kj$

Step 2: $CO(g) + ½\ O_2(g) \longrightarrow CO_2(g)$ **(2)** $\Delta H°_{298} = -283\ kJ$

Sum: $C(s) + ½\ O_2(g) + CO(g) + ½\ O_2(g) \longrightarrow CO(g) + CO_2(g)$ $\Delta H°_{298} = -394\ kJ$

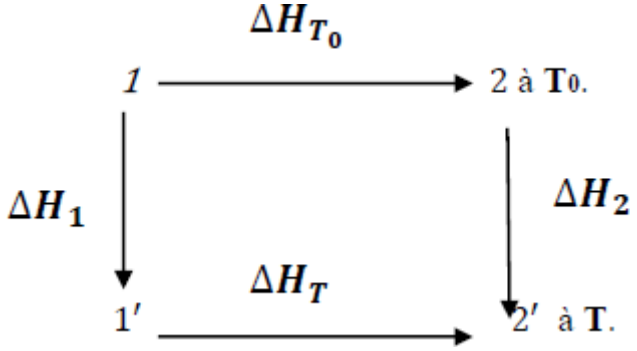
Because the CO produced in Step 1 is consumed in Step 2, the net change is:

$$C(s) + O_2(g) \longrightarrow CO_2(g)\ \ \Delta H°_{298} = \Delta H°_{298}(1) + \Delta H°_{298}(2)$$

6.5Influence of temperature on reaction enthalpy (Kirchhoff's law)

Or a transformation moving a thermodynamic system from an initial state (1) to a final state (2). Assuming that it is carried out at constant pressure and at a temperature T0 with a quantity of heat $\Delta \boldsymbol{HT0}$.

Knowing $\boldsymbol{C_{P1}}$ *et* $\boldsymbol{C_{P2}}$, what will be the enthalpy $\Delta \boldsymbol{HT}$ of this reaction at temperature 'T'?



According to the cycle:

$\Sigma \Delta Hi = 0$ so $\Delta HT0 + \Delta H2 - \Delta HT - \Delta H1 = 0$ $\Delta HT - \Delta HT0 = \Delta H2 - \Delta H1$

$$\Delta H_1 = \int_{T1}^{T2} n_1\, C_{p1} dT \quad and\ \Delta H_2 = \int_{T1}^{T2} n_2\, C_{p2} dT$$

$$\Delta H_1 = n_1 C_{p1} dT \quad and\ \Delta H_2 = n_2 C_{p2} dT$$

In a general way :

If we know $\Delta \boldsymbol{HT0}$ and we want to calculate $\Delta \boldsymbol{HT}$, simply integrate the previous equation and we will obtain:

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$$\Delta H_T = \Delta H_{T0} + \int_{T0}^{T} \Delta C_p dT \text{ Loi de KIRCHHOF}$$

With: $\boldsymbol{\Delta CP} = \Sigma \boldsymbol{n}\mathrm{C}_{\boldsymbol{P}}\,(\boldsymbol{Products}) - \Sigma \boldsymbol{n}\mathrm{C}_{\boldsymbol{P}}\,(\boldsymbol{r}\,\mathrm{e}\boldsymbol{act}\mathrm{ant}\boldsymbol{s}).$

- Cp is generally a function of temperature.
- In the case where there is a phase change in the interval [T0-T], the enthalpies of phase change must be taken into account in the calculation of the enthalpy.
- If Cp is not a function of temperature (Cp=cst) we will therefore have:

$$\Delta H_T = \Delta H_{T0} + \int_{T0}^{T} \Delta C_p dT$$

$$\Delta H_T = \Delta H_{T0} + \Delta n Cp \Delta T$$

Application :

The enthalpy of combustion of methane at 25°C is ΔH298°= −890.34 KJ.

Determine the enthalpy of the reaction at 100°C in the case where the water formed is still liquid, and in the case where it is gaseous

We give:

Cp (CH_4) = 35.31 ($J.mol^{-1}.K^{-1}$).

Cp (CO_2) = 37.2 ($J.mol^{-1}.K^{-1}$).

Cp (O_2) = 29.4 (J.mol-1.K^{-1}).

Cp (H_2O (liquide)) = 75.28 ($J.mol^{-1}.K^{-1}$).

Cp (H_2O (gaz)) = 33.6 ($J.mol^{-1}.K^{-1}$).

ΔHvap= 43.89 ($KJ.mol^{-1}$).

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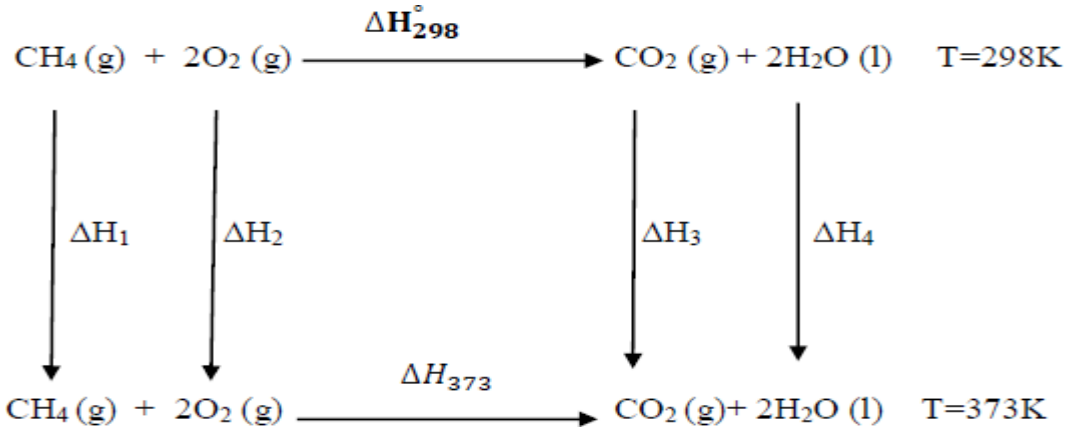
Solution :

1) In the case where the water formed is liquid:



We have: $\Delta H_{373} = \Delta H298° + \int \Delta CP\, 373298 dT = \Delta H298° + \Delta CP \Delta T$

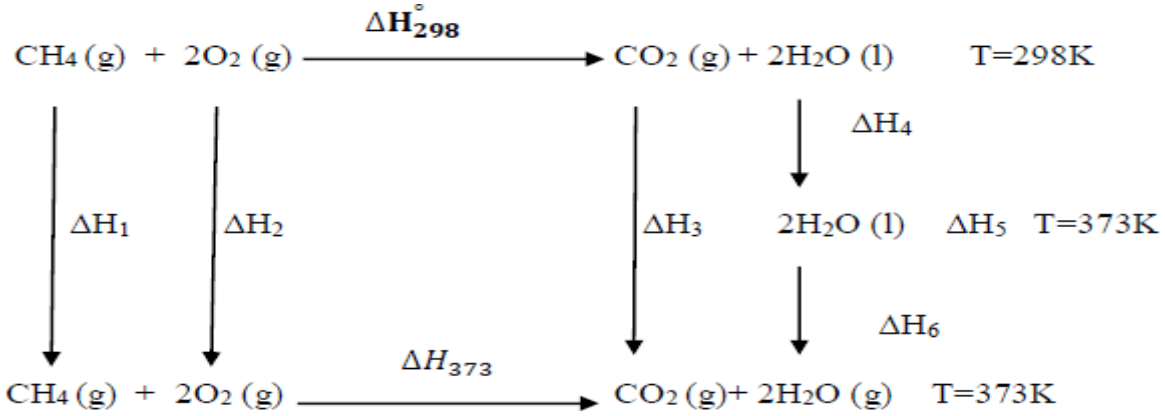
Calculation of $\boldsymbol{\Delta C_P}$:

$\Delta C_P = 2(H_2O(l)) + C_P(CO_2) - 2C_P(O_2) - C_P(CH_4) = 93.65$ J.K^{-1}

$\Delta H_{373} = 890.34 - 93.65 * 10 - 3(373 - 298) = -883.316$ KJ

$\Delta H_{373} = -883.316$ KJ

2) In the case where the water formed is gaseous:



We have: $\Delta H_{373} = \Delta H^{\circ}_{298} + \int_{298}^{373} \Delta CP\, dT = \Delta H^{\circ}_{298} + \Delta C_P \Delta T + 2\Delta H_{vap}(H2O)$

v
a
p

6. Enthalpies

Calculation of $\boldsymbol{\Delta C_P}$:

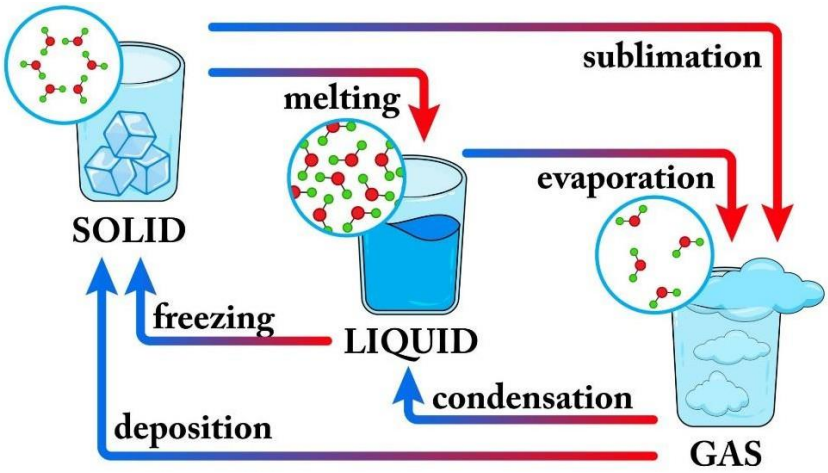
$\Delta C_P = 2C_p(H_2O(l)) + C_P\ (CO_2) - 2C_P(O_2) - C_P(CH_4) = 93.65\ J.K^{-1}$

$\Delta H_{373} = -890.34 + 93.65 * 10^{-3}(373-298) + 2 * 43.89 = -795.53 Kj$

Or: $\Sigma \Delta H_i = 0$ so $\Delta H1 + \Delta H_2 + \Delta H_{373} + \Delta H_{298} + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 = 0$

Enthalpy of change of state:

When a pure body undergoes a change of state (fusion, vaporization, liquefaction, sublimation, solidification), the temperature remains constant during this phase change.



The enthalpy of a mole of a pure substance (A) passing from T1 to T2 while undergoing fusion and vaporization is given by the following diagram:

$$\underset{T_1}{A(sol)} \xrightarrow{\Delta H1} \underset{T_{mel}}{A(sol)} \xrightarrow{\Delta Hfus} \underset{T_{mel}}{A(liq)} \xrightarrow{\Delta H2} \underset{T_{vap}}{A(liq)} \xrightarrow{\Delta Hvap} \underset{T_{vap}}{A(vap)} \xrightarrow{\Delta H3} \underset{T_2}{A(vap)}$$

$$\Delta H_{T1 \to T2} = \int_{T1}^{Tmel} C_P(sol)\,dT + \Delta H_{mel} + \int_{Tmel}^{Tvap} C_P(liq)\,dT + \Delta H_{vap} + \int_{Tvap}^{T2} C_P(vap)\,dT$$

$$\Delta H_{T1 \to T2} = \int_{T1}^{Tmel} nc_P(sol)dT + n\Delta H_{mel} + \int_{Tmel}^{Tvap} nc_P(liq)dT + n\Delta H_{vap} + \int_{Tvap}^{T2} nc_P(vap)dT$$

$\Delta \boldsymbol{H}$mel or Lmel: Latent heat of melting.

$\Delta \boldsymbol{Hvap}$ or Lvap: Latent heat of vaporization.

6.6 Enthalpy of combustion

The standard enthalpy of combustion noted ΔHcomb° of a compound or a simple body is the heat released during the oxidation reaction by O2 to form CO2 gas and liquid H2O.

Example:

Determination of the enthalpy of combustion of benzene: What is the value of the enthalpy of combustion of benzene (C6H6)? Data:

$\Delta Hf°(C_6H_6)=80$ KJ.mol^{-1}

$\Delta Hf°(CO_2)=-400$KJ.mol^{-1}

$\Delta Hf°(H_2O)=-240$KJ.mol^{-1}

$$C_6H_6\ (g) + 15/2\ O_2\ (g) \longrightarrow 6CO_2\ (g) + 3H_2O\ (l)$$

$\Delta Hcomb° = \Delta Hf°(products) - \Delta Hf°(reactants)$

$\Delta Hcomb° = 6\Delta Hf°(CO_2)+3\Delta Hf°(H_2O) - \Delta Hf°(C_6H_6) - 15/2\ \Delta Hf°(O_2)$ ΔHcomb°

$= 6(-400)+ 3(-240) - 80 - 152(0) = -3200KJ.mol^{-1}$

Δ**Hcomb**°<0: Exothermic reaction.

6.7 Bond energy or enthalpy

The dissociation of a gaseous molecule AB corresponds to the breaking of the chemical bond between the atoms A and B and to obtaining two atoms A and B free and in the gaseous state. Energy must be supplied to the system to carry out this dissociation. The enthalpy of the dissociation reaction in the gas phase is therefore positive. It is the energy that the system receives to dissociate into atoms in the gas state:

$$\boldsymbol{AB(g) \longrightarrow A(g) + B(g) \quad \Delta H°dissociation > 0}$$

This enthalpy of dissociation is called binding energy. It is denoted $\Delta Hdi(A-B)°$or D(A– B) The bond energy or bond enthalpy is an energy released (negative) during the formation of a bond from isolated gaseous atoms. It is expressed in J.mol^{-1}.

Example:

H2 (g) ➔ H(g) + H(g) ΔHdiss(H-H) = 436,4 kJ/mol

HCl(g) ➔ H(g) + Cl(g) ΔHdiss(H-Cl) = 431,9 kJ/mol

N2 (g) ➔ N(g) + N(g) ΔHdiss(N≡N) = 941,4 kJ/mol

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Bond enthalpy reflects the strength of the bond. It therefore depends on:
The length of the link, the nature of the link and the polarity of the link If we consider the opposite reaction:

$$A\ (g) + B\ (g) \xrightarrow{\Delta(A-B)} A\text{-}B$$

$$\Delta(\boldsymbol{A-B})° = -\Delta\boldsymbol{Hdiss}(\boldsymbol{A-B})°\ .$$

Application:

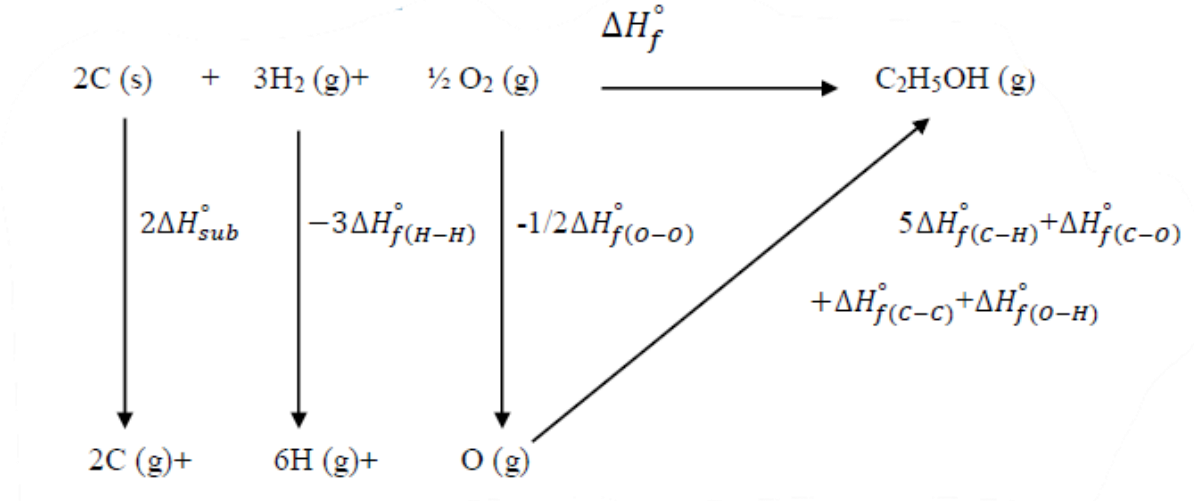
The standard enthalpy of formation of ethanol C2H5OH, $\Delta Hf° = -239$ KJ.mol^{-1}.
Calculate the bond energy of C-O in ethanol.

Data: $\Delta Hsub°(c)$= 717 KJ.mol^{-1}.

A-B bond	H-H	O-H	C-H	C-C
$\Delta\boldsymbol{H_f}\ (\boldsymbol{A-B})°$ **(KJ.mol^{-1})**	-435	-460	-414	-347

From the structural formula of the ethanol molecule we find:

- One C-C bond:$\Delta Hf(C-C)°$
- One C-O bond: $\Delta(C-O)°$
- One O-H bond: $\Delta(O-H)°$
- Five C-H bonds: $\Delta(C-H)$



$\Delta Hf°=\mathbf{2}\Delta Hsub°-\mathbf{3}\Delta(H-H)°-\mathbf{12}\Delta Hf(O-O)°+\mathbf{5}\Delta Hf(C-H)°+\Delta Hf(C-O)°+\Delta Hf(C-C)$

$+\Delta(O-H)°.$

$\Delta Hf(C-O)°=\Delta Hf°-\mathbf{2}\Delta Hsub°+\mathbf{3}\Delta Hf(H-H)°+\mathbf{12}\Delta Hf(O-O)°-\mathbf{5}\Delta Hf(C-H)°-\Delta Hf(C-C)°$

$-\Delta(O-H)°$

$$\Delta(\boldsymbol{C-O})°= \textbf{- 200 KJ.mol}^{\textbf{-1}}.$$

6.8 The Carnot cycle

Let us go back to our piston and pebbles system depicted on Fig.4.1 and modify it as described on Fig 4.5.

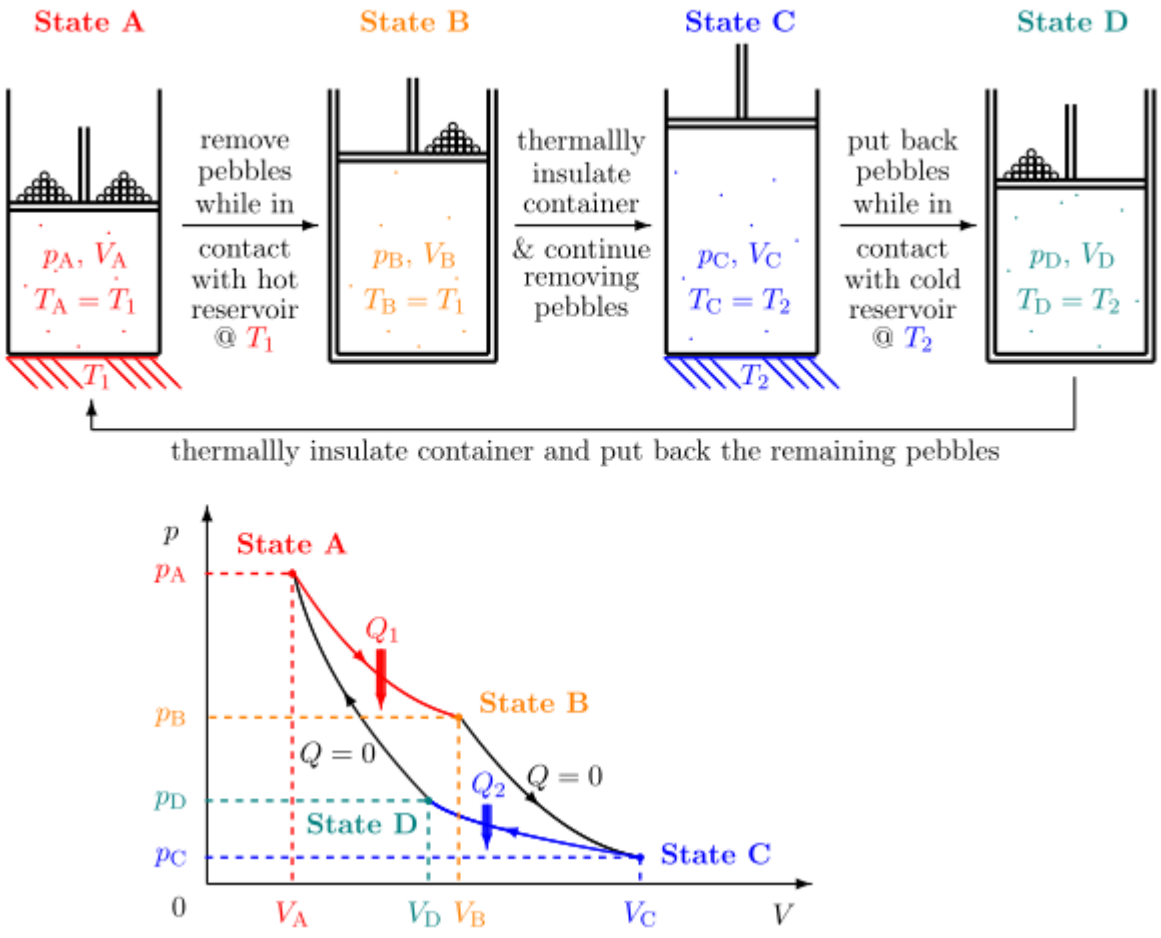


Figure 6.1: Carnot cycle for an ideal gas (top part of the figure) together with its diagram representation (bottom part).

As the system is in thermal contact with a *reservoir*† from State A to State B, its temperature remains constant on that path, and $T_B = T_1 = T_A$. It is called an *isothermal* process and given the equation of state of the ideal gas, it describes a hyperbola in the p V diagram (red curve in bottom part of Fig. 4.5 which is called an *isotherm*). As one is removing some pebbles on top of the piston, the gas expands, so that $V_B > V_A$ and $p_B < p_A$. We have previously established that the amount of work done by the gas is the area under the path in the p V diagram, $W_{AB} < 0$. For an ideal gas, the internal energy U is a function of the temperature alone, so the change in internal energy along an isothermal path, $\Delta U = 0$. Therefore, the first law allows us to write that the amount of heat $Q_1 = W_{AB} > 0$ (thick red arrow entering the cycle in Fig. 4.5). This is quite an intuitive result: the system must draw heat from the reservoir to do work if it is to operate at a constant temperature.

From State B to State C, one continues to remove pebbles, but this time from a container which is thermally insulated rather than in contact with a reservoir. This means that $Q = 0$ on this path, and the process is called *adiathermal*. If it is also reversible (as is our case here), then it is called *adiabatic* (black curve in the bottom part of Fig. 4.5, called an *adiabat*‡). Work is still being done by the gas as it expands (the area under the BC path is non nil), so $V_C > V_B$, $p_C < p_B$ and $W_{BC} < 0$. Applying the first law yields $\Delta U = W_{BC} < 0$ and therefore, as for an ideal gas U T, we have $T_C = T_2 < T_1$: the gas has cooled.Now we start reversing processes to get back to the original state and complete the cycle. From State C to State D, we place the system back in contact with a reservoir, but this time a cold one, with temperature $T_2 = T_C$. We then put back some of the pebbles. Reasoning in a similar manner than for the A B path, albeit in the reverse direction as the system is now compressed, we conclude that $T_D = T_2 = T_C$, $V_D < V_C$, $p_D > p_C$ and $W_{CD} > 0$. $\Delta U = 0$ along this isotherm therefore the first law tells us that $Q_2 = W_{CD} < 0$ (thick blue arrow exiting the cycle in Fig. 4.5): the system has dumped heat in the reservoir. Finally, we remove the reservoir, thermally insulate the system and put back the remaining pebbles to go from State D back to the original State A. Similarly to what took place on the B C path, $Q = 0$ on this adiabat (the other black curve in the bottom part of Fig. 4.5) and as the gas is compressed further, $V_A < V_D$, $p_A > p_D$, $W_{DA} > 0$. Applying the first law, we deduce $\Delta U = W_{DA} > 0$ and thus $T_A = T_1 > T_2$ for our ideal gas: it has heated. Summarising what happened along one entire Carnot cycle loop, we have $\Delta T = \Delta U = 0$ and $W_{tot} = W_{AB} + W_{BC} + W_{CD} + W_{DA} < 0$ (W_{tot} is the area within the cycle ABCD in Fig. 4.5) so that $Q_{tot} = -W_{tot} = Q_1 + Q_2 > 0$.

6.4 Limitations of first law of thermodynamics

First law of thermodynamics based on law of energy conservation has proved to be a powerful tool for thermodynamic analysis. But over the period of time when it was applied to some real systems, it was observed that theoretically first law stands valid for the processes which are not realizable practically. It was then thought that there exist certain flaws in first law of thermodynamics and it should be used with certain limitations. Therefore, it is obvious that Ist law of thermodynamics has certain limitations as given below:

(i) First law of thermodynamics does not differentiate between heat and work and assures full convertibility of one into other whereas full conversion of work into heat is possible but the vice-versa is not possible.

(i) First law of thermodynamics does not explain the direction of a process. Such as theoretically it shall permit even heat transfer from low temperature body to high temperature body which is not practically feasible. Spontaneity of the process is not taken care of by the first law of thermodynamic

7. Entropy

Course contents

- Entropy
- Entropy and Microstates
- Predicting the Sign of ΔS
- The Second and Third Laws of Thermodynamics
- Free Energy

7. Entropy

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (Figure 7.1) published the results of an extensive study regarding the efficiency of steam heat engines. In a later review of Carnot's findings, Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the reversible heat (qrev) and the kelvin temperature (T). The term reversible process refers to a process that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be "reversed") by an infinitesimally small change is some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as irreversible.

Figure 7.1 Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

Similar to other thermodynamic properties, this new quantity is a state function, and so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property entropy (S) and defined its change for any process as the following:

$$\Delta S = Q_{rev} / T$$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

7.1 Entropy and Microstates

As for other state functions, the change in entropy for a process is the difference between its final (Sf) and initial (Si) values:

$$\Delta S = S_f - S_i = k \ln W_f - k \ln W_i = k \ln W_f W_i$$

For processes involving an increase in the number of microstates, $W_f > W_i$, the entropy of the system increases, $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $W_f < W_i$, yield a decrease in system entropy, $\Delta S < 0$.

7.2 Predicting the Sign of ΔS

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure 7.2. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{liquid} > S_{solid}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

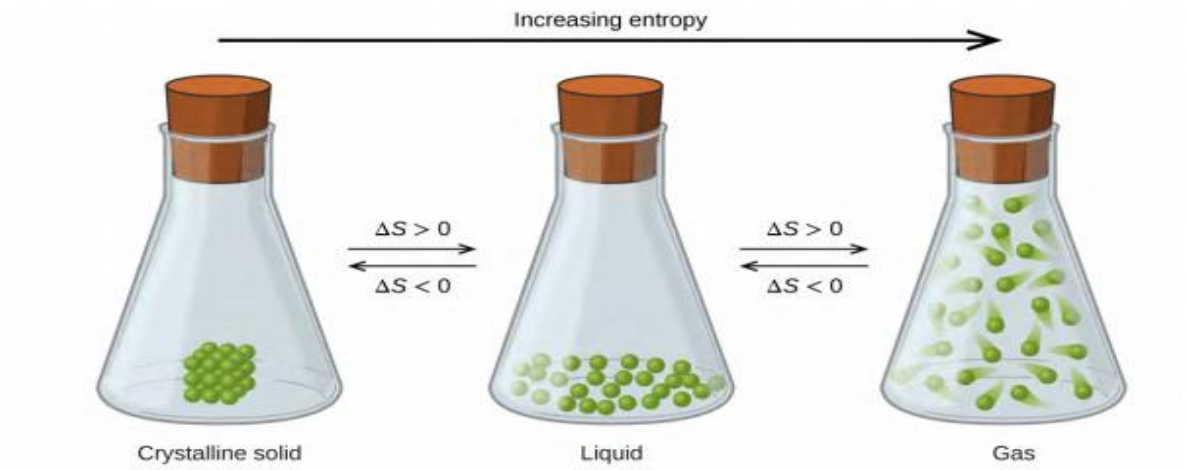


Fig 7.2 The entropy of a substance increases (ΔS > 0) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases (ΔS < 0) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the vapor or gas phase. The atoms or molecules occupy a much greater volume than in the liquid phase; therefore each atom or molecule can be found in many more locations than in the liquid (or solid) phase. Consequently, for any substance, Sgas > Sliquid > Ssolid, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$. the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature .

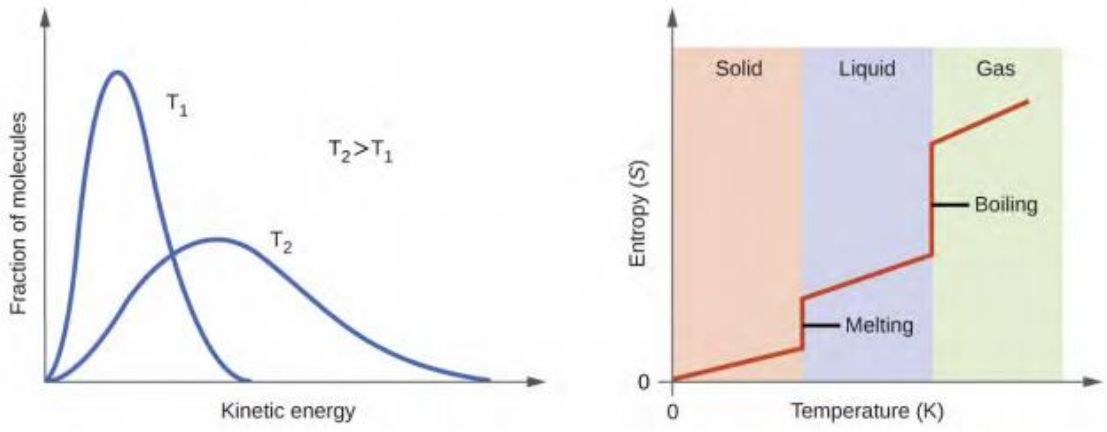


Fig 7.3 Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy.

The entropy of a substance is influenced by structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle's mass and the spacing of quantized translational energy levels (which is a topic beyond the scope of our treatment). For molecules, greater numbers of atoms (regardless of their masses) increase the ways in which the molecules can vibrate and thus the number of possible microstates and the system entropy.

Finally, variations in the types of particles affects the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions

that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

7.3 The Second and Third Laws of Thermodynamics

By the end of this section, you will be able to State and explain the second and third laws of thermodynamics • Calculate entropy changes for phase transitions and chemical reactions under standard conditions The Second Law of Thermodynamics In the quest to identify a property that may reliably predict the spontaneity of a process, we have identified a very promising candidate: entropy. Processes that involve an increase in entropy of the system ($\Delta S > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include the surroundings, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

$$\mathbf{\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}}$$

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. This is always observed to occur spontaneously. Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{sys} = -Q_{rev} / T_{sys} \text{ and } \Delta S_{surr} = Qrev / T_{surr}$$

The arithmetic signs of qrev denote the loss of heat by the system and the gain of heat by the surroundings. Since $T_{sys} > T_{surr}$ in this scenario, the magnitude of the entropy change for the surroundings will be greater than that for the system, and so the sum of ΔSsys and ΔS_{surr} will yield a positive value for ΔS_{univ}. This process involves an increase in the entropy of the universe.

2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. This is never observed to occur spontaneously. Again designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{sys} = Q_{rev} / T_{sys} \text{ and } \Delta S_{surr} = -Q_{rev}\, T_{surr}$$

The Second Law of Thermodynamics

$\Delta S_{univ} > 0$	spontaneous
$\Delta S_{univ} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{univ} = 0$	reversible (system is at equilibrium)

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are infinitely more massive (the earth's atmosphere). As a result, qsurr is a good approximation of qrev, and the second law may be stated as the following:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + Q_{surr} / T$$

This limiting condition for a system's entropy represents the third law of thermodynamics: the entropy of a pure, perfect crystalline substance at 0 K is zero. We can make careful calorimetric measurements to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. Standard entropies are given the label S_{298° for values determined for one mole of substance at a pressure of 1 bar and a temperature of 298 K. The standard entropy change (ΔS°) for any process may be computed from the standard entropies of its reactant and product species like the following:

$$\Delta S^\circ = \sum \nu S298^\circ \text{ (products)} - \sum \nu S298^\circ \text{ (reactants)}$$

Here, ν represents stoichiometric coefficients in the balanced equation representing the process. For example, ΔS° for the following reaction at room temperature

$$mA + nB \longrightarrow xC + yD,$$

is computed as the following:

$$= \left[\left[xS_{298^\circ}(C) + yS_{298^\circ}(D) \right] \right] - \left[\left[mS_{298^\circ}(A) + nS_{298^\circ}(B) \right] \right]$$

Table 7.1 lists some standard entropies at 298.15 K. You can find additional standard entropies in Appendix G.

Standard Entropies (at 298.15 K, 1 atm)

Substance	S°_{298} (J mol^{-1} K^{-1})
carbon	
C(*s*, graphite)	5.740
C(*s*, diamond)	2.38
CO(*g*)	197.7
$CO_2(g)$	213.8
$CH_4(g)$	186.3
$C_2H_4(g)$	219.5
$C_2H_6(g)$	229.5
$CH_3OH(l)$	126.8
$C_2H_5OH(l)$	160.7
hydrogen	
$H_2(g)$	130.57
H(*g*)	114.6
$H_2O(g)$	188.71
$H_2O(l)$	69.91
HCl(*g*)	186.8
$H_2S(g)$	205.7
oxygen	
$O_2(g)$	205.03

7.4. **Free Energy**

One of the challenges of using the second law of thermodynamics to determine if a process is spontaneous is that we must determine the entropy change for the system and the entropy change for the surroundings. An alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the **Gibbs free energy change (G)** (or simply the free energy), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G = H - TS$$

Free energy is a state function, and at constant temperature and pressure, the standard free energy change (ΔG°) may be expressed as the following:

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

We can understand the relationship between this system property and the spontaneity of a process by recalling the previously derived second law expression:

$$\Delta S_{univ} = \Delta S + Q_{surr}/T$$

7. Entropy

The first law$_{univ}$ requires that

$Q_{surr} = -Q_{sys}$,

and at constant pressure $q_{sys} = \Delta H$, and so this expression may be rewritten as the following:

$$\Delta S_{univ} = \Delta S - \Delta H/ T$$

ΔH is the enthalpy change of the system. Multiplying both sides of this equation by −T, and rearranging yields the following:

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

Comparing this equation to the previous one for free energy change shows the following relation:

$$\Delta G = -T\Delta S_{univ}$$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔSuniv. summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Relation between Process Spontaneity and Signs of Thermodynamic Properties

$\Delta S_{univ} > 0$	$\Delta G < 0$	spontaneous
$\Delta S_{univ} < 0$	$\Delta G > 0$	nonspontaneous
$\Delta S_{univ} = 0$	$\Delta G = 0$	reversible (at equilibrium)

calculation of free energy changes for physical and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute standard free energy changes according to the following relation.

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

Free energy changes may also use the standard free energy of formation (ΔGf °), for each of the reactants and products involved in the reaction. The standard free energy of formation is the free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpies of formation, ΔGf ° is by definition zero for elemental substances under standard state conditions. The approach to computing the free energy change for a reaction using this approach is the same as that demonstrated previously for enthalpy and entropy changes. For the reaction

$$mA + nB \longrightarrow xC + yD,$$

the standard free energy change at room temperature may be calculated as

$\Delta G298\,^{\circ} = \Delta G^{\circ} = \sum \nu\, \Delta G_{298^{\circ}}$ (products) $- \sum \nu\, \Delta G_{298^{\circ}}$ (reactants) $= \left[\left[x\Delta G_{f^{\circ}}(C) + y\Delta G_{f^{\circ}}(D) \right] \right] - \left[\left[m\Delta G_{f^{\circ}}(A) + n\Delta G_{f^{\circ}}(B) \right] \right]$.

Temperature Dependence of Spontaneity As was previously demonstrated in this chapter's section on entropy, the spontaneity of a process may depend upon the temperature of the system.

Summary of the Four Scenarios for Enthalpy and Entropy Changes

	$\Delta H > 0$ (endothermic)	$\Delta H < 0$ (exothermic)
$\Delta S > 0$ (increase in entropy)	$\Delta G < 0$ at high temperature $\Delta G > 0$ at low temperature Process is spontaneous at high temperature	$\Delta G < 0$ at any temperature Process is spontaneous at any temperature
$\Delta S < 0$ (decrease in entropy)	$\Delta G > 0$ at any temperature Process is nonspontaneous at any temperature	$\Delta G < 0$ at low temperature $\Delta G > 0$ at high temperature Process is spontaneous at low temperature

.table 7.2 There are four possibilities regarding the signs of enthalpy and entropy changes

For a system at equilibrium, Q = K and $\Delta G = 0$, and the previous equation may be written as

$0 = \Delta G^{\circ} + RT \ln K$ (at equilibrium) $\Delta G^{\circ} = -RT \ln K$ or $K = e - \Delta G^{\circ} RT$

This form of the equation provides a useful link between these two essential thermodynamic properties, and it can be used to derive equilibrium constants from standard free energy changes and vice versa. The relations between standard free energy changes and equilibrium constants are summarized .

Relations between Standard Free Energy Changes and Equilibrium Constants

K	ΔG°	Comments
> 1	< 0	Products are more abundant at equilibrium.
< 1	> 0	Reactants are more abundant at equilibrium.
= 1	= 0	Reactants and products are equally abundant at equilibrium.

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy change versus the extent of the reaction (for example, as reflected in the value of Q), equilibrium is established when the system's free energy is minimized . If a system is present with reactants and products present

in nonequilibrium amounts (Q ≠ K), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.

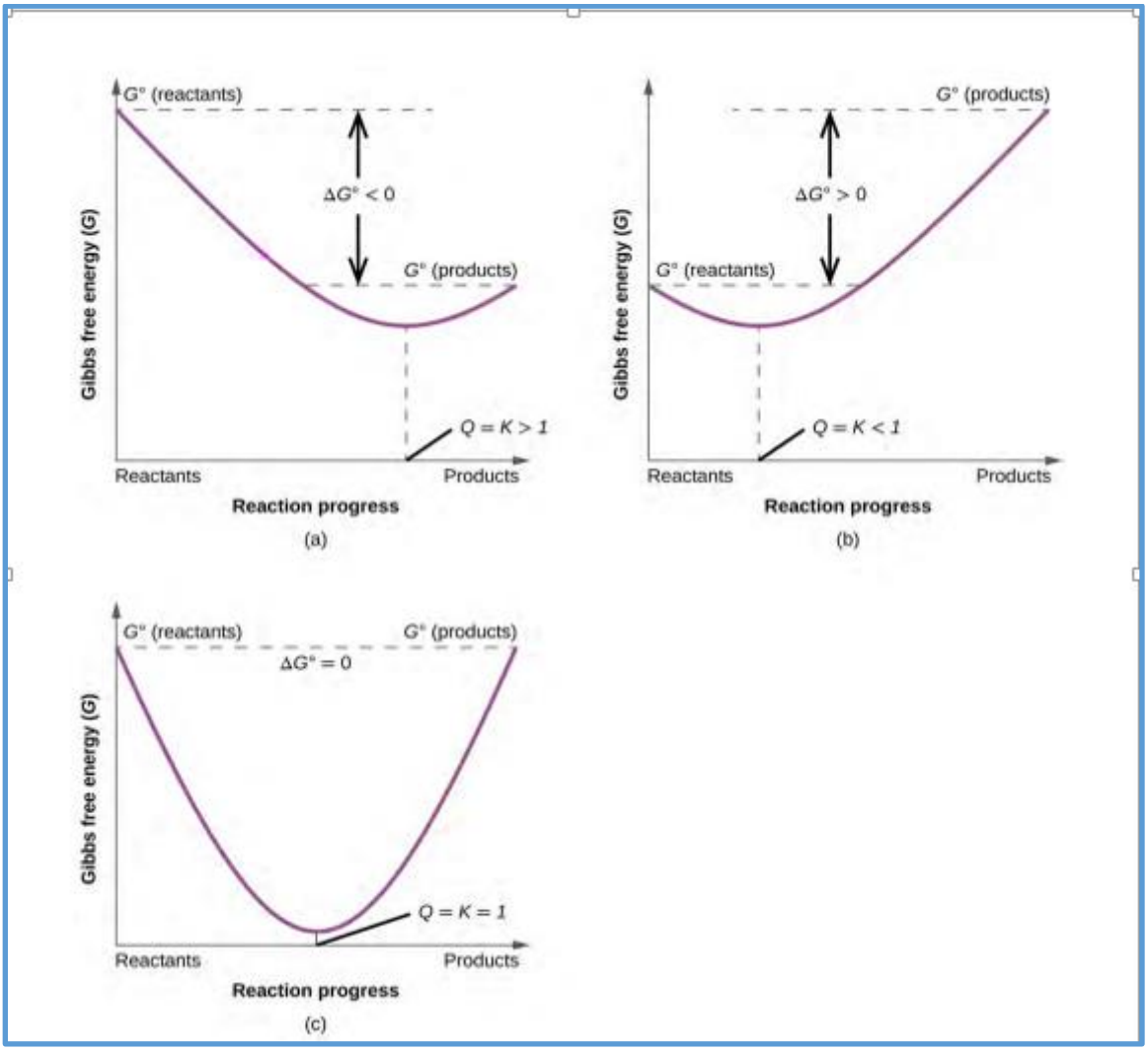


Figure 7.1 These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium.

TEXT BOOKS AND REFERENCES

Textbooks referred to in the development of each unit are presented at the end of the units. However, a list of some General references is presented below:

- Atkins, P. and De Paula, J. (2010)Atkins'PhysicalChemistry.NinthEdition.Oxford University Press. UK.
- Engel T. and Reid, P. (2005). Physical Chemistry. Pearson Cummings. San Francisco.New York.
- Leite, F. L.; Bueno, C. C.; Da Róz, A. L.; Ziemath, E. C.; Oliveira, O. N. (2012). "Theoretical Models for Surface Forces and Adhesion and Their Measurement Using Atomic Force Microscopy". International Journal of Molecular Sciences. 13 (12): 12773.
- Levine, N. I. (2009). Physical Chemistry.5thEdition.Higher Education. Boston.
- Mathew, P. (2004). Advanced Chemistry, Cambridge low price edition. Cambridge UniversityPress, UK.
- Margenau, H. and Kestner, N. (1969) Theory of intermolecular forces, International Series of Monographs in Natural Philosophy, Pergamon Press, ISBN 1483119289
- Monk, P. (2004). Physical Chemistry: Understanding the Chemical World. John Wileyand Sons Ltd. England.
- Ryan, L and Norris, R. (2014). Cambridge international AS and A level chemistry. CambridgeUniversity Press, U
- Pobell,, F. (2007). Matter and Methods at Low Temperatures, Springer-Verlag, Berlin,
- BOOCK CHEMISTRY OPENSTAX COLLEGE RICE UNIVERSITY 6100 Main Street MS-375 Houstron, Texas 77005