CHEMICAL ENGINEERING THERMODYNAMICS I
02. DEFINITIONS AND CONCEPTS

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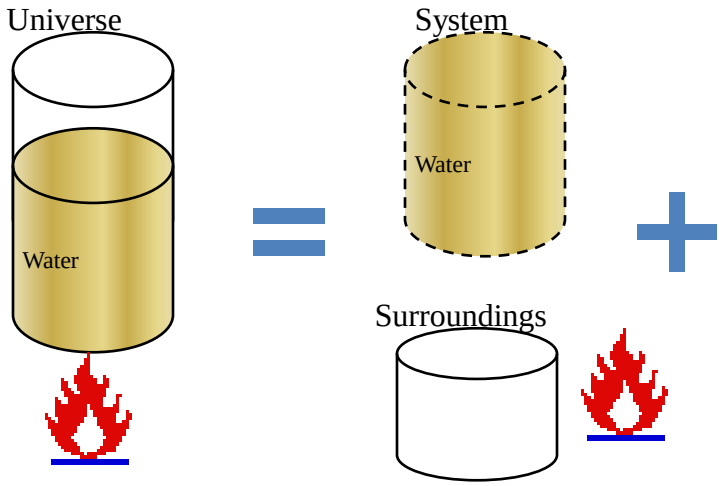
Outline

- What is a system?
- Contact Mechanisms.
- Thermodynamic Variables and properties.
- States.
- Processes.
- Path and state functions.

System, Surroundings and Universe

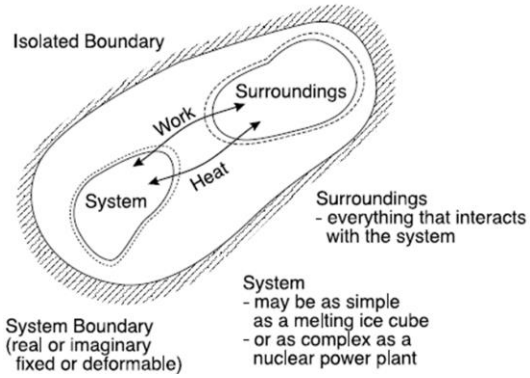
- A **system** is a three dimensional region of space bounded by arbitrary surfaces called **walls** or **boundaries** which delineate the portion of the universe we are interested in studying.
- The **surroundings (or environment)** is the region of physical space outside the arbitrarily selected boundaries of the system.
- The **universe** is the system and its surroundings.

Universe = System + Surroundings



Walls and Boundaries

- The **walls** or **boundaries**
  - May be real or imaginary
  - May change size or shape
  - May be at rest or in motion

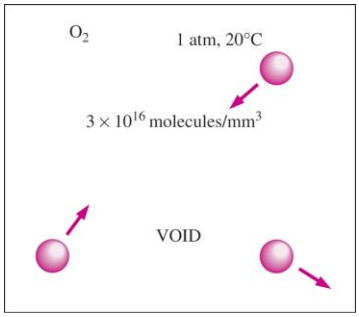


Types of Systems

- **Isolated**
  - Changes in the surroundings do not lead to changes in the system i.e. there is no mode of contact between the system and its surroundings.
- **Closed**
  - Mass is not allowed to be exchanged between the system and its surroundings.
- **Adiabatic**
  - The system is prevented from being in thermal contact with its surroundings.
- **Open**
  - Mass is allowed to be exchanged between the system and its surroundings.

Continuum

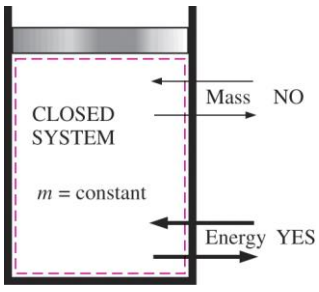
- Matter is made up of atoms that are widely spaced in the gas phase. Yet it is very convenient to disregard the atomic nature of a substance and view it as a continuous, homogeneous matter with no holes, that is, a **continuum**.
- The continuum idealization allows us to treat properties as point functions and to assume the properties vary continually in space with no jump discontinuities.
- This idealization is valid as long as the size of the system we deal with is large relative to the space between the molecules.
- This is the case in practically all problems.
- In this text we will limit our consideration to substances that can be modeled as a continuum.

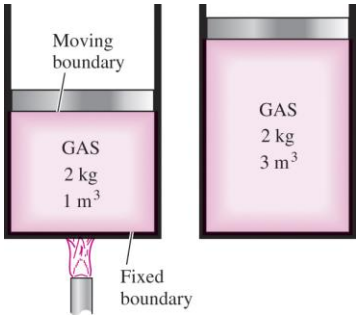


Despite the large gaps between molecules, a substance can be treated as a continuum because of the very large number of molecules even in an extremely small volume.

Control Mass

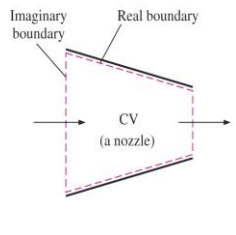
- **Closed system** (**Control mass**): A fixed amount of mass, and no mass can cross its boundary.



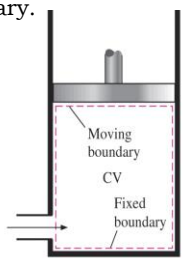


Control Volume

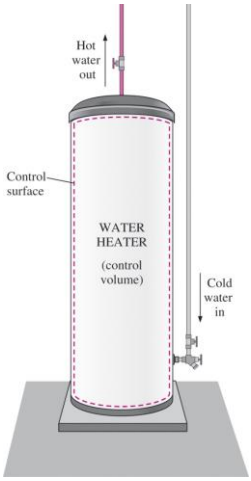
- **Open system (control volume):** A properly selected region in space.
  - Usually encloses a device that involves mass flow such as a compressor, turbine, or nozzle.
  - Both mass and energy can cross the boundary of a control volume.
  - Control surface: The boundaries of a control volume. It can be real or imaginary.



(*a*) A control volume with real and imaginary boundaries



(*b*) A control volume with fixed and moving boundaries



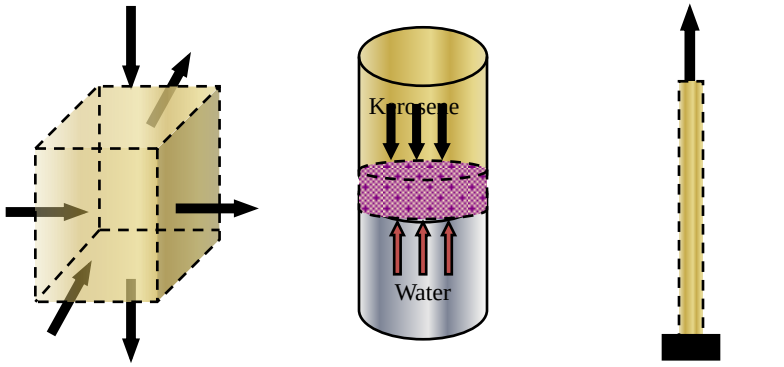
Contact Mechanisms

- The system can be in contact with its surroundings by three distinct mechanisms:
  - **Mechanical contact**
    - Changes in the pressure in the surroundings leads to change in the pressure of the system.
  - **Thermal contact**
    - Changes in the temperature in the surroundings leads to change in the temperature of the system.
  - **Material/Chemical** contact
    - The system and surroundings are able to exchange matter.

Intensive, Extensive and Conjugate Variables

- **Intensive variables**
  - Variables that are independent of the size of the system e.g. T, P, Density etc.
  - Can vary throughout the system (local distributions, nonisotropic).
- **Extensive variables**
  - Variables that scale with the size of the system, and are proportional to its volume, if other conditions are kept constant e.g. mass, volume, total energy etc.
  - Can be transformed into intensive variables by dividing by the total mass/moles or total volume to obtain **specific** properties.
- Extensive and intensive variables tend to come in pairs (**conjugate variables**). The incremental work done on a body is the product of an intensive variable and the increment in the conjugate extensive variable.

Conjugate Variables



a) Pressure & Volume **b) Interfacial tension & area** **c) Tension & length**

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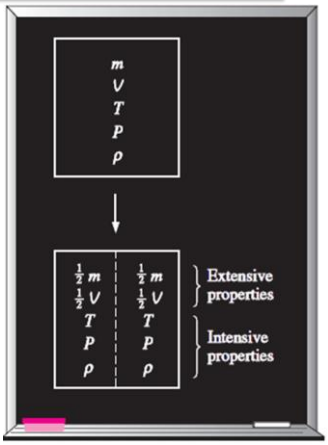
Work = Force × Displacement

System	Intensive	Extensive
Generalized	Generalized force (X)	Generalized displacement (x)
Fluid	Pressure (P)	Volume (V)
Wire (Rubber band)	Tension (F)	Length (l)
Film	Surface or interfacial tension (g)	Area (A)

Thermodynamic Properties

- A system is characterized by thermodynamic variables called properties which can either be intensive or extensive.
- A ***property*** is a macroscopic characteristic of a system such as mass, volume, energy, pressure, and temperature to which a numerical value can be assigned at a given time without knowledge of the previous behavior (*history*) of the system.
- Any of the intensive variables of the equilibrium system e.g. T, P, specific volume, specific energy etc. is a **state variable**.
- The value of any state variable depends only on the equilibrium state of the system, not on the path by which the equilibrium state was reached.

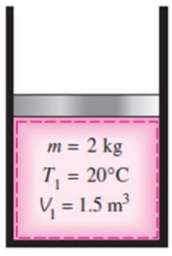


Extrinsic and Intrinsic Properties

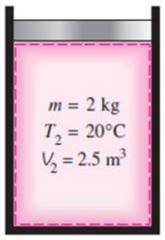
- Properties can be split into two classes
  - **Extrinsic** properties are quantities whose value is **independent of the nature** of the substance within the system boundaries e.g., translational and rotational velocities of a body around its center
  - **Intrinsic** properties are quantities whose value **depend on the nature** of the substance composing the system e.g., density, pressure, and temperature.

Thermodynamic State

- The **thermodynamic state** of a system is the condition of the system as characterized by the values of its properties.
- A **state property** is a property that only depends on the thermodynamic state of the system, not the path taken to get to that state.
- Specifying two state variables uniquely determines the values of all other state variables of an equilibrium, single-component, single-phase system.
- At a given state, all the properties of a system have fixed values.
- If the value of even one property changes, the state will change to a different one.



(a) State 1



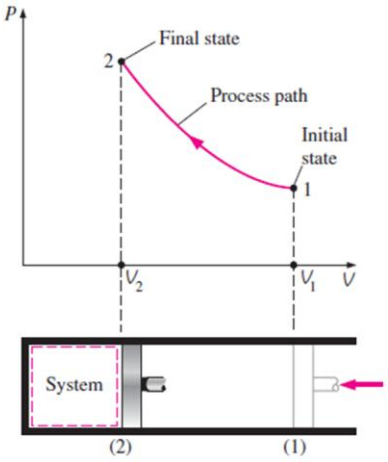
(b) State 2

Thermodynamic Processes and Paths

- **Process**
  - A change or a sequence of changes in the thermodynamic state of the system.
- **Process Path**
  - The specific series of states through which the system passes.
- **Quasistatic process**
  - A process passing through a succession of equilibrium states.
- **To describe a process completely, one should specify the initial and final states, as well as the path it follows, and the interactions with the surroundings.**

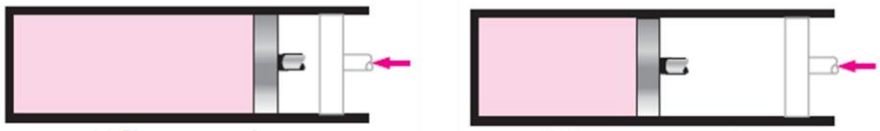
Process diagrams plotted by employing thermodynamic properties as coordinates are very useful in visualizing the processes.

Some common properties that are used as coordinates are temperature T, pressure P, and volume V (or specific volume v).



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

- When a process proceeds in such a manner that the system remains infinitesimally close to an equilibrium state at all times, it is called a quasistatic, or quasi-equilibrium process.
- A quasi-equilibrium process can be viewed as a sufficiently slow process that allows the system to adjust itself internally so that properties in one part of the system do not change any faster than those at other parts.



(*a*) Slow compression (quasi-equilibrium)

(*b*) Very fast compression (nonquasi-equilibrium)

Reversible Processes

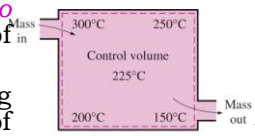
- **Reversible processes**
  - Processes which are quasistatic and for which no dissipative forces are present.
  - Alternatively: these processes in which a second process could be performed so that the system and surroundings can be restored to their initial states with no change in the system or surroundings.
- Reversible processes are possible only if driving forces are infinitesimal (infinitely slow). **An idealization which we approach but we can never attain**.
- Some factors which render **processes irreversible (natural processes)** are friction, unrestrained expansion of gasses, heat transfer through a finite temperature difference, mixing, chemical reaction etc.

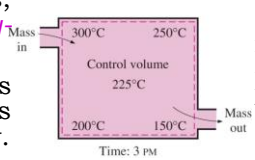
Iso -- Processes

- Iso means constant
  - **Isothermal** process occurs at constant **temperature**.
  - **Isobaric** process occurs at constant **pressure**.
  - **Isochoric** (isometric) process occurs at constant **volume**.
  - **Isentropic** process occurs at constant **entropy**.
  - **Isenthalpic** process occurs at constant **enthalpy**.

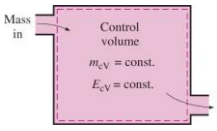
The Steady-Flow Process

- The term *steady* implies *no change with time*. The opposite of steady is *unsteady*, or *transient*.
- A large number of engineering devices operate for long periods of time under the same conditions, and they are classified as *steady-flow devices*.
- **Steady-flow process**: A process during which a fluid flows through a control volume steadily.
- Steady-flow conditions can be closely approximated by devices that are intended for continuous operation such as turbines, pumps, boilers, condensers, and heat exchangers or power plants or refrigeration systems.





During a steady-flow process, fluid properties within the control volume may change with position but not with time.



Under steady-flow conditions, the mass and energy contents of a control volume remain constant.

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Cyclic Processes I

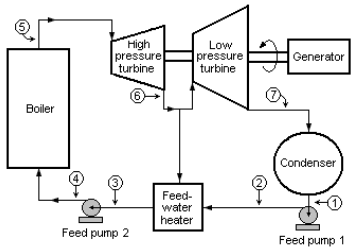
- **Cyclic process**
  - A process such that the system passes through a sequence of states, ending up back in its original state.
  - Mathematically, the cyclic process can be represented for any property as

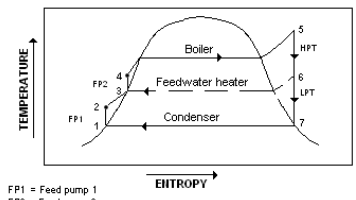
$$\oint d\mathbf{y} = 0$$

- Conversely, if the integral of a quantity dy over an arbitrary cycle is zero, then the quantity y is a property.
- At the conclusion of a cycle all properties have the same values they had at the beginning. Consequently, over the cycle the system experiences no net change of state.

Applications of Cyclic Processes

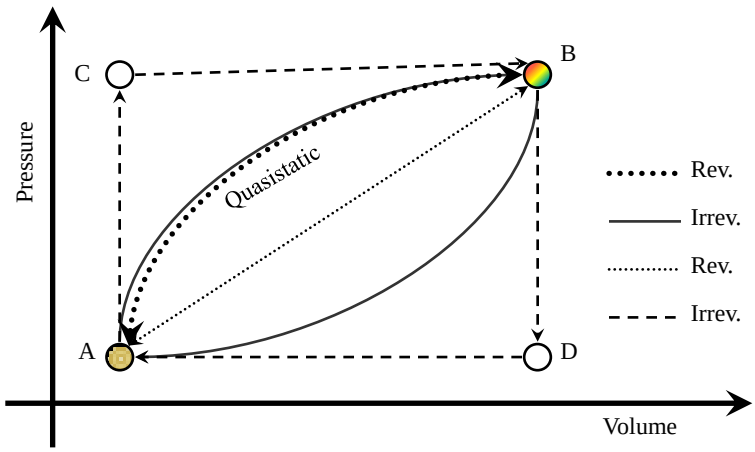
- Cycles that are repeated periodically play prominent roles in many areas of application.
  - steam circulating through an electrical power plant executes a cycle.
  - Refrigerants in a domestic or industrial plant passes through a cycle.





FP1 = Feed pump 1
FP2 = Feed pump 2
HPT = High pressure turbine
LPT = Low pressure turbine

Cyclic Processes II



State Versus Path Functions

- **State functions**
  - Properties of the **system** i.e. properties a substance can possess e.g. *T*, *P*, *S*, *U*, *V*, *H*, *A*, and *G*.
  - Have **exact differentials** (value depends on current state).
- **Path (Process) functions**
  - Properties of a **process** i.e. properties only a process can possess e.g. heat and work.
  - have **inexact differentials** (value depends on how change occurs).

Review

Temperature

- ✓ Temperature Scales
- ✓ International Temperature Scale

Pressure

- ✓ Variation of Pressure with Depth
- ✓ Manometers
- ✓ Other Pressure Measurement Devices
- ✓ Barometer and Atmospheric pressure

Unit and Dimensions

Please refer to the Principle course or the fluid mechanics course for the details.

Note: You will be asked about this in quizzes and exams

Zeroth Law of Thermodynamics

- The zeroth law of thermodynamics states that if two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other.
- Serves as a basis for the validity of temperature measurement.
- By replacing the third body with a thermometer, the zeroth law can be restated as two bodies are in thermal equilibrium if both have the same temperature reading even if they are not in contact.
- The Zeroth Law thus defines a property (temperature) and describes its behavior

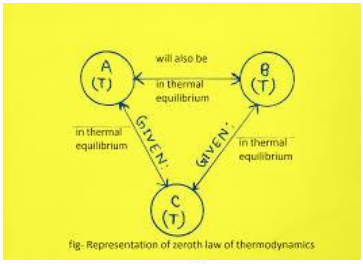
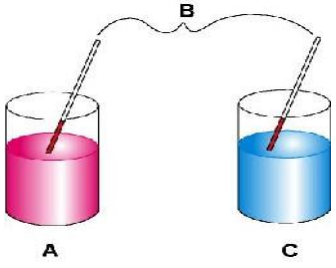


fig- Representation of zeroth law of thermodynamics



Concept Summary

- Define a system, surroundings and universe. Also, know their contact mechanisms.
- Know different kinds of systems and distinguish between them.
- Define intensive and extensive variables and their relation with specific properties.
- Define what is a reversible process.
- Distinguish between state functions versus path functions.
- Know the phase rule and apply it to different situations.
- Define what is a phase and know the different phases of matter.