Zeroth law of thermodynamics

Thermal equilibrium

Temperature

Reversibility

Content last lecture

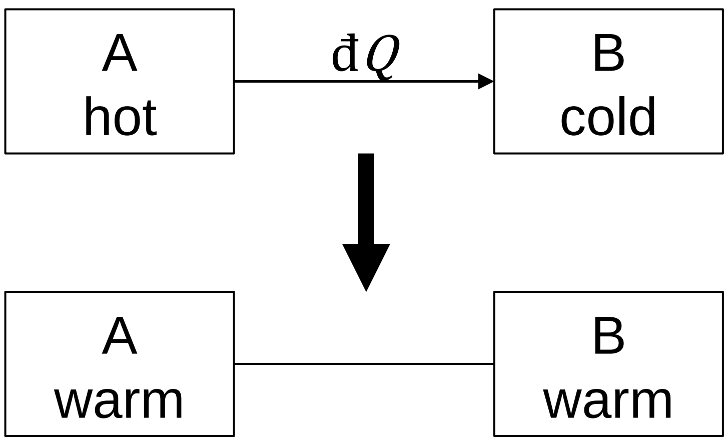
- Systems
- Variables
- Equations/Functions of State

Laws of Thermodynamics

4 “Laws of thermodynamics” summarise many observations:

Zeroth Law	-	meaning of temperature (thermal equilibrium);
First Law	-	conservation of energy;
Second Law	-	entropy and how energy can be used;
Third Law	-	absolute zero of temperature. (not covered here)

0^{th} Law of Thermodynamics



equilibrium is reached when no further changes occur

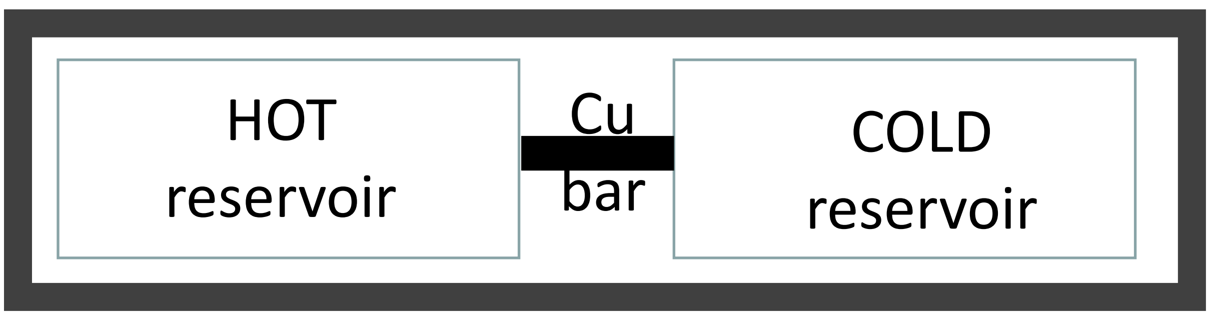
Zeroth law: If two systems A and B are separately in thermal equilibrium with a third system, C, then they are also in equilibrium with each other.
(thermometers work)

Thermal equilibrium

Two systems are in thermal equilibrium when no heat is flowing e.g. they have the same temperature

heat flowing $\not\Rightarrow$ temp chang

This is different to a steady state!
(temperature is not changing, but heat is constantly flowing)



reservoir: body so big doesn't change temp

Mathematical interpretation of zeroth law

Take 2 systems (p_1,V_1), (p_2,V_2) and reference system (p_3,V_3).

1 & **3** in eq^m. $\Rightarrow F_1(p_1,V_1,p_3,V_3) = 0$ (equation of state) (1)
$(p_3,V_3$ fixed; fix V_1 and wait for p_1 to settle)

2 & **3** in eq^m. $\Rightarrow F_2(p_2,V_2,p_3,V_3) = 0$. (2)

Can solve (1) for, e.g, p_3: $p_3 = f_1(p_1,V_1,V_3)$ (3)
or (2): $p_3 = f_2(p_2,V_2,V_3)$ (4)

So, clearly, $f_1(p_1,V_1,V_3) = f_2(p_2,V_2,V_3)$ (5)

$$f_1(p_1,V_1,V_3) = f_2(p_2,V_2,V_3) \qquad (5)$$

Can in principle solve (5) for p_1: $$p_1 = g(p_2,V_1,V_2,V_3) \qquad (6)$$

1 & **2** in eq^m. $\Rightarrow F_3(p_1,V_1,p_2,V_2) = 0$ if we use the Zeroth Law. (7)

Can solve this for p_1 as well: $$p_1 = f_3(p_2,V_1,V_2) \qquad (8)$$

But (8) says p_1 doesn't depend on V_3, so V_3 cannot appear in (6) and also not in (5).

Therefore $$f_1(p_1,V_1) = f_2(p_2,V_2) \qquad (5')$$

So, for any system x in thermal equilibrium with reference system **3**, we can write $$f_x(p_x,V_x) = \Theta \qquad (9)$$

where Θ = const. called the *empirical temperature*

<u>systems in thermal eq^m. have the same temperature</u>.

Equation (9) allows us to plot *isotherms* for the system.

Zeroth law says that temperature can be defined.

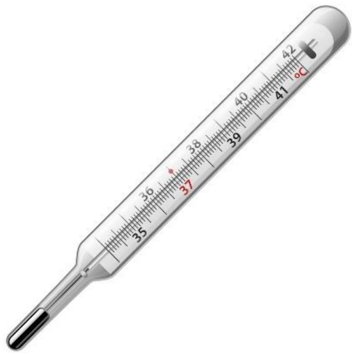
Doesn't give meaning of Θ, i.e. larger Θ means "hotter".

It says "thermometers work", because Θ can be measured.

If 2 systems have the same Θ then there will be no heat flow between them.

How do we measure temperature?

- Thermometer



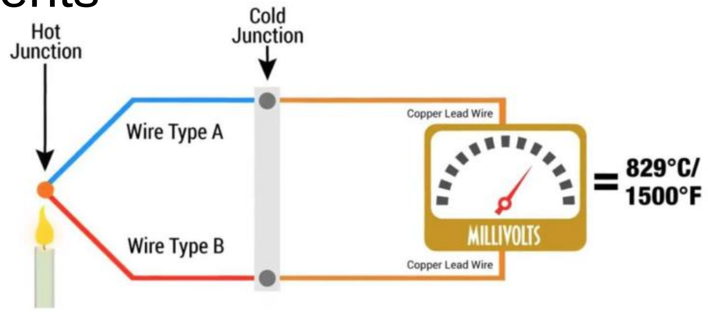
- Pyrometer

- thermocouple

Picture taken from https://www.omega.com/en-us/resources/thermocouple-hub

How do we measure temperature?

- Thermometer
  - Measures the change in volume in a reference substance (e.g. mercury or ethanol)
- Pyrometer
  - Measures intensity of radiation
  - Usually used for very hot or distant measurements
- thermocouple



  - Uses Seebeck effect

How do we measure temperature?

- So temperature device measures some change of a physical property in another material

- But, what is the temperature scale and who came up with it?

Picture taken from Wikipedia

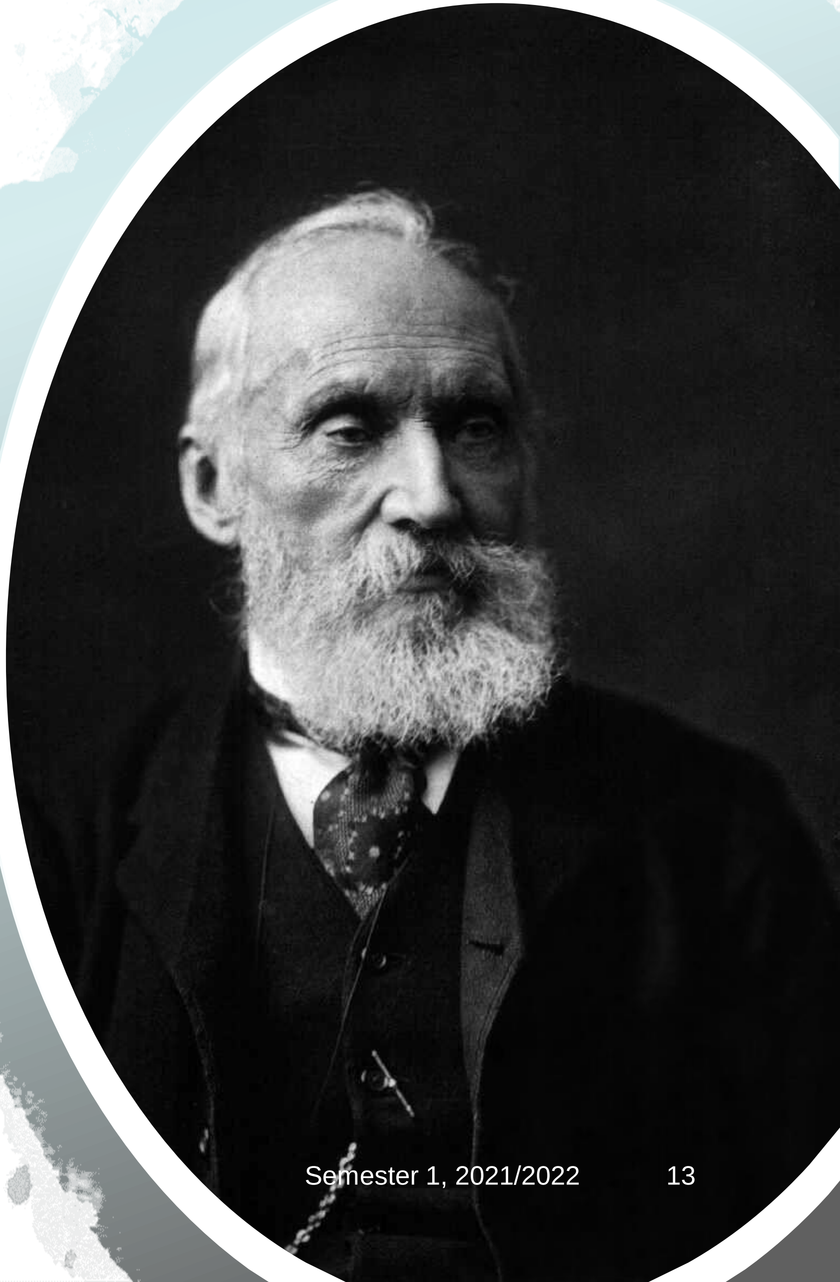
How do we measure temperature?

- Celsius:
    - Initially defined by the melting (0 °C) and boiling point (100 °C) of water
    - Between 1954 and 2019 temperature scale was define between absolute zero (-273.15 °C) and the triple point of water (0.01 °C, 611.657 Pa)
    - Since 2019 re-defined according to re-definition of Kelvin scale

Picture taken from Wikipedia

How do we measure temperature?

- Kelvin:
    - 0 K defined as absolute zero
    - Second point is 1/273.16 of triple point of water (until 2019) step size is equal to Celsius scale
    - Since 2019 re-defined via Boltzmann constant



Picture taken from Wikipedia

How do we measure temperature?

- Fahrenheit:
  - Derived from Rømer scale
    - 0 °R melting point of brine (H_2O+NH_4Cl)
    - 60 °R boiling point of H_2O
    - Later defined melting point of ice to be exactly 7.5 °R
  - 0 F melting point of brine
  - 96 F temperature of “hot blood”
  - 32 F melting point of ice

Thermodynamic reversibility

- If compress gas quickly $\Rightarrow$ generate heat
- Not reversible
- Compress very slowly
  - At each point gas is infinitesimally close to thermodynamic equilibrium (quasi-static process)
  - Each point can be described by thermodynamic variables (functions of state)
- Reversible processes are quasi-static processes where no dissipative forces such as friction and no hysteresis* are present.
- Direction of reversible processes can be reversed by infinitesimally small steps in the opposite direction

*Hysteresis: when process is reversed and system does not return to original state

Thermodynamic reversibility

A thermodynamic process is *reversible* if the process is

(i) *quasi-static* and

(ii) there is no *hysteresis* and no memory of the previous state.

In a *quasi-static* process, every intermediate state is an equilibrium state.

Example: a line in a p-V diagram always shows a quasi-static process.

If we make a *fast* change in V, shock waves in the gas $\Rightarrow$ p is not uniform (no unique value to plot) $\Rightarrow$ process is not reversible: $đW > -p\,\mathrm{d}V$.