Classical Thermodynamics

"Concerned with the relationships between certain macroscopic properties of a system at equilibrium"
— Hill

"The study of the restrictions on the possible 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: valid irrespective of assumptions about existence or type of forces between molecules

PROVIDED THAT THE ASSUMPTIONS OF EQUILIBRIUM ARE SATISFIED

Statistical Mechanics

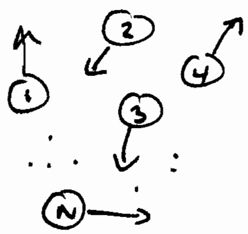
"The molecular theory of macroscopic properties of thermodynamic systems"
— Hill

"The theory with which we analyse the behavior of natural or spontaneous fluctuations" — Chandler

- relates microscopic properties to macroscopic observables
- rigorous results are difficult to obtain
- Increasing usefulness because of advent of numerical simulations to obtain properties

Question

The energy of a macroscopic mechanical system (e.g. weights in gravitational field) is a well-defined quantity [ability to produce work]. However, for a thermodynamic system, one needs to be extremely careful about the "energy."



N molecules – $N \simeq O(10^{23})$

Is the energy $\stackrel{?}{=} \sum_{\text{all molecules}} \frac{1}{2} m u^2$

How can it be measured?

Is thermodynamic "energy" equivalent to mechanical energy (i.e. with respect to ability to produce work)

→ Answers to be provided shortly

Definitions

System: A well-defined contiguous region of space. Does not have to be of fixed volume or contents.

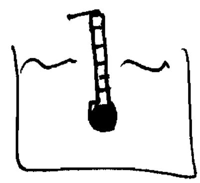
Environment: {The universe} – {The system}

Boundary: Zero-volume surface dividing system + environment

How do we characterize a system?

<u>Primitive (observable) properties</u>: The result of a standardized macroscopic measurement on a system that does not change any properties (disturb it).

Example: standard "thermometer" measure length of column of liquid in tube after a certain amount of time has passed



Example of measurable non-primitive property: image of atoms in an STM (not macroscopic)

Example of macroscopic non-primitive property: energy (not measurable)

Classification of Boundaries	System
permeable / impermeable to mass	open / closed
movable / rigid	(not) constant - volume
permeable / impermeable to "heat"* *defined by observing changes to thermometric temperature	adiabatic / diathermal

Example

Hermetically sealed glass bottle containing He gas :

environment:
1 bar
300K

Is this an open or closed system?

$D \simeq 10^{-8}\ cm^2/s$ diffusion coefficient of He through glass

$L \simeq 0.2 cm$ glass thickness

$t = L^2/D = 46$ days

Depending on time scale of observation,

$t \ll 50$ days → closed
$t \gg 50$ days → open
} both valid!

In the first case, $t \ll 50$ days $P_{\text{"final"}} = 2$ bar

In the second case $t \gg 50$ days $P_{\text{"final"}} = 1$ bar

Thermodynamic reasoning, by itself, cannot tell you which one is a "better" description – only comparison with experiment will tell you if your assumptions are not correct.

Definitions (Continued)

<u>Simple Systems</u>: No external fields, no internal boundaries

<u>Composite Systems</u>: Two or more simple systems considered together.

<u>Internal restraints</u>: Related to the "time scale" issue discussed previously. Barriers to heat or mass transfer, or slow chemical reactions

For example, $O_2 + H_2$ at 0°C, 1 bar, in the absence of a catalyst do not react to form H_2O. When dealing with such a system, the absence/presence of catalyst is an internal restraint.

POSTULATES

A minimal set of empirically justified statements about the behavior of macroscopic systems.

[The specific set is not unique - other sets would also work, just as in axioms of geometry]

I For closed, simple systems with given internal restraints, there exist <u>stable equilibrium states</u> which can be fully characterized by the values of <u>two</u> independently variable primitive properties in addition to the masses of chemical species initially charged

II All systems, simple and composite, in processes for which there is no effect on the environment, will change in such a way as to approach a single stable equilibrium state for each subsystem. In the limiting condition, the entire system is said to be at equilibrium.

Postulate II forms the basis for the "second Law" of Thermodynamics.

Thermodynamic Processes

Change of state of a system: Change in at least one primitive property

Path: Description of all states a system traverses during a change of state. If all intermediate states are equilibrium states the path is termed "quasi-static"

Nomenclature

Intensive (per mole or unit of mass) versus Extensive (total) properties:

$\underline{V}$ $\underline{E}$ $\underline{U}$ are extensive (exception: N)

V E U " intensive