Thermodynamics

Lecture : Introduction thermodynamics

Grade: 1th Class

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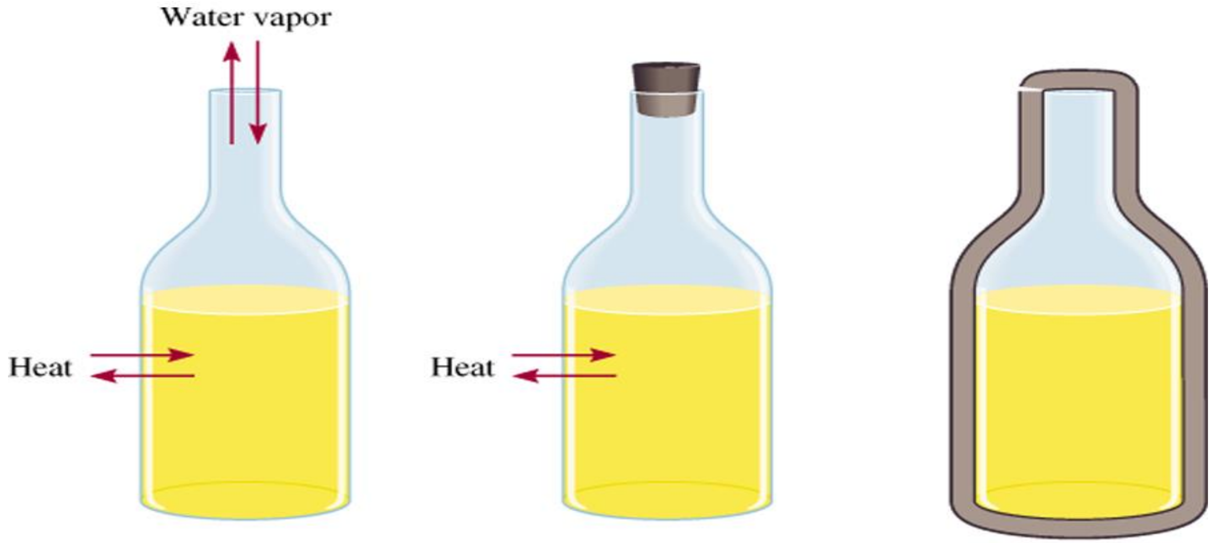
Introduction to thermodynamics

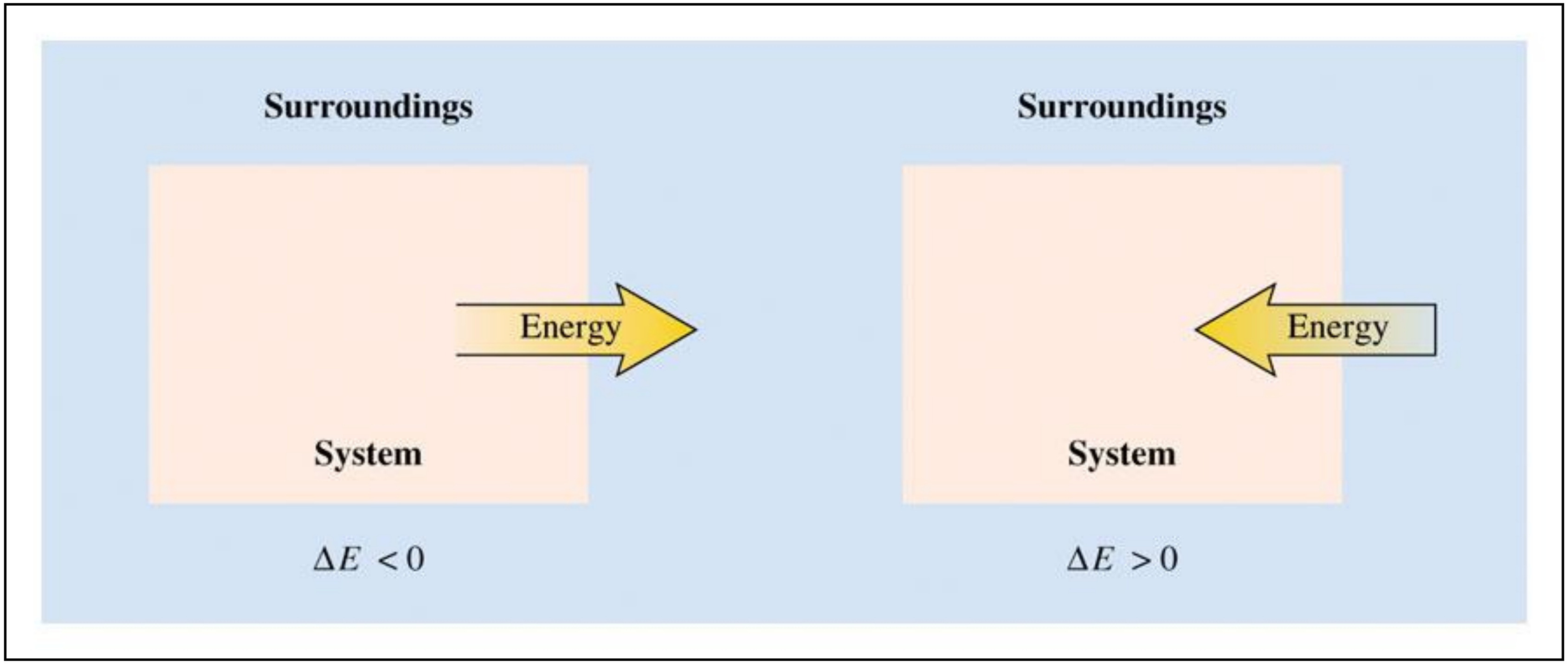
Thermochemistry is part of a broader subject called thermodynamics

The *system* is the specific part of the universe that is of interest in the study.



	open	closed	isolated
Exchange:	mass & energy	energy	nothing

Thermodynamics: Systems and Surroundings



A thermodynamic system is the part of the universe that is under consideration. A boundary separates the system from the rest of the universe, which is called the surroundings. A system can be anything that you wish it to be, for example a piston, and engine, a brick, a solution in a test tube, a cell, an electrical circuit, a planet, etc.

Thermodynamics

- “the branch of science that deals with energy levels and the transfer of energy between systems and between different states of matter”

Temperature

- In thermodynamics, temperature is **always** represented in Kelvins

- K = ºC + 273.15

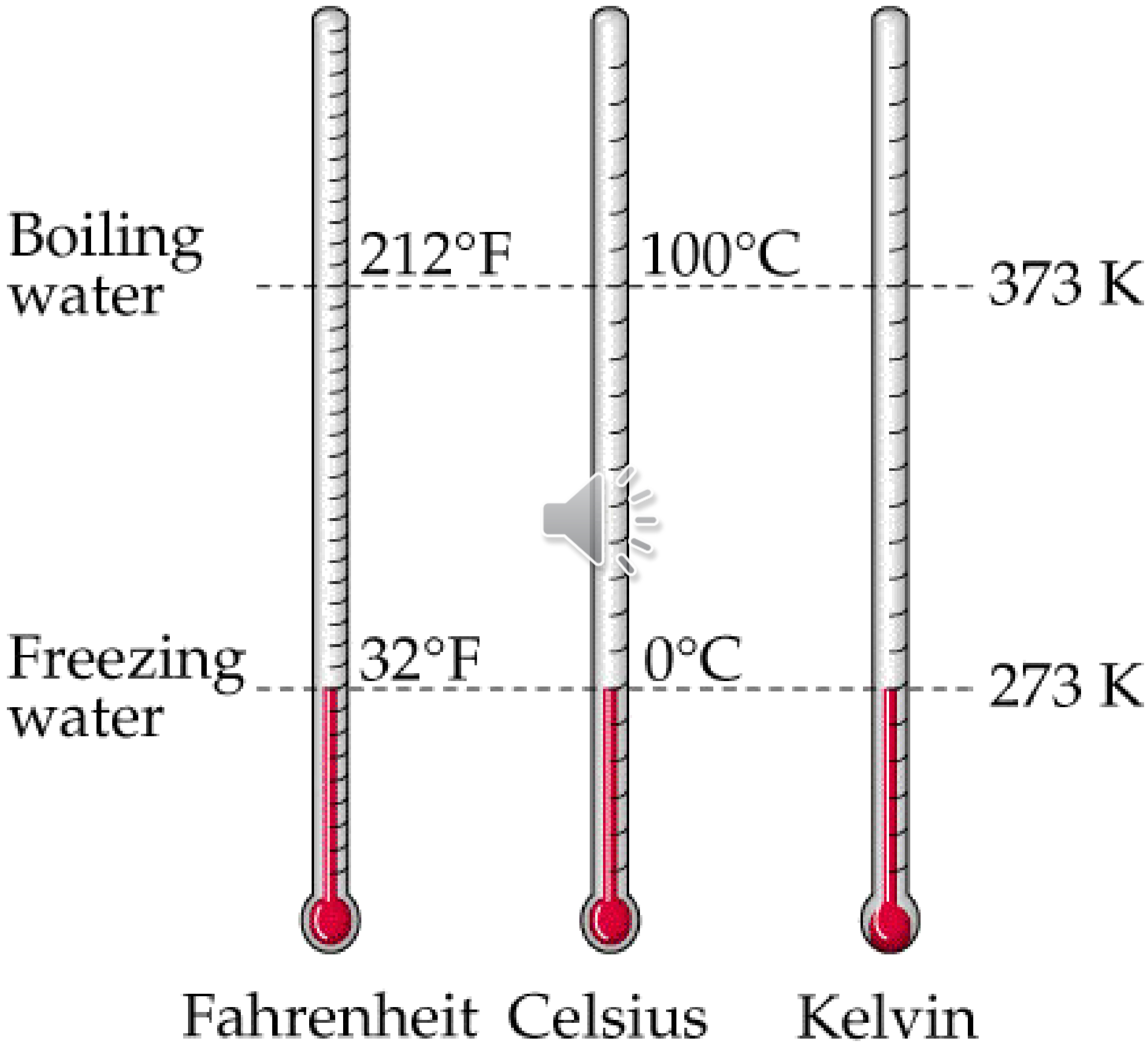
Scales

Temperature normally measured in degrees [º] using one of the following scales:

- Fahrenheit [º**F**].
- Celsius or centigrade[º**C**].
- Kelvin [ºK].

The relationships between the different temperature scales are: -

Celsius to Fahrenheit	$[^\circ F] = [^\circ C] \times {}^9/_5 + 32$
Fahrenheit to Celsius	$[^\circ C] = ([^\circ F] - 32) \times {}^5/_9$
Celsius to Kelvin	$[K] = [^\circ C] + 273$
Kelvin to Celsius	$[^\circ C] = [K] - 273$


Boiling water
212°F
100°C
373 K
Freezing water
32°F
0°C
273 K
Fahrenheit
Celsius
Kelvin

Heat

- The origin of thermodynamics dealt with heat
- Thermo considers heat, and really ANY energy as though it were an indivisible fluid, always flowing from higher to lower energies
- Ergo → signs are + when energy flows from surroundings to the system and – when energy flows from system to surroundings

Work

- Work is another kind of energy
- Different from heat
- Can flow in and out of a system and invoke changes
- Imagine the energy required to lift a book – that work changes the potential energy of the book, but is not related to heat…

Heat (q) and Work (w)

$\Delta E = q + w$

- **q** = Heat absorbed by the system
  - ✓ If $q > 0$, heat is absorbed
  - ✓ If $q < 0$, heat is given off
- **w** = Work done on the system

- Increase the energy of a system by heating it ($q>0$) or by doing work on it ($w>0$).

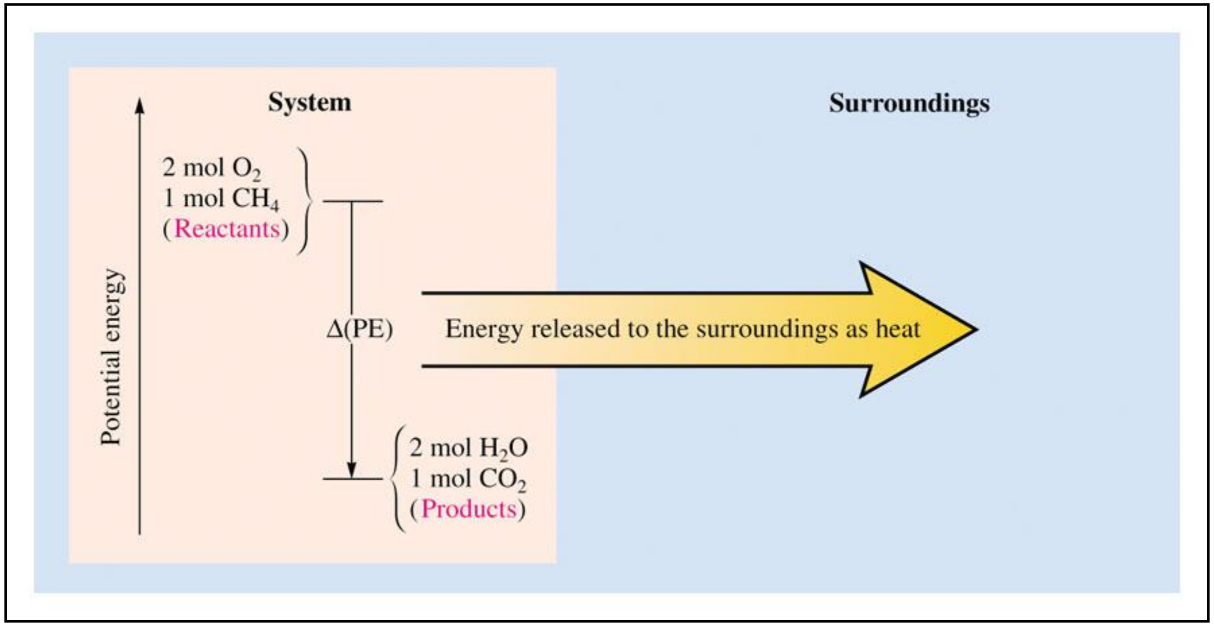
Work

- **w** = Force x distance
  = (Pressure x area) x distance
  = pressure x **$\Delta V = P\Delta V$**

Work is Pressure-Volume work (P-V)

Exothermic reactions release energy to surroundings (by heating the surroundings)

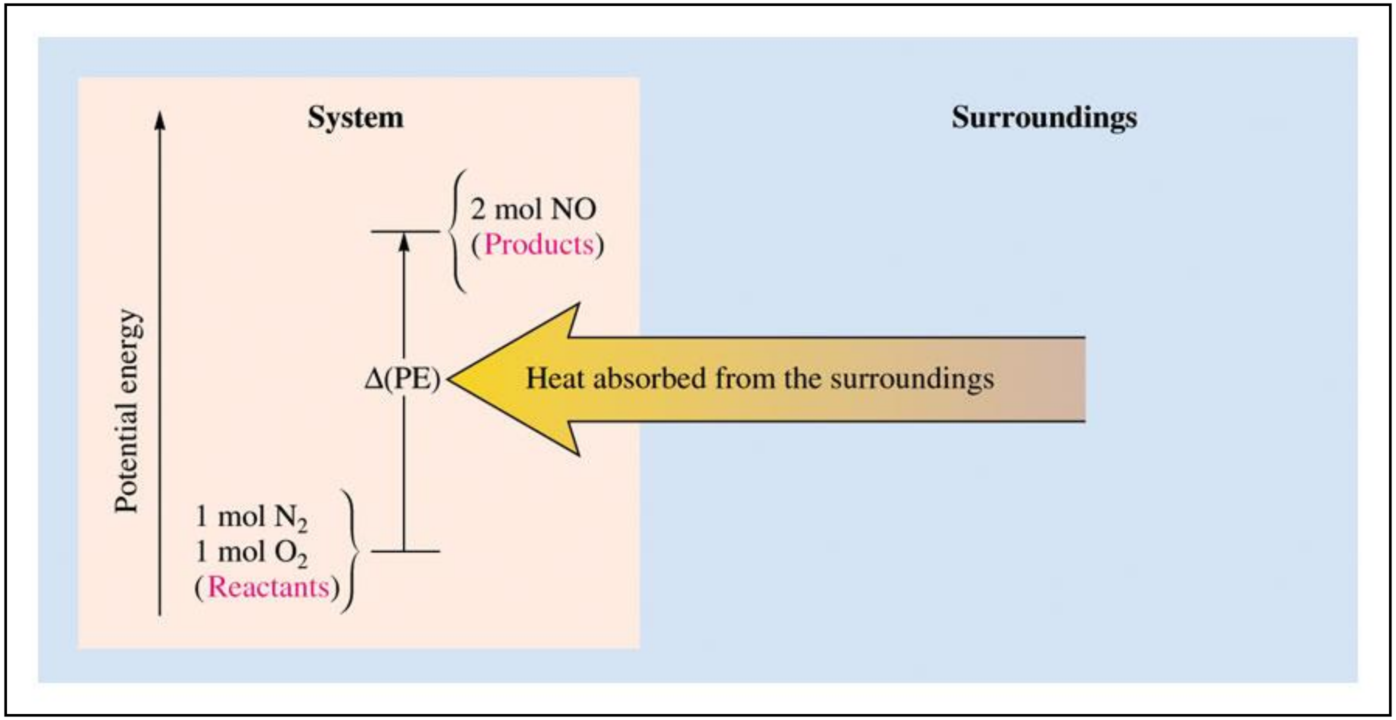
$CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (g)$ **+ heat**



In an **exo**thermic process, the energy stored in chemical bonds/molecular interactions is converted to thermal energy (random kinetic energy).

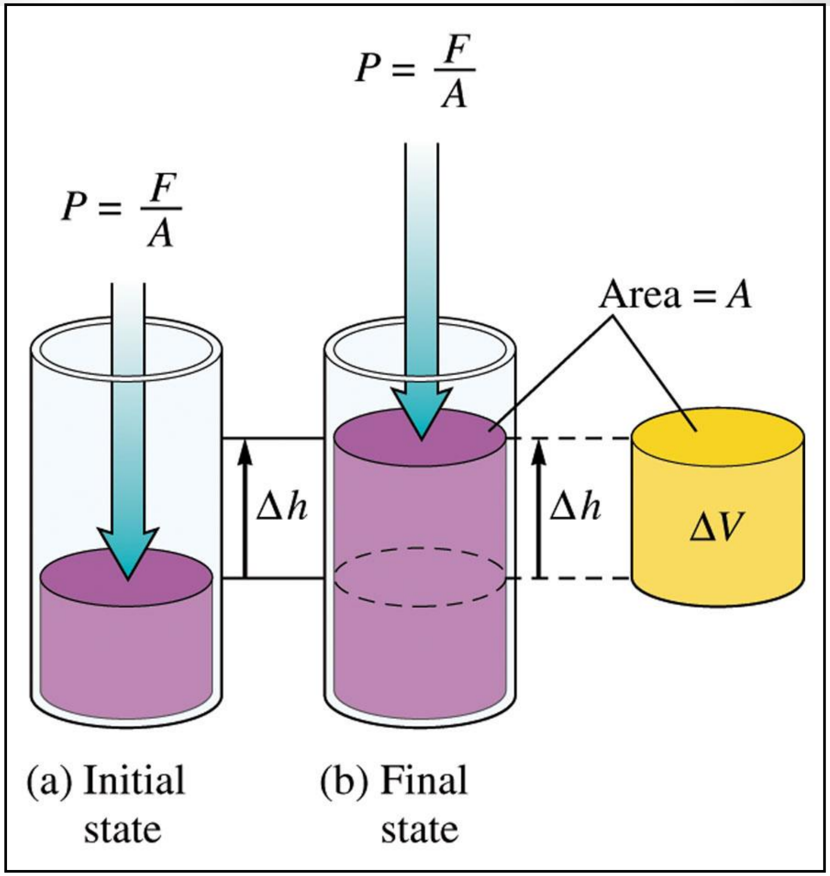
Endothermic reactions absorb energy

$N_2\ (g) + O_2\ (g)$ **+ Energy (heat)** $\rightarrow 2\ NO\ (g)$



An endothermic reaction consumes heat and stores energy in the chemical bonds/molecular interactions of the products.

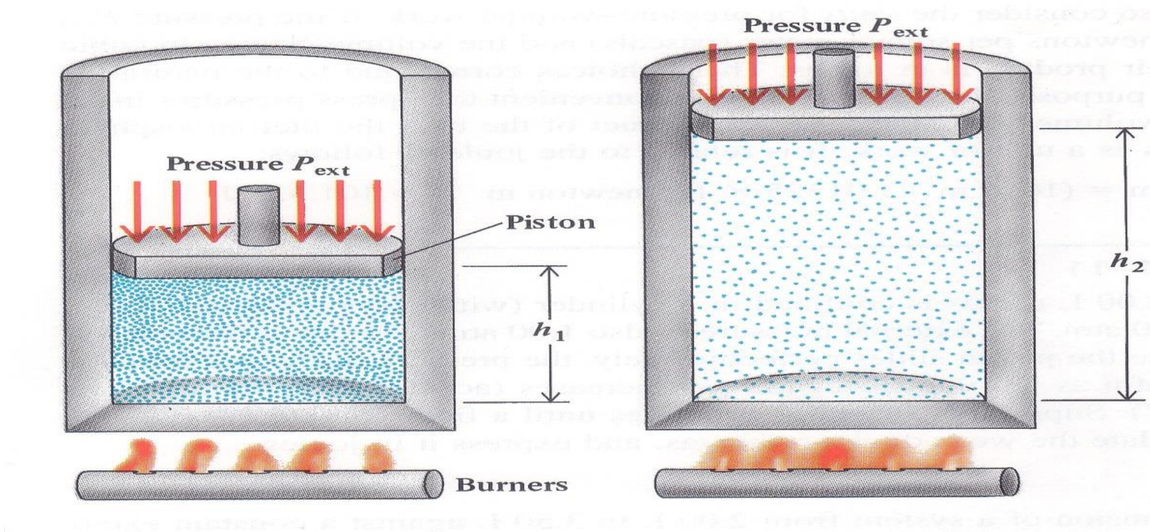
Work



$$w = F \times \Delta h \qquad P = F/A$$

$$P \times A \times \Delta h \qquad \Delta V = A\,\Delta h$$

$$W = P\,\Delta V$$



- Force exerted by heating $= P_1A$
  - Where P_1 is the pressure inside the vessel
  - Where A is the Area of the piston

$$P_{ext} = P_1 \text{ if balanced}$$

$$w = F \times d = F \times \Delta h = P \times A \times \Delta h$$

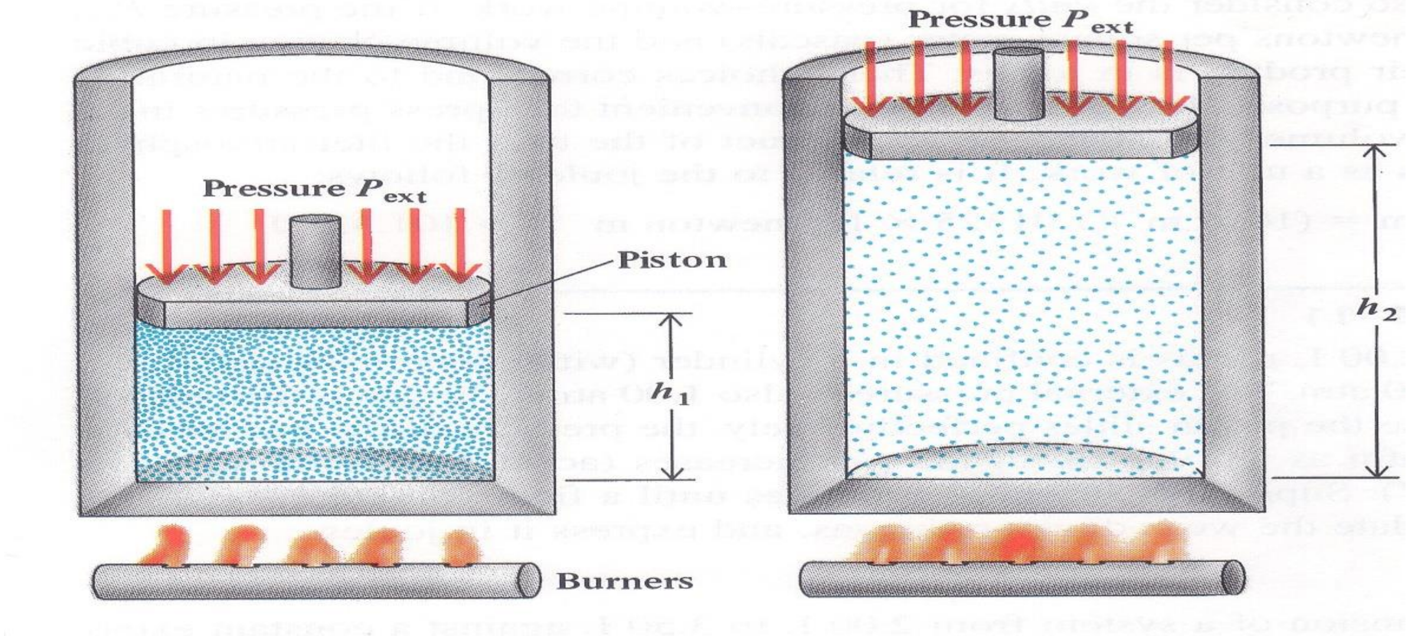
$$\Delta V = A\,\Delta h$$

$$w = -P_{ext}\,\Delta V$$

- Units are atm·L or L atm
- **Where 1 L atm = 101.3 Joules**

ratio of Gas law constants

$$= \frac{\dfrac{8.3145\ \text{J}}{\text{K mol}}}{\dfrac{0.08206\text{L atm}}{\text{K mol}}} = \frac{101.3\text{J}}{\text{L atm}}$$



- Expansion (w<0)
  - The system does work on the surroundings.

- Compression (w>0)
  - The surroundings do work on the system.

Energy

- Many ways to describe energy changes in thermodynamics
- Originally developed to describe changes in heat and ‘work’ (think a steam engine piston)
- Energy flow also describes chemical reactions in systems – but since there is no energy ‘particle’ we must do all of this in a relative sense i.e. one think has more ‘energy’ than another and wins…

Energy

- Energy is the capacity to do work.

- **Energy** is a **state property**, which means it depends on the initial and final state, not the path between them.

$$\Delta E = E_{final} - E_{initial}$$

$$\Delta E_{rxn} = E_{products} - E_{reactants}$$

The nature of energy and types of energy

Energy is : *the capacity to do work*

Work " directed energy change resulting from a process "

work = **force x distance**

Types of energy **:** **.** *Radiant energy*

- *Thermal energy*
- *Chemical energy*
- *Nuclear energy*
- *Potential energy*
- *Kinetic energy*

6-1- Types of energy

- *Radiant energy* comes from the sun and is earth's primary energy source
- *Thermal energy* is the energy associated with the random motion of atoms and molecules
- *Chemical energy* is the energy stored within the bonds of chemical substances
- *Nuclear energy* is the energy stored within the collection of neutrons and protons in the atom
- *Potential energy* is the energy available by virtue of an object's position
- *Kinetic energy* consists of various types of molecular motion and the movement of electrons within molecules.

Enthalpy

- Heat is a means by which **energy is transferred.**
- For processes carried out at constant pressure, the heat absorbed equals a change in **Enthalpy,** **ΔH**.

$$q_p = \Delta H \quad \text{Enthalpy Change}$$

(p denotes constant pressure)

- **Enthalpy** is a **state property**, which means it depends on its initial and final state, not the path between them.

$$\Delta H = H_{final} - H_{initial}$$

$$\Delta H_{rxn} = H_{products} - H_{reactants}$$

Enthalpy

- $\Delta E = q + w = \Delta H + w$ (at constant P)

- If a chemical reaction occurs in solution with no PV work (no change in V), then w=0 and
  $\Delta E = \Delta H$.

- ΔH for a reaction may be either positive (absorbs heat from surroundings) or negative (disperses heat to the surroundings).

- For a gas phase reaction, where **ΔV** is allowed, then **ΔE** $\neq$ **ΔH.**

Phase Changes

Phase changes (are not chemical reactions) but involve enthalpy changes

Melt ice: $H_2O(s) \rightarrow H_2O(l)$ $\Delta H_{fusion} = +6$ kJ at 0C

ΔH_{fusion} is positive means endothermic (add heat)

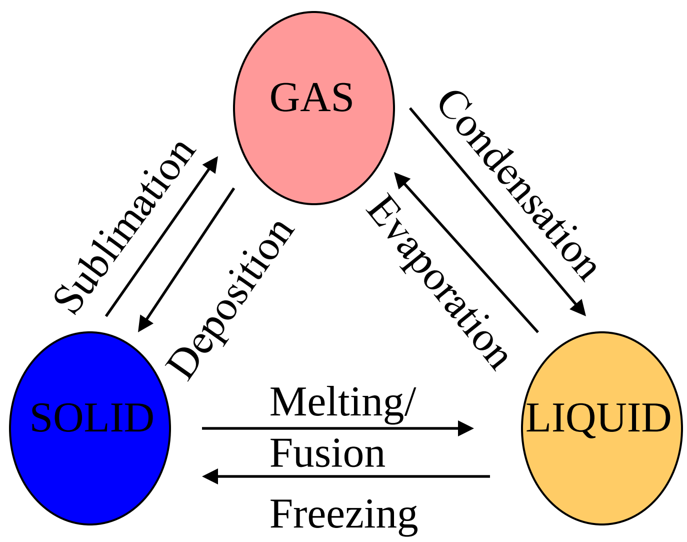
if reversed

$H_2O(l) \rightarrow H_2O(s)$ $\Delta H_{freeze} = -6$ kJ

$\Delta H_{freeze} = -\Delta H_{fusion}$

$\Delta H_{vaporization} = -\Delta H_{condensation}$

$\Delta H_{sublimation} = -\Delta H_{deposition}$



Thermodynamics Equilibrium

Q: Define thermodynamic equilibrium system

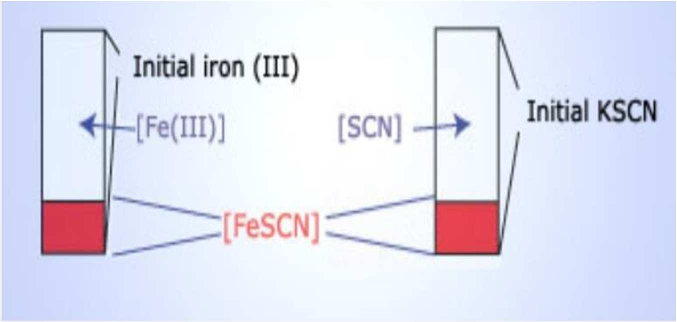
Thermodynamics Equilibrium

A system is said to be in thermodynamic equilibrium if it maintains

a. **Thermal Equilibrium (Equality of Temperature)**

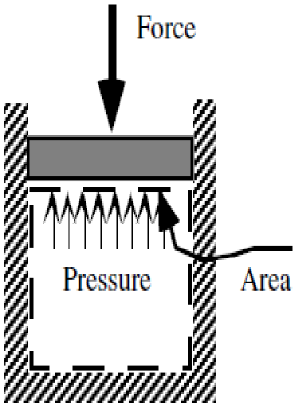
b. Mechanical Equilibrium (Equality of Forces / Pressure)

c. Chemical Equilibrium (Equality of Chemical Potential)

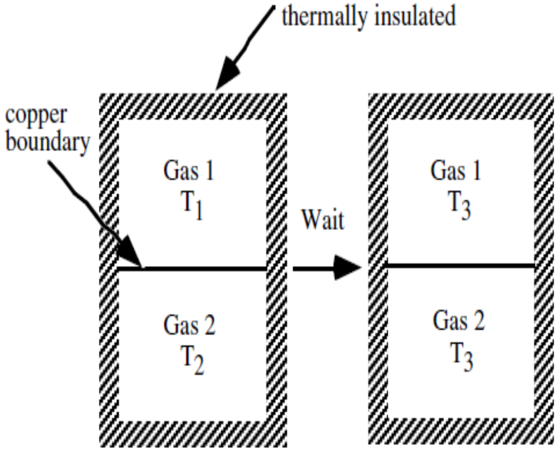


Chemical equilibrium

Same concentration in two systems



mechanical equilibrium
(force balances pressure times area)



thermal equilibrium
(same temperature)

Thermodynamics Equilibrium types

Between the system and surroundings, if there is no difference in

▪ Pressure	→	Mechanical equilibrium
▪ Potential	→	Electrical equilibrium
▪ Concentration of species	→	Species equilibrium
▪ Temperature	→	Thermal equilibrium

No interactions between them occur.
They are said to be in equilibrium.

Thermodynamic equilibrium implies all those together.
A system in thermodynamic equilibrium does not deliver anything.

Definition Of Temperature and Zeroth Law Of Thermodynamics

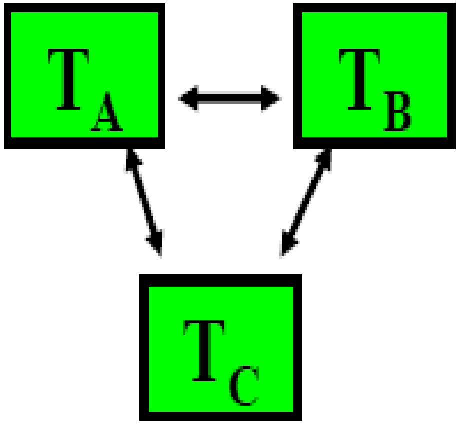
- **Temperature** is a property of a system which determines the degree of hotness.
- Obviously, it is a relative term.

Example g: A hot cup of coffee is at a higher temperature than a block of ice. On the other hand, ***ice is hotter than liquid hydrogen.***

- Two systems are said to be equal in temperature, when there is no change in their respective observable properties when they are brought together. In other words, "when two systems are at the same temperature they are in thermal equilibrium" (They will not exchange heat).

Zeroth Law

If two systems (say A and B) are in thermal equilibrium with a third system (say C) separately (that is A and C are in thermal equilibrium; B and C are in thermal equilibrium) then they are in thermal equilibrium themselves (that is A and B will be in thermal equilibrium with each other.



Q: State Zeroth law of thermodynamics.

Ans. It states if the bodies A and B are in thermal equilibrium with a third body C separately, then the two bodies A and B shall also be in thermal equilibrium with each other.

Explanation of Zeroth Law

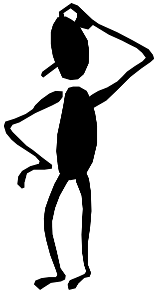
- Let us say TA,TB and TC are the temperatures of A,B and C respectively.
- A and C are in thermal equilibrium. TA= TC
- B and C are in thermal equilibrium. TB= TC

Consequence of ‘0’th law

- A and B will also be in TA=TB
- Looks very logical
- All temperature measurements are based on this Law.

Q: How Zeroth law of thermodynamics is applied in thermometry?

Ans. Zeroth law states that if two systems are each in thermal equilibrium with a third system separately then two systems are also in thermal equilibrium with each other It provide the basis for the measurement of temperature of a system.



A sample of nitrogen gas expands in volume from 1.6 L to 5.4 L at constant temperature. What is the work done in joules if the gas expands (a) against a vacuum and (b) against a constant pressure of 3.7 atm?

$$w = -P\,\Delta V$$

(a) $\Delta V = 5.4\text{ L} - 1.6\text{ L} = 3.8\text{ L}$ $\qquad P = 0\text{ atm}$

$$W = -0\text{ atm} \times 3.8\text{ L} = 0\text{ L•atm} = 0\text{ joules}$$

(b) $\Delta V = 5.4\text{ L} - 1.6\text{ L} = 3.8\text{ L}$ $\qquad P = 3.7\text{ atm}$

$$w = -3.7\text{ atm} \times 3.8\text{ L} = -14.1\text{ L•atm}$$

$$w = -14.1\ \cancel{\text{L•atm}} \times \frac{101.3\text{ J}}{1\cancel{\text{L•atm}}} = -1430\text{ J}$$

Do You Have Any Questions?