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Thermodynamics (Equilibria)

and its applications to pharmaceutical systems

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Outlines

- Objectives
- Terminology
- Thermodynamics laws
- Gibbs Free Energy
- Summary

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Objectives

- Theory of thermodynamics.
- Understanding of 1st, 2nd and 3rd laws of thermodynamics and their uses.
- Calculation of free energy.

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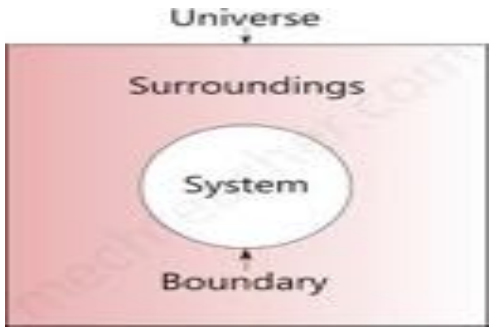
Thermodynamics

- **Interconversions of various forms of energy.**
- **Forms of energy:** mechanical , chemical, electrical, and radiant.
- **Terms:**

❖ A ***system*** in thermodynamics is a well-defined part of the universe that one is interested in studying.

❖ ***Surroundings*** are the rest of the universe, separated from the system by ***boundaries***.



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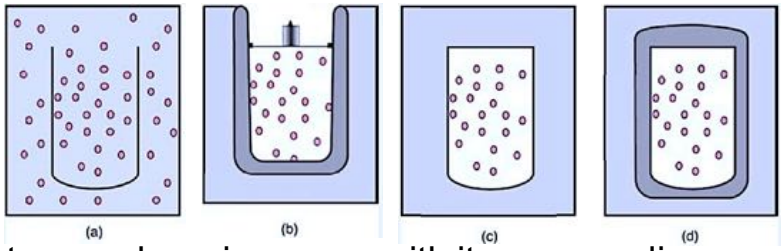
Systems classification



a) Open system exchanging mass with its surroundings
b) Closed system exchanging work with its surroundings;
c) Closed system exchanging heat its surroundings;
d) Isolated system, in which neither work nor heat can be exchanged through boundaries.

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Properties of a system

- Properties of a system is a measurable characteristic of a system that is in equilibrium:

- ***Intensive*** – These are independent of the amount of mass: e.g: **Temperature**, **Pressure**, and **Density**,

- ***Extensive*** – These are varies directly with the mass e.g: **mass**, **volume**, **energy**, **enthalpy.**

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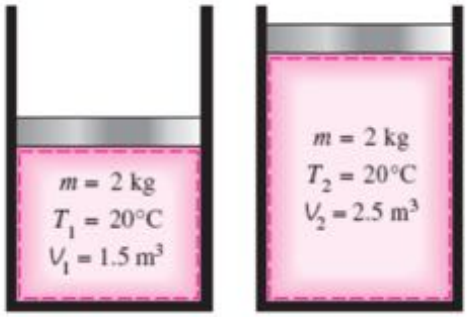
Thermodynamic state

- It is the state of the system with definite value of dependent variable.
- State variables are : **Pressure**, **Temperature**, and **Volume**.

- E_1 is the thermodynamic state of 1 g of water under 1 atm and 10ºC
- E_2 is the thermodynamic state of 1 g of water under 5 atm and 150ºC



(a) State 1 (b) State 2

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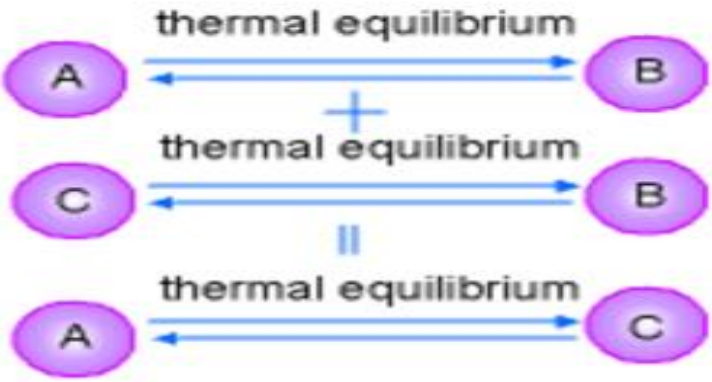
Zeroth Law of Thermodynamics

" If two bodies are in thermal equilibrium with a third body, there are also in thermal equilibrium with each other."



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First Law of Thermodynamics

- **It is the statement of conservation of energy**
- **It is transformed from one to another**
- **It can not created nor destroyed**

Energy = (Mass change) x (Velocity of light)^2

$$\Delta E = E_2 - E_1 = Q + W$$

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Internal energy

- **Isothermal** process: any reaction is said to be conducted isothermally, when the temperature is kept constant.
- **Adiabatic** process: any reaction is said to occur adiabatically, when the heat is neither lost nor gained during a process.
- **T/F with explanation**:
  - In an adiabatic process when work is done by the system and the internal energy decreases, temperature must fall.
  - The internal energy of an isolated system is constant.
  - For a thermodynamic cycle the net heat supplied to the system equals the net work done by the system.
  - In an isolated system, Q=–W

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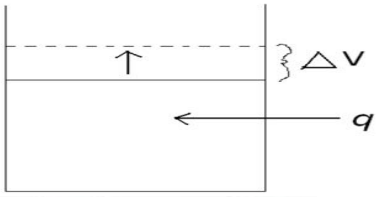
Work

- It is produced by varying the volume of the system against constant external pressure.
- Expansion or Compression.

$$W = -P_{ex} * \Delta V$$



- Reversible Process:

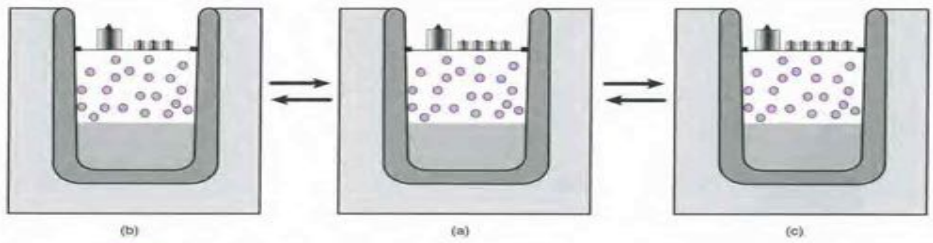


Fig. 3–3. A reversible process: evaporation and condensation of water at 1 atm in a closed system. (*a*) System at equilibrium with P_{ex} = 1 atm; (*b*) expansion is infinitesimal; (*c*) compression is infinitesimal.

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Maximum work

- The work done by a system in an isothermal expansion process is at a maximum when it is done reversibly.
- No work is accomplished if an ideal gas expands freely into a vacuum, where $P_{ext} = 0$, because any work accomplished depends on the external pressure.