



Thermodynamics is the only physical theory of universal content which I am convinced, within the areas of applicability of its basic concepts, will never be overthrown

A. Einstein 1949

Lecture TOPIC 1 (Finn : 1.1-1.9)

Synopsis: Preview, and introduction. Systems, surroundings and thermodynamic variables; work and equilibrium introduced. Temperature and the Zeroth law of Thermodynamics.

A short list of things you already know

- Phases of matter: solids, liquids and gases
- Temperature. Thermometers, Kelvin and Celsius scales, absolute zero.
- Ideal gases. Kinetic theory; Maxwell-Boltzmann velocity distributions; degrees of freedom and equipartition theorem.
- Non-ideal gases. Lennard-Jones type interaction; van der Waals approach; instability in PV isotherms; phase coexistence.
- Liquid phase; vapour pressure; surface tension.
- Properties of materials: compressibility, heat capacity, thermal expansivity, latent heat
- Transport phenomena: Bernoulli equation; thermal and electrical conductivity.
- Elasticity and deformations. Young's modulus; sound waves; bulk modulus;

You should also have seen these definitions, shortly we'll see why they are incomplete. Compressibility $\kappa = -\frac{1}{V} \frac{dV}{dP}$; bulk modulus $K = -V \frac{dP}{dV}$; heat capacity $C = \frac{dQ}{dT}$; thermal expansivity $\beta = \frac{1}{V} \frac{dV}{dT}$.

Main postulate of thermodynamics

Isolated systems settle into **equilibrium states** having uniform **macroscopic** properties, eg uniform pressure P , uniform density $\rho = \text{mass}/V$, uniform magnetisation etc. If we disturb the system we will get the same response independent of where we carry out the measurement, eg uniform thermal conductivity, compressibility, conductivity, etc

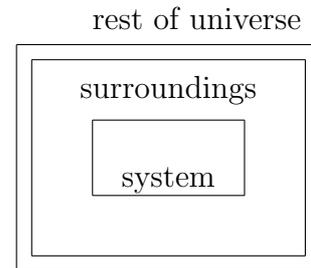
Definition: An equilibrium state is one in which all the bulk physical properties do not change with time and are uniform throughout the system.*

* for the special case where there is phase separation the system comprises homogeneous portions, with uniform properties in each portion.

Some definitions

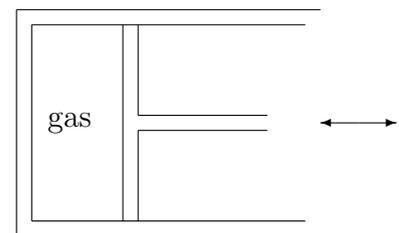
Sample of interest = the **system**,
interacts with **surroundings**,

System and surroundings are separated by some kind of **boundary** wall.



Closed system

System cannot exchange matter with its surroundings, but may exchange energy
e.g. a fixed mass of compressible fluid in a cylinder closed by a moveable ideal piston (ideal = no leaks).

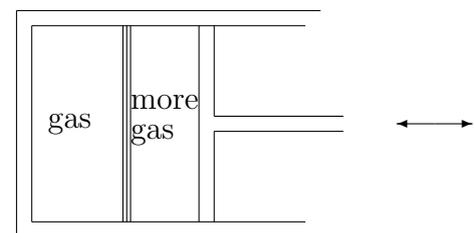


Isolated system

No exchange of matter or energy with surroundings. e.g. piston fixed in position, and piston and cylinder insulated so there is no heat conduction.

Thermal and Mechanical equilibrium

Consider the arrangement opposite: two gas systems are separated by a rigid wall. If the right-hand gas sample is compressed (an external force pushes the insulated piston in) the values of its state variables will change. Pressure and temperature will increase.



- If the wall between the two gas samples is **rigid** and **adiabatic**, meaning there is no movement or transfer of heat energy across it, the left hand sample will be unchanged.
- If the rigid wall allows heat flow, the samples come into thermal equilibrium and have the same temperature (different pressure).
- If the wall is **adiabatic** but movable, the samples come into mechanical equilibrium and have the same pressure (different temperature).

Mechanical Equilibrium = *Work done = movable wall*

Thermal Equilibrium = *Heat exchange = thermally conducting wall*

While the process is occurring, the systems are not in equilibrium, because their bulk physical properties are changing.

State functions and state variables

The various properties that can be quantified without disturbing the system eg internal energy U and V , P , T are called state functions or state properties. Properties whose absolute values are easily measured eg. V, P, T are also called state variables.

Intensive and extensive variables

An intensive property is a property of a system or of a material itself. It is independent of how much of the material is present. e.g. **density, temperature, pressure, specific heat capacity**.

An extensive property is proportional to the amount of material. e.g. **mass, energy, volume, heat capacity**.

Often, these are distinguished these by using small letters for intensive properties, and large for extensive ones. In doing calculations, it is very important to be careful with units here: e.g. volume/mole, volume/kg and volume/atom are all intensive quantities.

Other Thermodynamic variables

Different systems may have other key thermodynamic variables to those necessary to specify the state of a fluid, e.g. for an elastic band held under tension, the value of the tension \mathcal{F} and the length L of the band are also needed to describe its mechanical state (and are much more relevant than P and V).

Fractional changes and absolute values

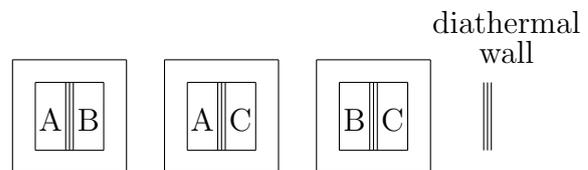
Some thermodynamic quantities (e.g. Volume) have an obvious zero. Others (e.g. Temperature) have a less-obvious zero. For these quantities it makes sense to talk about fractional changes.

Other quantities including internal energy, have no obvious choice of zero - consider e.g. adding the rest mass energy to an ideal gas. It provides a big extra contribution, but whether we include it or not, the *measurable* quantities of the ideal gas do not change. We are free to choose the zero, but then should never use ratios.

Notice that some materials properties are log derivatives, e.g. $\kappa = -\frac{d \ln V}{dP} = -\frac{1}{V} \frac{dV}{dP}$. Log derivatives relate the fraction by which something has changed, rather than the absolute amount, so only make sense when a reference state (e.g. zero) is well defined.

Zeroth Law

Suppose that two systems (A,B) which are thermally isolated from their surroundings are put in thermal contact (connected by a diathermal wall) and allowed to reach thermal equilibrium: i.e. their pressure and volume reach equilibrium values.



Experimental observation: if A and a third suitable system C are similarly brought into thermal equilibrium, this results in no change in the values of the state variables of A, then it is observed that B and C, if put in thermal contact are also in thermal equilibrium with each other. This observation can be repeated for fourth, fifth, ... systems (D, E, ...). and is summarised as the **Zeroth Law of Thermodynamics**:

Zeroth Law: If each of two systems is in thermal equilibrium with a third system they are in thermal equilibrium with each other.

Zeroth law requires the Existence of Temperature

If many systems are in thermal equilibrium with each other, they must have the same value of some property (state variable). This property is called the thermodynamic temperature T .

The temperature of a system is a property that determines whether or not that system would be in thermal equilibrium with other systems.

For two systems to be in complete thermodynamic equilibrium, they must have a common temperature **and** show no **net** (1) exchange of material (no diffusion), (2) chemical reaction (chemical equilibrium), (3) unbalanced force (mechanical equilibrium) (4) charge flow (electromagnetic equilibrium).

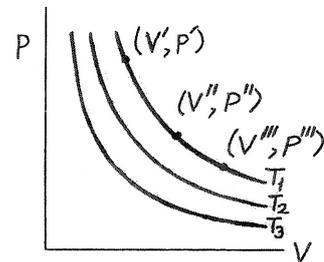
System at equilibrium is fully specified by two variables and Equation of State

For a fixed amount of simple material, only *two* state variables are required to specify an equilibrium state, so temperature must be a function of P and V : $T = T(P, V)$. Equivalently we can also write $P = P(V, T)$ and $V = V(P, T)$ where $P(V, T)$ and $V(P, T)$ are material dependent functions. The relationship between P, V and T is an example of an **equation of state**, and depends on the material.

The equation of state for n moles of ideal gas can be written as $T = T(P, V) = PV/nR$.

Indicator diagram / Isotherms

A system comprising a fixed mass of gas can exist in a number of equilibrium states corresponding to the same temperature T but with different values of its pressure and volume: (P', V') , (P'', V'') , (P''', V''') , The line through plotted values $T(V, P) = T_i, \dots$ is called an isotherm. An isotherm can be drawn for each value of T_i . For given P, V a system has only one temperature, so different isotherms cannot cross.



Three Temperatures are all the same

Remarkably, the “Temperature” related to the kinetic energy of an ideal gas, the “Temperature” which determines thermal equilibrium, and the “Temperature” which appear in statistical distributions (Boltzmann, Fermi-Dirac and Bose-Einstein) *are all the same*.

Statistical Redefinition Kelvin = Joule/Boltzmann

If temperature is kinetic energy, we have the relationship $m\overline{v^2} = 3k_B T$. Equivalently the equipartitioned energy of any degree of freedom is $k_B T/2$. To relate Kelvins to Joules requires an accurate measurement of k_B , e.g. from the speed of sound in ideal gas:

$$c_0 = \sqrt{\left(\frac{\partial P}{\partial \rho}\right)_s} = \sqrt{\frac{\gamma P}{\rho}} = \sqrt{\frac{\gamma N_A k_B T}{M}} \implies k_B = \frac{M c_0^2}{\gamma T N_A}$$

where ρ is the density and M the molar mass. This was recently measured more accurately than the critical point of water can be, using low density limit of speed of sound in argon, by resonance of copper sphere whose diameter is known to 11.7nm (500 atoms).

(de Podesta et al 2013 Metrologia 50 354 <http://iopscience.iop.org/0026-1394/50/4/354>)