Chemical Engineering (Thermodynamics I) (UCH305)

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Lecture 4

Thermodynamic properties

Thermodynamic processes

<u>Outline</u>

- Temperature

- Thermodynamic Equilibrium

- Process, path

- Quasi-static or quasi equilibrium Process

- Various thermodynamic processes

- Cyclic process

- Static process

- Steady-state process

- Point (State) functions & Path functions

Temperature

➢ A **temperature** is an objective comparative measure of *hot* or *cold*.

➢ It is also defined as ***Degree*** of ***hotness*** of any system.

➢ It is measured by a *thermometer.*

➢ the most common scale of temperature:

▪ Celsius (denoted °C; formerly called *centigrade*),

▪ Fahrenheit (denoted °F), and,

▪ especially in science, Kelvin (denoted K).

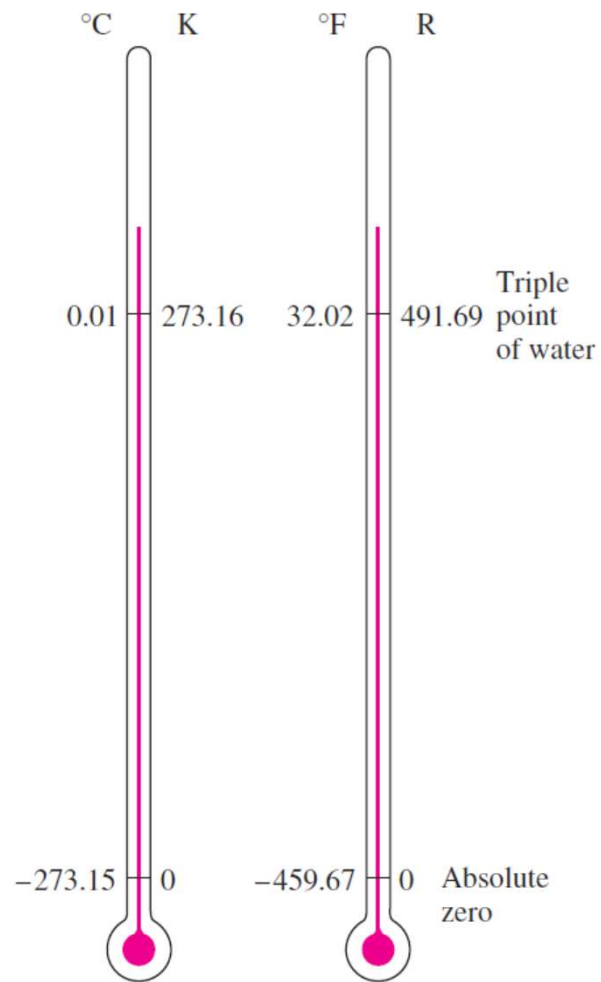A typical Celsius thermometer measures a winter day temperature of −17°C

Temperature scales

	°C	K	°F	°R
Normal H_2O Boiling point	100.00	373.15	211.95	671.67
Normal H_2O Ice point	0.00	273.15	32.00	491.67
Absolute zero	− 273.15	0.00	− 459.67	0.00

Comparison of temperature scales

°C	K	°F	R	
0.01	273.16	32.02	491.69	Triple point of water
−273.15	0	−459.67	0	Absolute zero

Temperature conversion

- $K = {}^oC + 273.15$

- ${}^oR = {}^oF + 459.67$

$$\frac{{}^oC}{100} = \frac{{}^oF - 32}{180}$$

$${}^oC = \frac{5}{9}\left({}^oF - 32\right) \longrightarrow {}^oC = 0.5556\left({}^oF - 32\right)$$

$${}^oF = \left(\frac{9}{5} \times {}^oC\right) + 32 \longrightarrow {}^oF = \left(1.8 \times {}^oC\right) + 32$$

- It is common practice to round the constant in:

  - Kelvin scale to 273, and that in
  - Rankine scale to 460.

- The temperature scales in the two unit systems are related by:

  - T (^{o}R) = 1.8 T (K)
  - T (^{o}F) = 1.8 T (^{o}C) + 32

- At the same time the differential in temperature:

  - ΔT (K) = ΔT (^{o}C)
  - ΔT (^{o}R) = ΔT (^{o}F)

State and Equilibrium

- Consider a system not undergoing any change.

- At this point, all the properties can be measured or calculated throughout the entire system.

- It gives us a set of properties that completely describes the condition, or the **state**, of the system.

- At a given state, all the properties of a system have fixed values.

A system at two different states

- If the value of even one property changes, the state will change to a different one.

- The figure shows a system at two different states.

$m = 2$ kg
$T_1 = 20°C$
$V_1 = 1.5$ m^3

(a) State 1

$m = 2$ kg
$T_2 = 20°C$
$V_2 = 2.5$ m^3
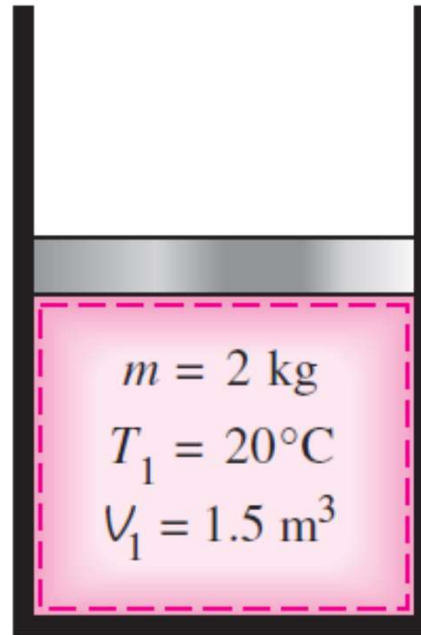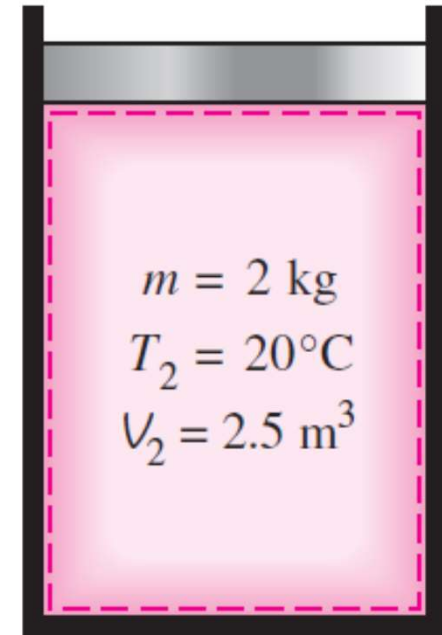
(b) State 2

Equilibrium

- Thermodynamics deals with *equilibrium* states.

- The word equilibrium implies a state of balance.

- In an equilibrium state there are no unbalanced potentials (or driving forces) within the system.

- A system in equilibrium experiences no changes when it is isolated from its surroundings.

- Thermodynamics deals with the equilibrium states, and not with dynamics of the system between such states.

- Thermodynamics doesn't say how long it will take to reach equilibrium or by which path system will attain equilibrium.
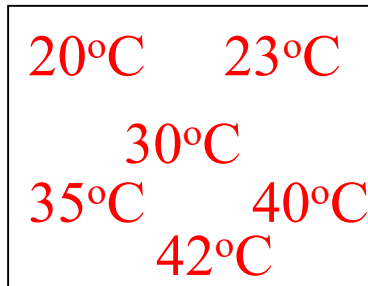
Types of equilibriums

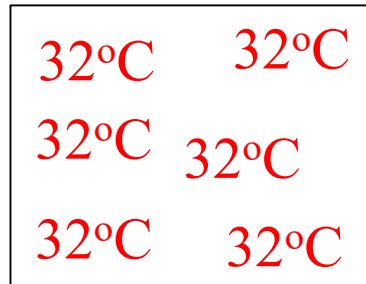➢ Thermal equilibrium

➢ Mechanical equilibrium

➢ Chemical equilibrium

Thermal equilibrium

➤ if the temperature is the same throughout the entire system,

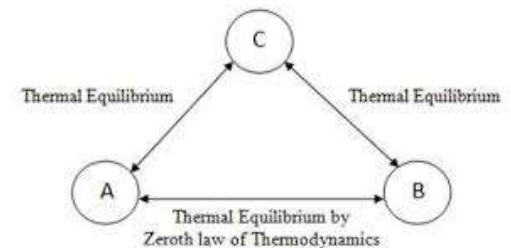➤ the system involves no temperature differential, which is the driving force for heat flow.

A closed system reaching thermal equilibrium.

20ºC   23ºC
    30ºC
35ºC   40ºC
    42ºC
	32ºC 32ºC
	32ºC 32ºC
	32ºC 32ºC

(a) Before

(b) After

Thermal Equilibrium   Thermal Equilibrium
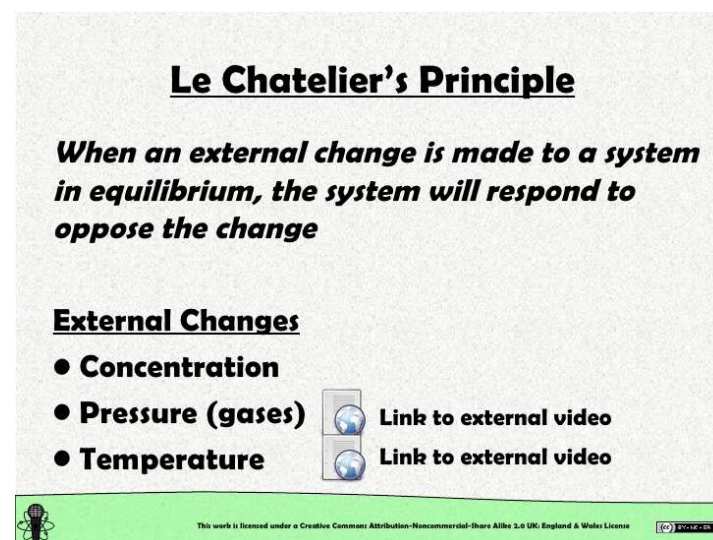
Thermal Equilibrium by
Zeroth law of Thermodynamics

Mechanical equilibrium

➢ if there is no change in pressure at any point of the system with time.

➢ the pressure may vary within the system with elevation as a result of gravitational effects.

Force of sled on tractor   Force of tractor on sled
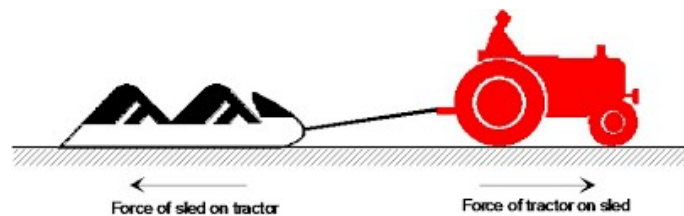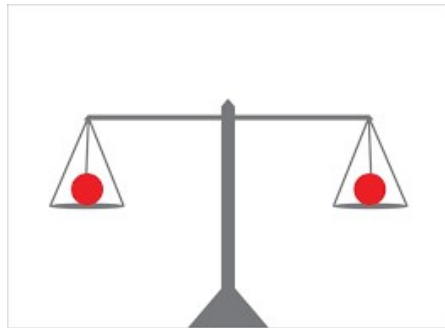
Chemical equilibrium

- if there is no chemical reaction or transfer of matter from one part of the system to another (diffusion) the system is said to exist in a state of chemical equilibrium.

CHEMICAL EQUILIBRIUM

$$AB + C \rightleftharpoons AC + B$$
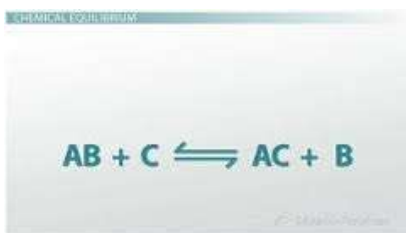
Le Chatelier's Principle

When an external change is made to a system in equilibrium, the system will respond to oppose the change

External Changes
- Concentration
- Pressure (gases)   Link to external video
- Temperature   Link to external video

The State Postulate

- The state of a system is described by its properties.

- But it is not needed to specify all the properties in order to fix a state.

- Once a sufficient number of properties are specified, the rest of the properties assume certain values automatically.

- That is, specifying a certain number of properties is sufficient to fix a state.

- The number of properties required to fix the state of a system is given by the **state postulate**:

The state of a simple compressible system is completely specified by two independent, intensive properties [T, specific volume (v)].

Nitrogen
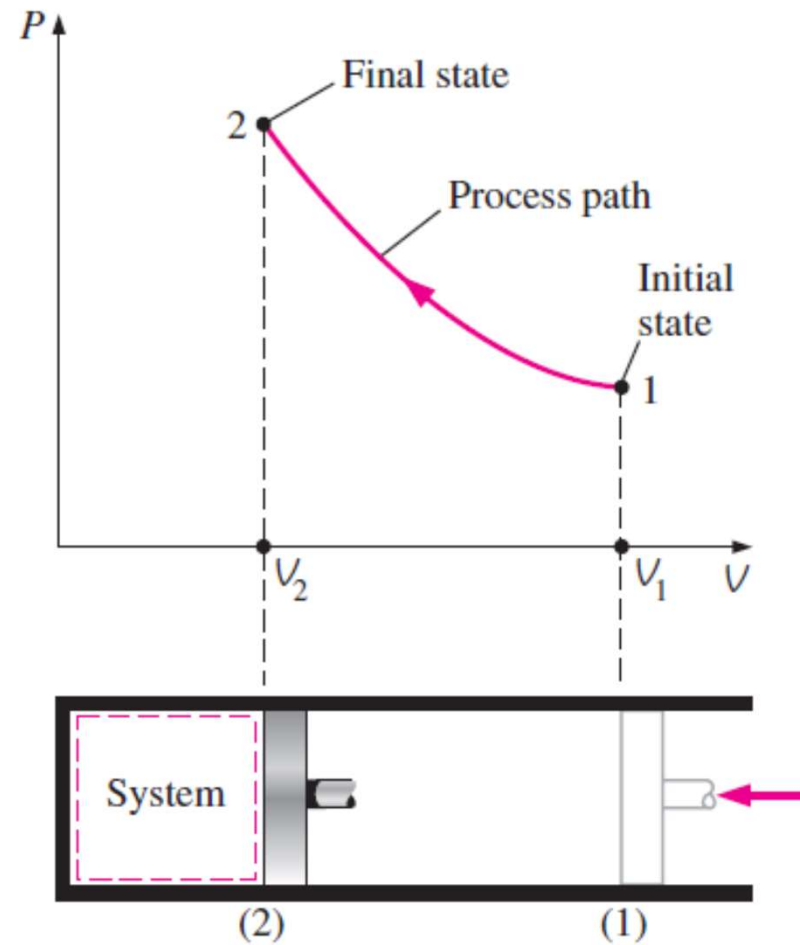$T = 25°C$
$v = 0.9 \text{ m}^3/\text{kg}$
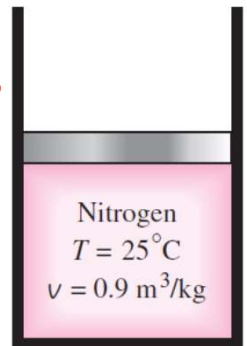
Processes and Path

➢ Any change that a system undergoes from *one equilibrium state* to *another equilibrium state* is called a ***process***.

➢ The series of states through which a system passes during a process is called the **path** of the process.

➢ To describe a process completely,

- it should specify the initial and final states of the process, as well as

- the path it follows, and

- the interactions with the surroundings.

Property A

State 2

Process path

State 1

Property B
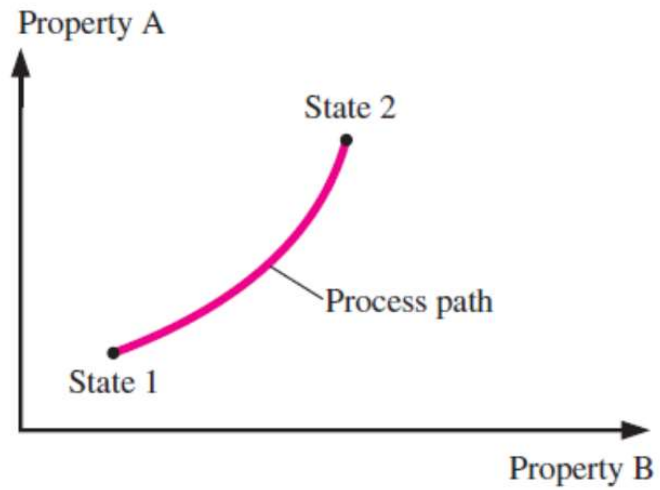
A process between states 1 and 2
and the process path.

P

Final state

2

Process path

Initial
state

1

V_2

V_1

V

System

(2)

(1)

The *P-V* diagram of a compression process.

References

1. *Rao, Y.V.C., Thermodynamics, Universities Press (2004).*

2. *Smith J. M. and Van Ness H. C., Chemical Engineering Thermodynamics, Tata McGraw-Hill (2007).*

3. *Nag, P.K., Engineering Thermodynamics, Tata McGraw Hill (2008) 3rd ed.*

4. *Cengel, Y. A. and Boles, M., Thermodynamics: An Engineeing Approach, Tata McGraw Hill (2008).*

Special Thanks to Professor D. Gangacharyulu.

Thank you for your Patience