What is Thermodynamics?

* The branch of physical science that deals with the relations between heat and other forms of energy [New Oxford American Dictionary]

* The branch of physical science concerned with equilibrium in materials systems [Encyclopaedia Britannica]

* The study of restrictions on the physical properties of matter that follow from the symmetry properties of the fundamental laws of physics [Callen]

→ relates observable, macroscopic properties to each other

→ Completely general, can be developed rigorously from a small number of postulates based on experimental observations

→ no need to invoke molecular hypothesis

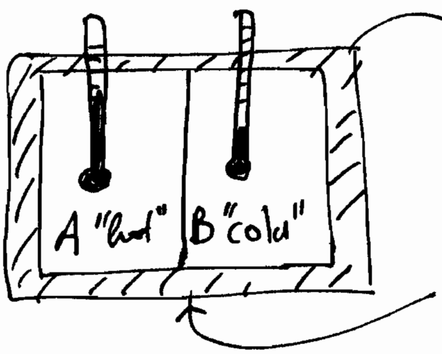
Why do Chemical Engineers need Thermodynamics?

It sets limits on allowable processes:

- at a certain T and P, will a liquid vaporize?
  will a crystal melt?
  will a protein unfold?
- what is the concentration of a pollutant in fish ~~fat~~ tissue?
- how much work is needed to compress a gas?

Temperature

* Need to quantify intuitive notion of "hot" and "cold"
* Standard measurement devices - e.g. liquid-in-glass thermometers w/ given dimensions + materials



"Zeroth Law" of thermodynamics: such systems reach the same thermometric temperature after a sufficiently long time has passed.

→ Allows construction of temperature scales given two reference points (e.g. melting + boiling of H_2O at atmospheric pressure)

Ideal-gas scale: $P\underline{V} = A\theta + B$

↑ molar volume (intensive)

Picking A, B defines temperature scale

If we set $B=0$, we obtain T, the "thermodynamic" temperature scale

→ $P\underline{V} = RT$ R: universal constant, $8.3145 \frac{J}{mol\,K}$

Common scale: θ (°C) 0°C ≡ melting of H_2O, 100°C ≡ boiling of H_2O

$$\boxed{\theta = T - 273.15}$$

Definitions

System: A well-defined region of space in which we are interested. Can be stationary or moving, a fixed volume or a given amount of matter

Surroundings (aka "environment"): {The Universe} − {the system}

Boundary: Surface dividing system and its surroundings may be physical (e.g. wall) or abstract

Systems are characterized in terms of the types of exchanges (flows) that occur across their boundaries:

open/closed: permeable / impermeable to mass flow (e.g. opened/unopened soda can)

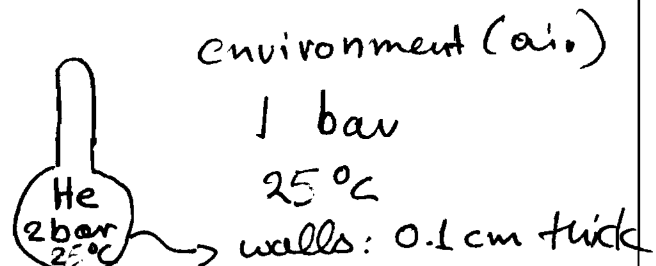
movable / rigid: constrain (or not) a system to a fixed volume

adiabatic / diathermal: impermeable / permeable to "heat" (defined by observing changes in θ)

A system surrounded by impermeable, rigid and adiabatic boundaries is isolated.

Example 1.1.

Hermetically sealed glass bottle containing He gas



Is this a closed or an open system?

Diffusion coefficient D of He through glass:

$D = 8\cdot10^{-9}\ cm^2/s \qquad \ell = 0.1\ cm$

Characteristic time? Dimensional analysis suggests:

$$t = \frac{\ell^2}{D} = \frac{0.1^2\ cm^2}{8\cdot10^{-9}\ cm^2/s} = 1.2\cdot10^6 s \simeq 14\,d$$

for "short" times $\ll$ 2 weeks → effectively closed

for "long" times $\gg$ 2 weeks → open to He

How about O_2 or N_2?

Thermodynamics cannot tell you if your assumptions about a system (e.g. closed or open) are correct. Only careful analysis (and eventually comparison with experiments).

Equilibrium States

Basic postulate: There exist stable equilibrium States for systems with given internal + external constraints (e.g. fixed volume, isolated etc), fully characterized by $\boxed{n+2}$ independent thermodynamic variables (3 for $n=1$, one-component)

* Huge reduction in # of variables relative to non-equilibrium states.