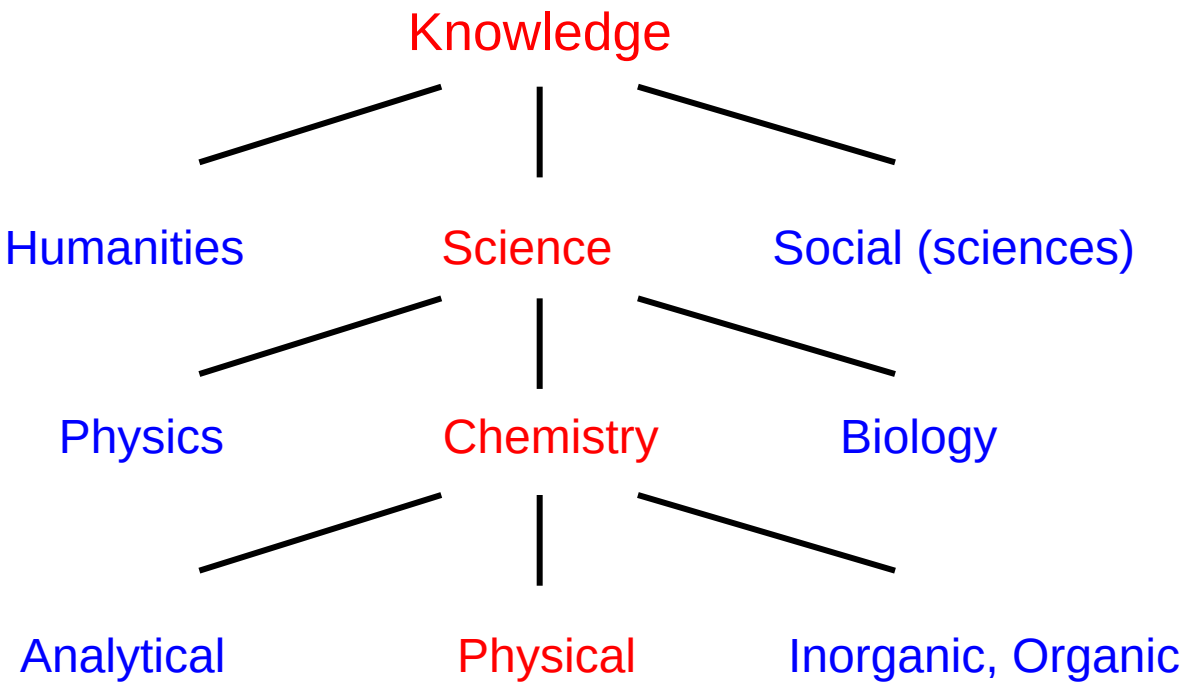
What is Thermodynamics?



Macroscopic
Thermodynamics

Molecular
Quantum Chemistry
Spectroscopy

Statistical Thermodynamics

Kinetics

Equilibrium *Change* *Structure*

Energy, Work and Heat

Energy is the capacity to do work.

Its classification into:

	kinetic	potential
	(by motion)	(by position)
e.g.	thermal	chemical, electrical

Is purely arbitrary!

Heat and work are *not* "types" of energy, but are processes involving *transfer* of energy. They appear and disappear at the system boundary. They are path variables.

Heat is the transfer of energy from one body to another of lower temperature.

Convention: if heat flows into the system, $q > 0$.

Work is the transfer of energy by some mechanism other than temperature difference.

Convention: if work is done on the system, $w > 0$.

Heat stimulates random motion.

Work stimulates organized motion.

Work "degrades" into heat.

- qualitative observations by Count Rumford (Ben Thompson)
- quantitative measurements by James Joule

Terminology 1

A system is a particular sample of matter or region of space.

An isolated system does not interact with its surroundings.

system + surroundings = universe

A closed system does not allow passage of mass over its boundaries, in contrast to…

An open system.

An adiabatic system has boundaries which permit no flow of heat. It is insulated.

A system is in a definite state when all its properties have definite values.

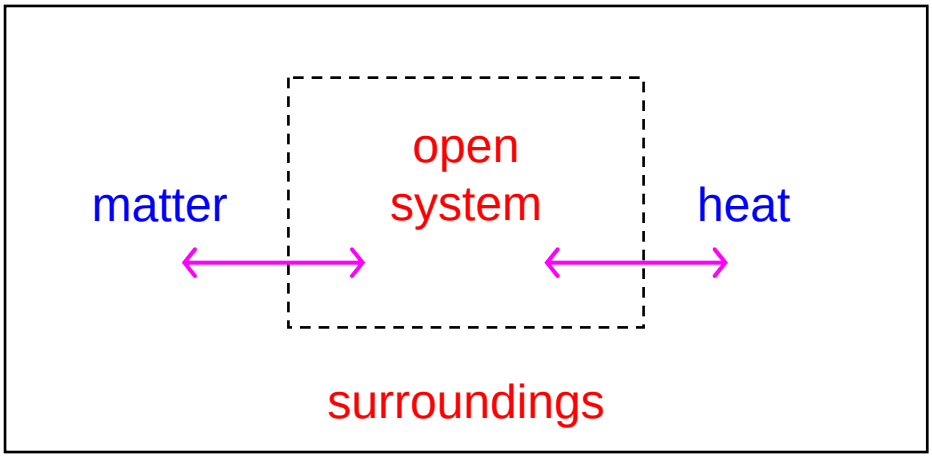
A system at equilibrium is time independent; it is not affected by the history of the system.

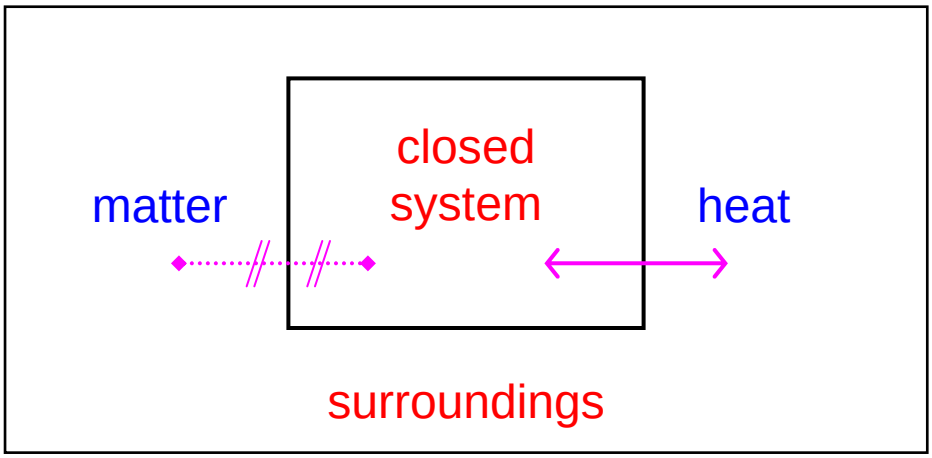
Extensive properties depend on the amount of substance in the system, e.g. n, V.

$$\text{Total Property} = \sum \text{property(part)}$$

Intensive properties are independent of amount, e.g. P, T.

$$\text{Total Property} = \text{property of part}$$


open
system
matter
heat
surroundings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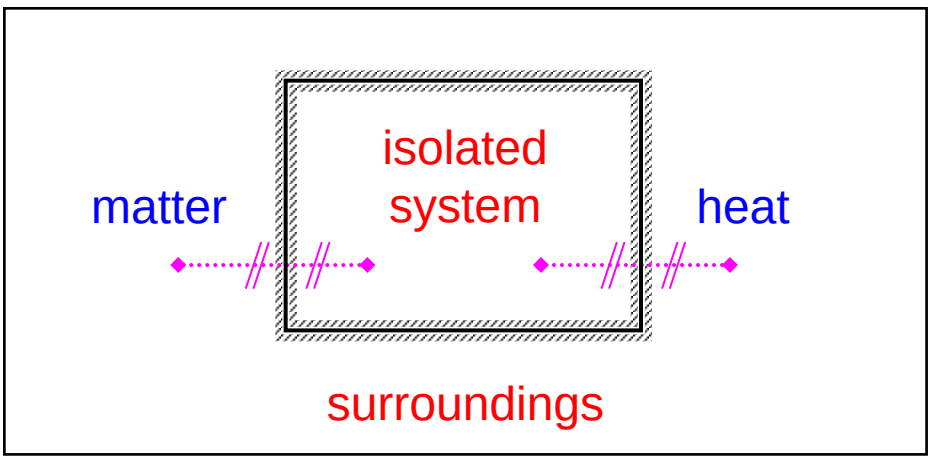
isolated
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Terminology 2

State variables (state functions) uniquely determine the state of a system at equilibrium. Two samples of a substance with the same state variables are in the same state.

The change in a state variable depends only on the initial and final states, *independent of path*.

Path functions depend on the process and therefore vary with path.

A cyclic process is one in which the initial and final states are the same, i.e. no change in the state variables.

In contrast, path functions generally have non-zero values for cyclic processes, dependent on the path.

A reversible process is one that can be reversed by an infinitesimal modification of a variable. The system is in equilibrium with the surroundings at all times. This is an idealized situation, useful as a theoretical limit, but…

All real processes are irreversible. It is possible to restore the system or the surroundings to their original states but not both.

An equation of state is the functional relationship between the properties of a system, e.g, the ideal gas law.

Ideal Gases -- Review

Ideal gases obey the ideal gas law:

$$PV = nRT$$

Pressure Pa $\equiv 1\ \text{N m}^{-2} \equiv 1\ \text{J m}^{-3} \equiv 1\ \text{kg m}^{-1}\ \text{s}^{-2}$

Volume m^3 $\equiv 10^3\ \text{dm}^3 \equiv 10^3$ litres

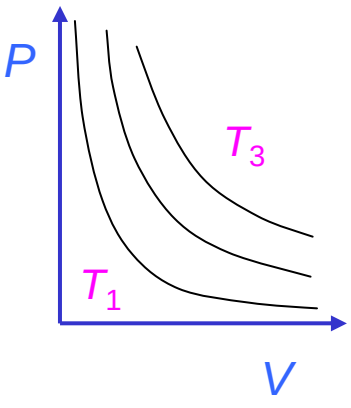
Temperature K

number of moles $n = \frac{w}{M} = \frac{N}{L}$ $L = 6.022 \times 10^{23}$ no. of atoms in 12 g ^{12}C

gas constant $R = 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}$

but if P is in atm ($\equiv 1.01325 \times 10^5$ Pa) and V in litres,

$$R = 0.08206\ \text{dm}^3\ \text{atm K}^{-1}\ \text{mol}^{-1}$$



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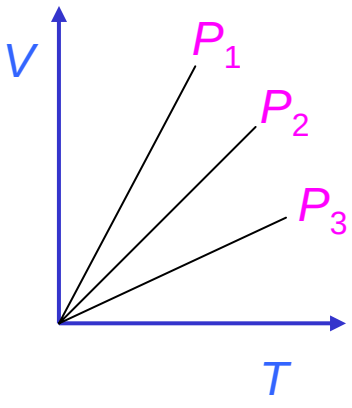

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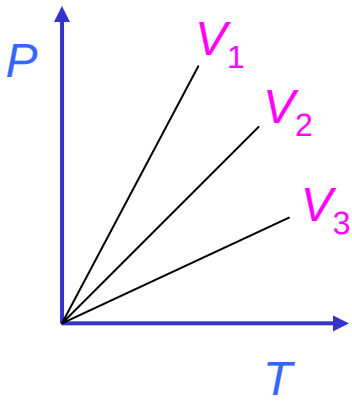

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Mixtures of Ideal Gases

If the ideal gas law applies to each component, i

$$P_i V = n_i RT$$

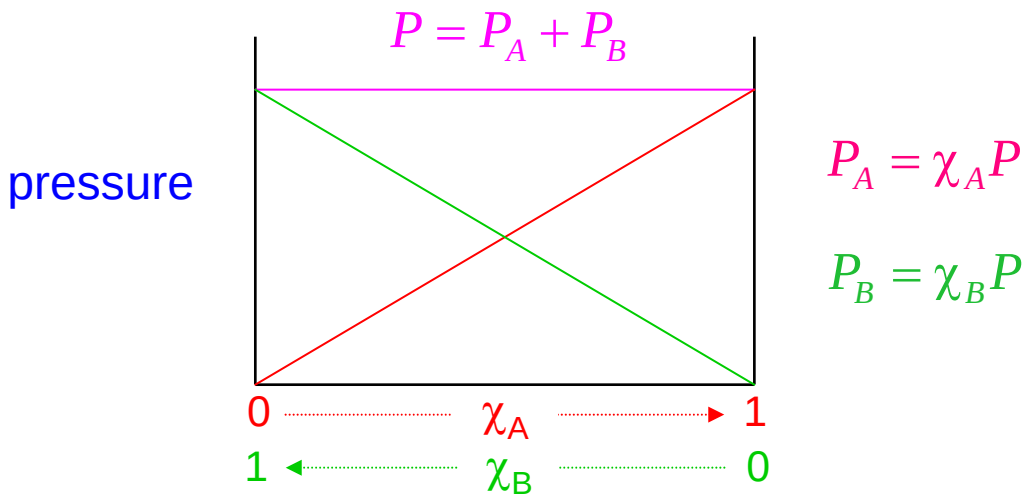
partial pressure

$$P_i = \frac{n_i RT}{V} = \frac{n_i P_{\text{tot}}}{n_{\text{tot}}} = \chi_i P_{\text{tot}}$$

Dalton's Law of Partial Pressures

$$\sum_i P_i = \frac{P_{\text{tot}}}{n_{\text{tot}}} \sum_i n_i = P_{\text{tot}}$$

e.g. for two components:



Real gases are ideal only at the low density limit. Why?