

Ministry of Higher Education
and Scientific Research

Al-Muthanna University

College of Science

Department of Chemistry



وزارة التعليم العالي والبحث
العلمي

جامعة المثنى

كلية العلوم

قسم الكيمياء

Physical Chemistry

المحاضرة 7

المرحلة الثانية

أ.د. حسن صبيح جبر

Thermodynamic introduction

Thermodynamics is a science and, more importantly, an engineering tool used to describe processes that involve changes in temperature, transformation of energy, and the relationships between heat and work. It is used to describe the performance of propulsion systems, power generation systems, and refrigerators, and to describe fluid flow, combustion, and many other phenomena.

Thermodynamics is the science of energy.

Thermodynamics = *Therme* + *Dynamis*
(Heat) (Power)

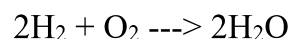
- Thermodynamics is the study of the effects of work, heat, and energy on a system
- Thermodynamics is only concerned with macroscopic (large-scale) changes and observations.

Thermodynamics outline

- System, Surrounding, State.
- Path Property, Reversible and Irreversible Process.
- Thermodynamic Work, Heat, Temperature, Thermal Equilibrium.
- Zeroth Law, First Law and Second Law of Thermodynamics.

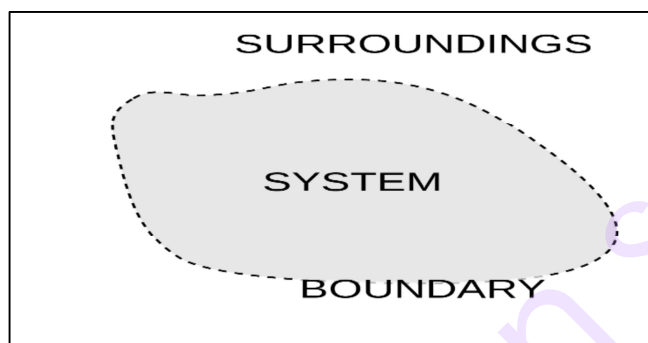
System & Surroundings

The **system** is the part of the universe we wish to focus our attention on. In the world of chemistry, the system is the chemical reaction. For example:

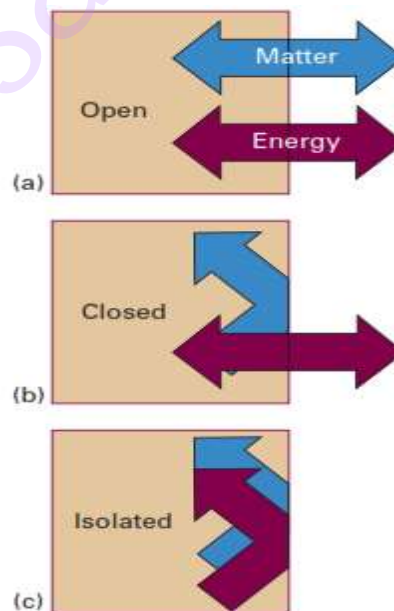
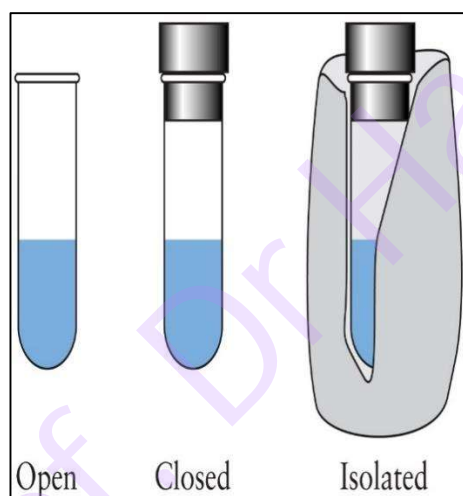


The **surroundings** are everything else; the rest of the universe. For example, say the above reaction is happening in gas phase; then the walls of the container are part of the surroundings.

Boundary is real / imaginary surface that separates the system from surroundings



Types of thermodynamic systems



- An **open system** may exchange both energy and matter with its surroundings.
- A **closed system** may exchange energy but not matter with its surroundings.
- An **isolated system** may exchange neither energy nor matter with its surroundings.

Properties of System

Any characteristic of a system is known as its **property**.

Intensive: independent on mass of system.

-e.g. Temperature, t , refractive index, n , density, ρ , state of matter

Extensive: dependent on mass of system.

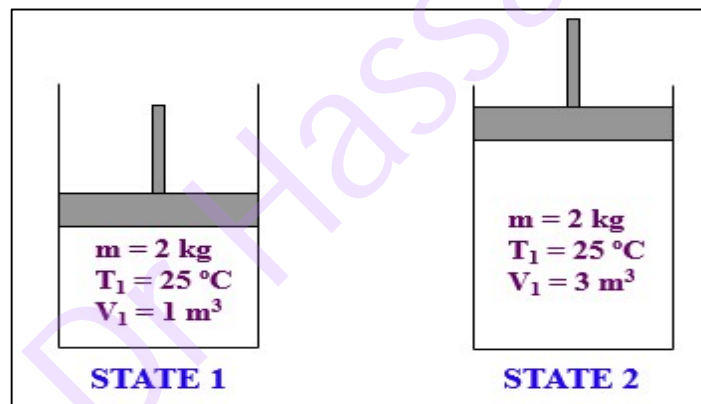
- e.g. pressure (p), amount of substance, mol, energy, E enthalpy, H entropy, S , Gibbs energy, G , heat capacity, C_p , Helmholtz energy, A , internal energy, E , mass, m , volume, V .

Specific: Extensive properties per unit mass.

- e.g. Sp. Vol ($v=V/m$), Sp. Enthalpy ($h=H/m$), specific heat capacity, μ .

State & Equilibrium

Set of properties to completely describe the condition of the system is known as its **state**.



EQUILIBRIUM : State of Balance

Thermal Equilibrium :

- NO Temperature Gradient throughout the system

Mechanical Equilibrium :

- NO Pressure Gradient throughout the system.

Phase Equilibrium :

- System having more than 1 phase.
- Mass of each phase is in equilibrium.

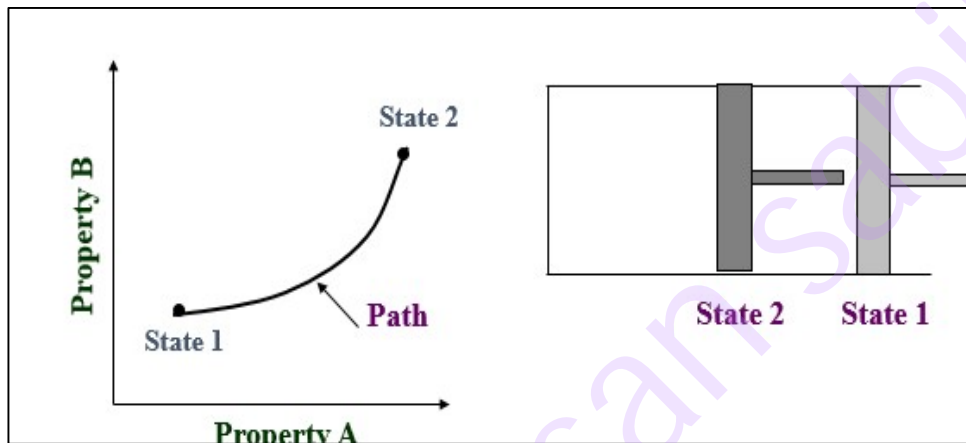
Chemical Equilibrium :

- Chemical composition is constant

Path & Process

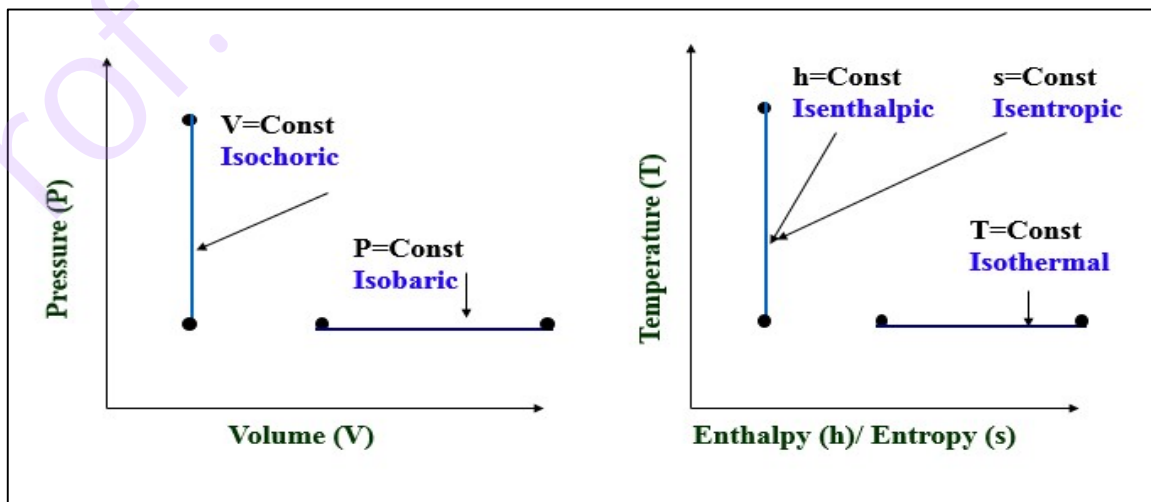
Any change a system undergoes from one equilibrium state to another is known as **PROCESS**.

Series of states through which system passes during the process is known as its **PATH**.



Thermal process

- Diathermic process allows heat flow into or out of the system.
- An adiabatic process prevents heat flow into or out of the systems.
- Isothermal implies constant temperature, T.
- Isobaric implies constant pressure, P.
- Isochoric implies constant volume, V.



Cycle:

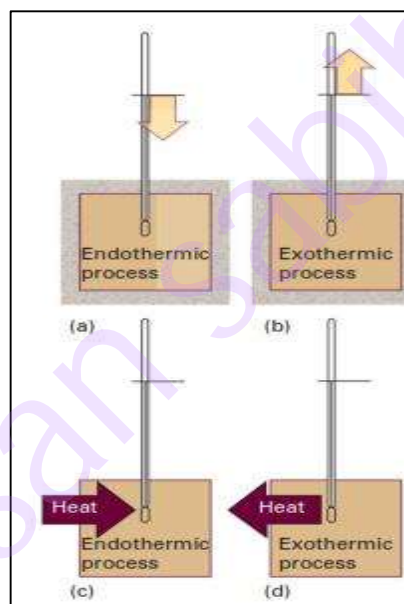
A system is said to have undergone a cycle if it returns to its original state at the end of the process. Hence, for a cycle, the initial and the final states are identical.

Exothermic process

A process that releases energy as heat into its surroundings. All combustion reactions are exothermic. (-q negative)

Endothermic process

A process in which energy is acquired from its surroundings as heat. An example of an endothermic process is the vaporization of water. (+q positive)



Reversible Process: Process that can be reversed without leaving any trace on the Surroundings. (spontaneously process)

i.e. Both, System and Surroundings are returned to their initial states at the end of the Process. This is only possible when net Heat and net Work Exchange between the system and the surroundings is ZERO for the Process.



Irreversible Process

Most of the Processes in nature are **irreversible**. (Non- spontaneously process). i.e. Having taken place, they cannot reverse themselves spontaneously and restore the System to its original State. e.g. Hot cup of coffee Cools down when exposed to Surroundings. But, Warm up by gaining heat from Surroundings. i.e. w/o external Heat supply.



State function

State functions do not depend on the path by which the system arrived at its present state. A state function describes the equilibrium state of a system.

$$\int_a^b dV = V_b - V_a$$

Differential of a **state function** is called

EXACT DIFFERENTIAL

EX) Energy (E), Enthalpy (H), Internal energy (U), Gibbs free energy (G),

Helmholtz free energy (F), Pressure (P), Temperature (T), Volume (V)

Entropy (S)

$$\int_a^b dW \neq W_b - W_a$$

$$= w$$

Differential of a **path function** is called

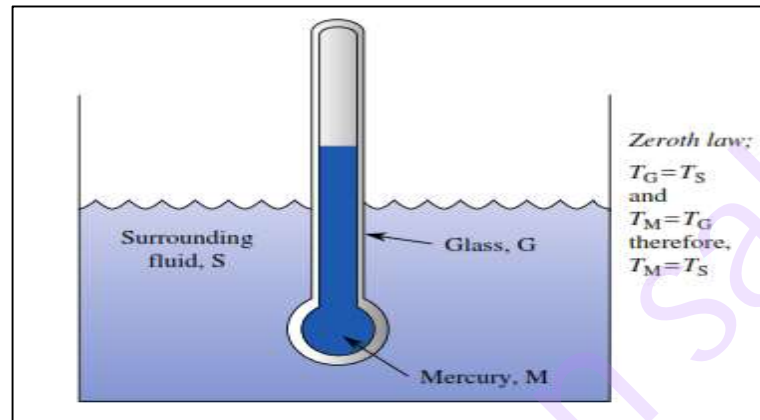
INEXACT DIFFERENTIAL.

EX) Work (w), Heat (q).

Note/ state functions are symbolized by uppercase (CAPITAL) letters.

ZEROth LAW OF THERMODYNAMICS

Consider three thermodynamic systems, A, B, and C. If system A is in thermal equilibrium with (i.e., is the same temperature as) system C and system B is in thermal equilibrium with system C, then system A is in thermal equilibrium with system B.



Q) Multiple choice

1- Chemical reactions that absorb heat energy are called _____ and have a _____ heat.

A. exothermic, positive B. exothermic, negative C. endothermic, positive.

2- The study of the effects of work, heat, and energy on a system is _____

A. efficiency B. thermodynamics C. equilibrium

Q) Explain the Types of thermodynamic systems

Q) Give an example for each of the following thermodynamic terms:

1- The thermodynamic system 2- Irreversible Process 3- state function

4- Path function 5- Reversible Process 6- Extensive properties

Q) What the differences between the State function and the Path function?

Q) Explain zeroth law of thermodynamics.