

Lecture four

BASICS OF THERMODYNAMICS OF LIVING SYSTEMS

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)

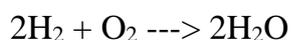
- Thermodynamics is the study of the effects of work, heat, and energy on a system
- Thermodynamics is only concerned with macroscopic (large-scale) changes and observations.

Thermodynamics outline

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

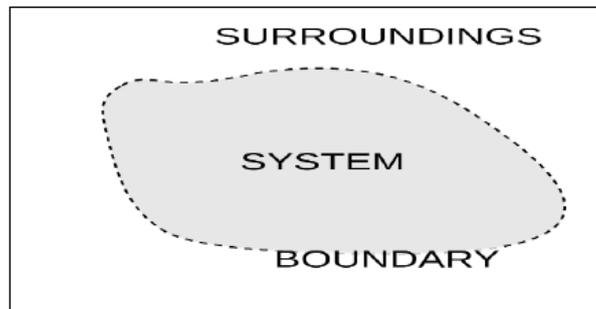
System & Surroundings

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:

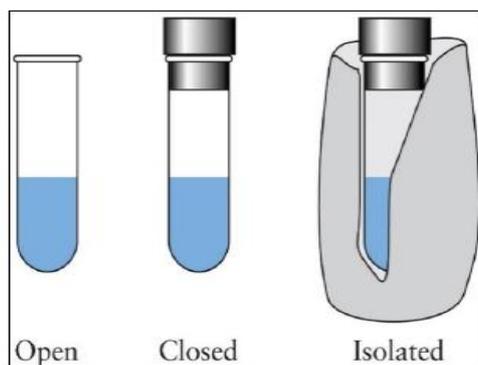


The surroundings are everything else; the rest of the universe. For example, say the above reaction is happening in gas phase; then the walls of the container are part of the surroundings.

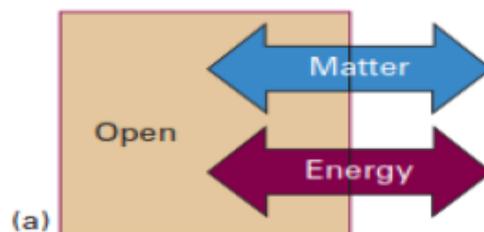
Boundary is real / imaginary surface that separates the system from surroundings



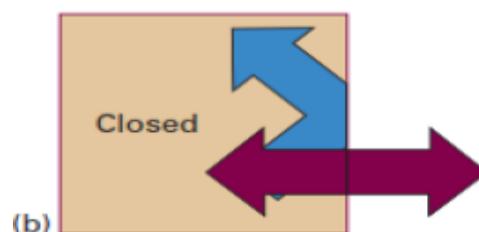
Types of thermodynamic systems



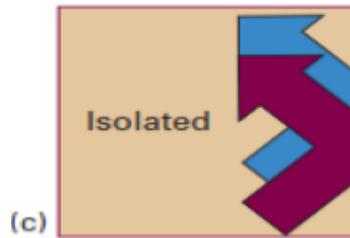
- An open system may exchange both energy and matter with its surroundings.



- 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.

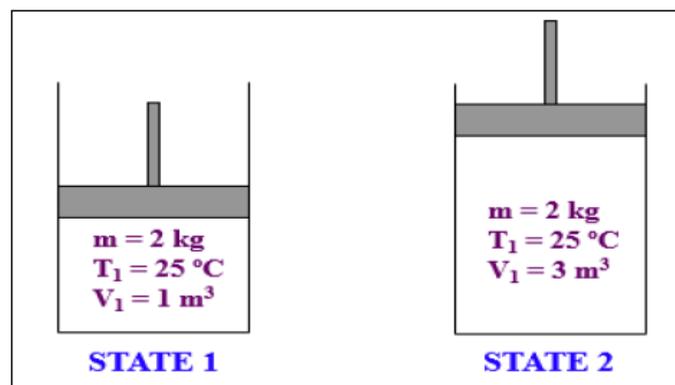
- e.g. pressure (p), amount of substance, mol, energy, E enthalpy, H entropy, S , Gibbs energy, G , heat capacity, C_p , Helmholtz energy, A , internal energy, E , mass, m , volume, V .

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.

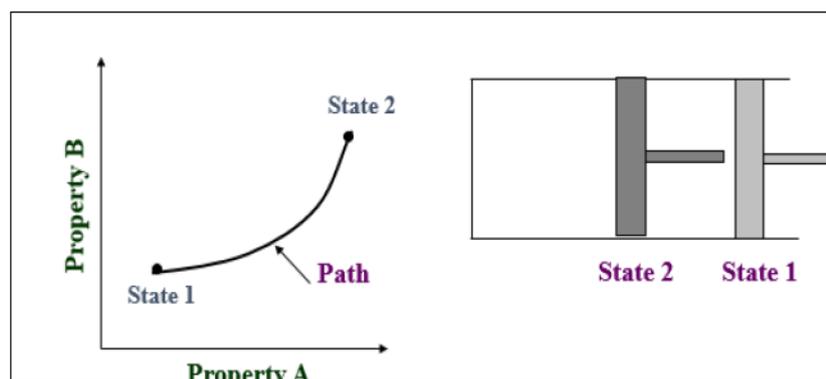
Chemical Equilibrium:

- 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

- Adiabatic – no heat transferred**
- Isothermal – constant temperature**
- Isobaric – constant pressure**
- Isochoric – constant volume**

a) Adiabatic Process

- An adiabatic process transfers no heat; therefore $Q = 0$
- $\Delta U = Q - W$
- When a system expands adiabatically, W is positive (the system does work) so ΔU is negative.

- When a system compresses adiabatically, W is negative (work is done on the system) so ΔU is positive.

b) Isothermal Process

- An isothermal process is a constant temperature process. Any heat flow into or out of the system must be slow enough to maintain thermal equilibrium
- For ideal gases, if ΔT is zero, $\Delta U = 0$
- Therefore, $Q = W$

– Any energy entering the system (Q) must leave as work (W)

c) Isobaric Process

- An isobaric process is a constant pressure process. ΔU , W , and Q are generally nonzero, but calculating the work done by an ideal gas is straightforward

$$W = P \cdot \Delta V$$

- Water boiling in a saucepan is an example of an isobar process

d) Isochoric Process

- An isochoric process is a constant volume process. When the volume of a system doesn't change, it will do no work on its surroundings. $W = 0$

$$\Delta U = Q$$

- Heating gas in a closed container is an isochoric process

Specific Heat Capacity

Specific Heat Capacity: The amount of energy needed to heat substances up. It can be thought of as a measure of how much heat energy is needed to warm the substance up.

Specific Heat Capacity (C) of a substance is the amount of heat required to raise the temperature of 1g of the substance by 1°C (or by 1 K). The units of specific heat capacity are $\text{J } ^\circ\text{C}^{-1} \text{ g}^{-1}$ or $\text{J K}^{-1} \text{ g}^{-1}$. Sometimes the mass is expressed in kg so the units could also be $\text{J } ^\circ\text{C}^{-1} \text{ g}^{-1}$ or $\text{J K}^{-1} \text{ kg}^{-1}$

The equation: The amount of heat energy (q) gained or lost by a substance = mass of substance (m) * specific heat capacity (C) * change in temperature (ΔT)

$$q = m * C * \Delta T$$

1.2.1. Heat Capacity of Ideal Gas

- C_V = heat capacity at constant volume

$$C_V = 3/2 R$$

- C_P = heat capacity at constant pressure

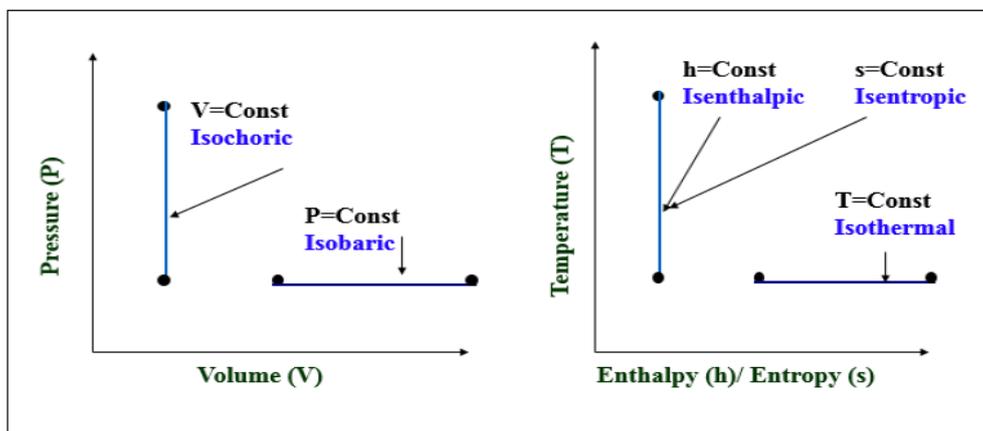
$$C_P = 5/2 R$$

- For constant volume

$$Q = n * C_V * \Delta T = \Delta U$$

- The universal gas constant

$$R = 8.314 \text{ J/mol. K}$$



Cycle:

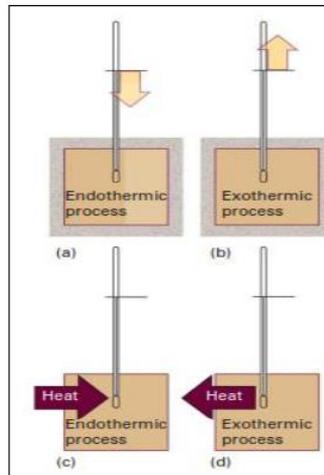
A system is said to have undergone a cycle if it returns to its original state at the end of the process. Hence, for a cycle, the initial and the final states are identical.

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

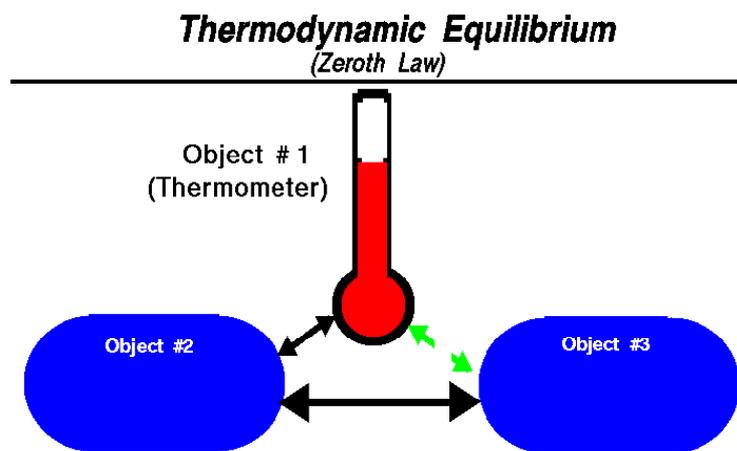
Differential of a path function is called “INEXACT DIFFERENTIAL”.

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

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

1. The Zeroth Law

- The First and Second Laws were well entrenched when an additional Law was recognized (couldn't renumber the 1st and 2nd Laws)
- If objects A and B are each in thermal equilibrium with object C, then A and B are in thermal equilibrium with each other
- Allows us to define temperature relative to an established standard



When two objects are separately in thermodynamic equilibrium with a third, they are in equilibrium with each other. Object in thermodynamic in equilibrium have the same temperature.