Thermodynamic Equilibrium

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Isolated systems & TD equilibrium

- Systems that cannot exchange BOTH matter and energy with the surrounding- Isolated
- TD equilibrium=None of the TD properties are changing with time at a measurable rate (Methods of TD, H. Reiss)
- Equilibrium is unique & is irrespective of the irreversible pathways via which the system reaches the equilibrium state
- Uniqueness of the equilibrium state for simple systems is easy to rationalize because the TD properties are related via an equation of state, f(TD variables)=0
- Reproducibility and relevant TD variables/properties is not straight forward in complex systems: Solids like thermally treated steel/glass that are strained during processing, heterogeneous systems…

Equation of state

- Ideal gas equation of state; PV=nRT
- Total number of independent variables can be chosen via "Gibbs phase rule", Degree of freedom (to be discussed in latter lectures);

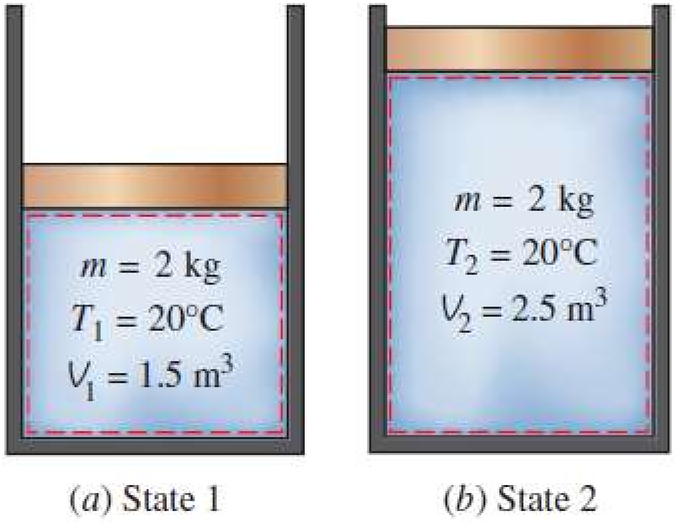


FIGURE 1–26
A system at two different states.

Fig: C & B: TD

TD equilibrium state

- At equilibrium state: no driving forces for change within the system.
- Thermal equilibrium: Temperature is uniform in the entire system & does not vary with time
- Mechanical equilibrium: Pressure is uniform in the entire system & does not vary with time
- Chemical equilibrium: Chemical composition of a system does not change with time, that is, no chemical reactions occur
- Phase equilibrium: For system with more than one phase, mass of different component in each phase does not change with time

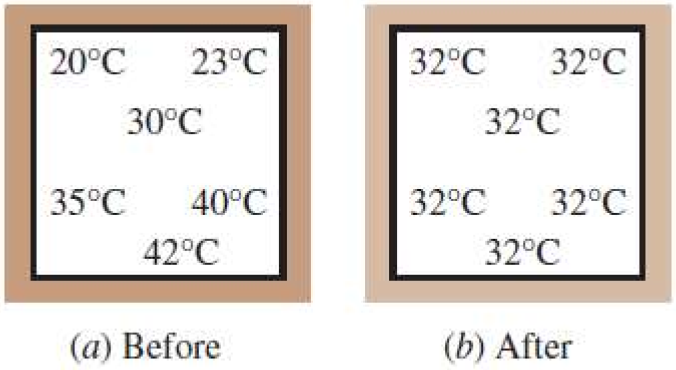
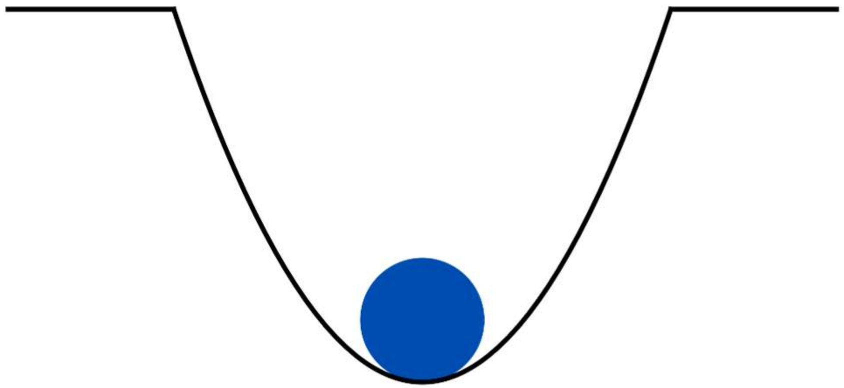


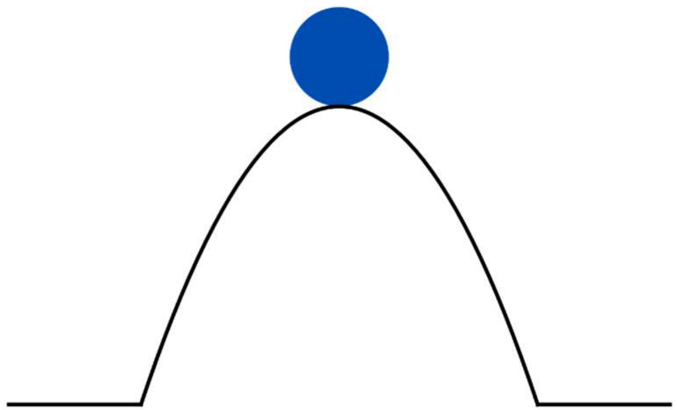
FIGURE 1–27
A closed system reaching thermal equilibrium.

Fig: C & B: TD

Avatars of TD states

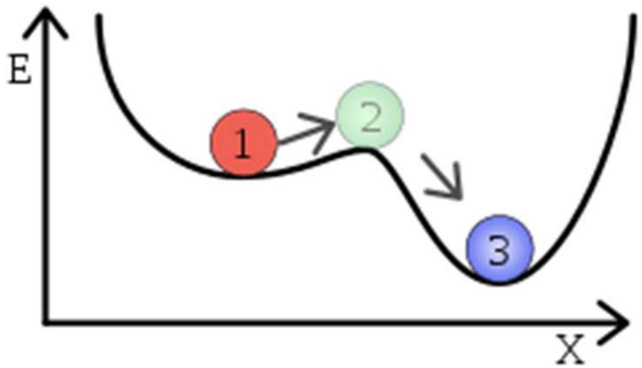


- Stable equilibrium & fluctuations



- Unstable & neutral equilibrium are rare in TD

- Metastable states do occur; Metastability is an internal constraint



Wikipedia

Transformation via quasi static/equilibrium states

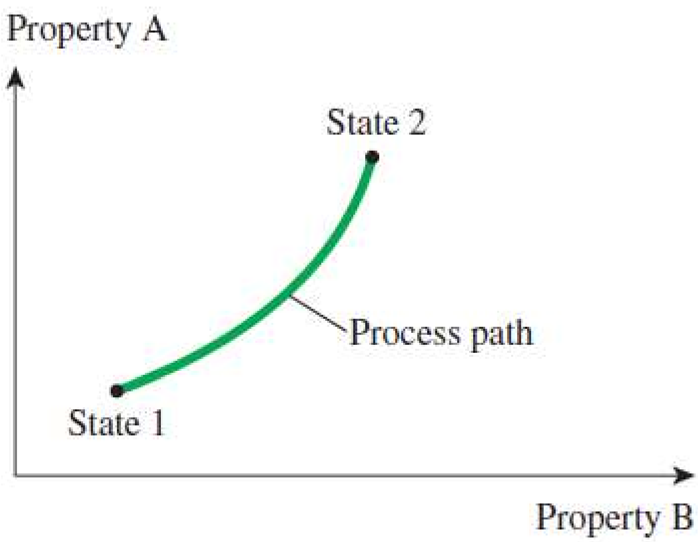


FIGURE 1–29
A process between states 1 and 2 and the process path.

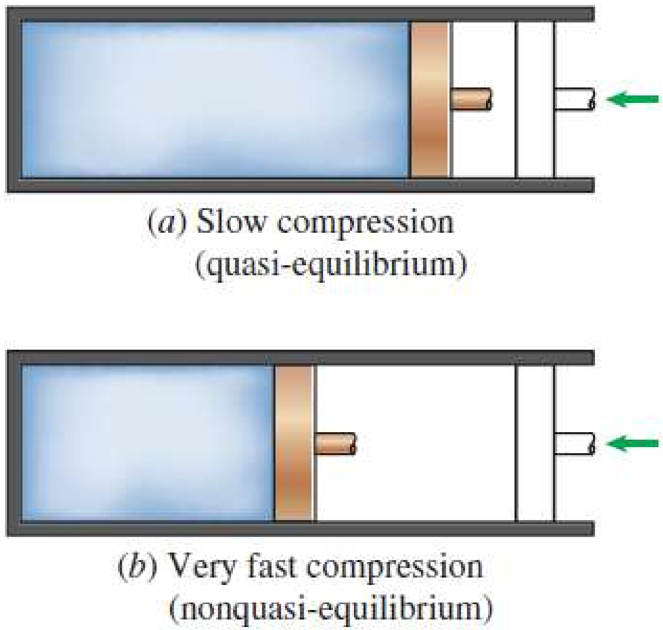


FIGURE 1–30
Quasi-equilibrium and nonquasi-equilibrium compression processes.

Fig: C & B: TD

Typical TD processes

- Isothermal process
- Isobaric process
- Isochoric (or isometric) process
- Cycle: Linear cyclic motion of a piston to rotary motion of the wheel...

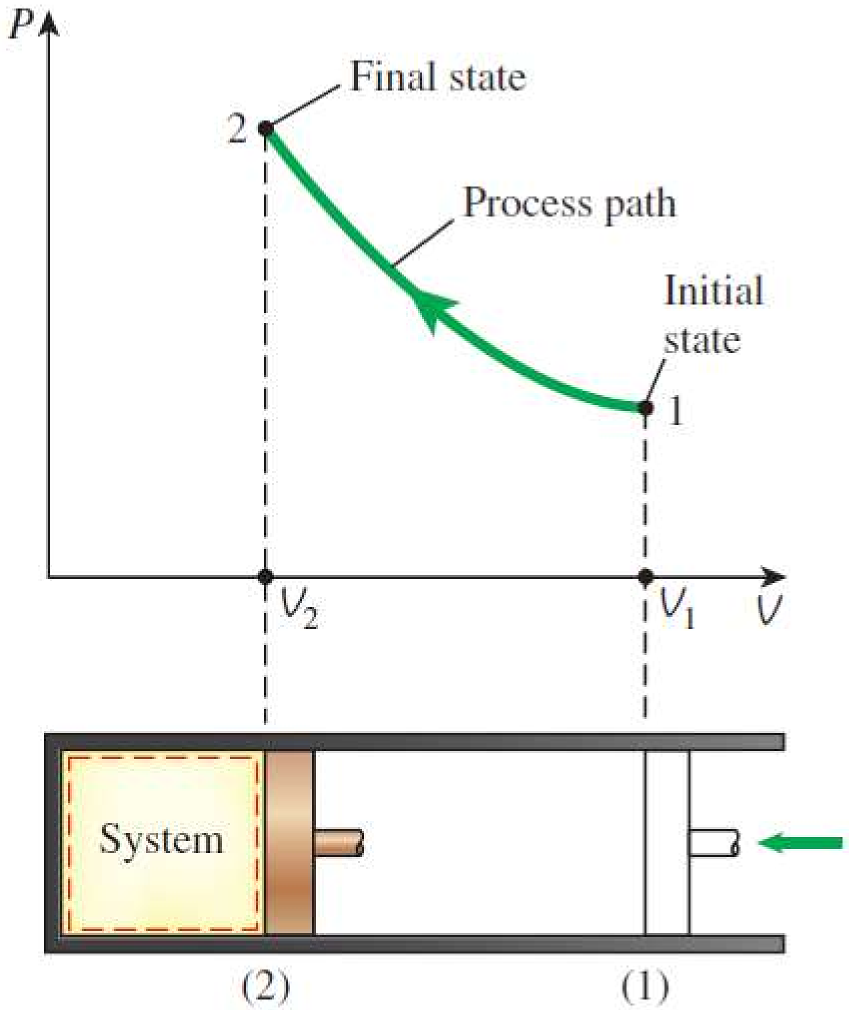


FIGURE 1–31

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

Fig: C & B: TD