Thermodynamics (over next 3 weeks)

Study: temperature, heat, entropy
converting heat ⟷ mechanical work.

Historically, developed before understanding gases & matter as collections of atoms or molecules. Found everything concerning temperature, heat, energy, mechanical work, and entropy could be described in terms of a few simple "laws."

Statistical mechanics (Maxwell, Boltzmann, Gibbs) showed:

$$\left(\begin{array}{c}\text{energy conservation} \\ + \text{ statistics of lots} \\ \text{of particles}\end{array}\right) \longrightarrow \left(\begin{array}{c}\text{laws of thermodynamics} \\ \text{for macroscopic systems}\end{array}\right)$$

e.g. heat ⟷ energy stored in internal disordered moving about of atoms & molecules.

temperature & entropy ⟵ average properties ~~of~~ associated with lots of particles, average energy stored in internal disor.

<u>Temperature</u> : "Zeroth law of thermodynamics"

"Every body X can be given a temperature T_X. Two bodies in thermal equilibrium have the same temperature"

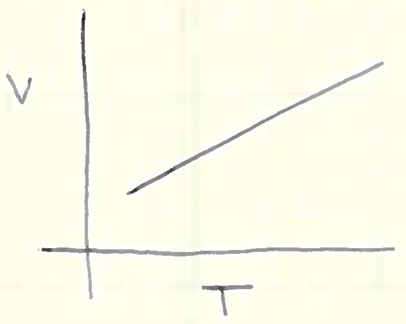
or

"If bodies A and B are in thermal equilibrium with a third body C, then A & B are in thermal equilibrium with each other."

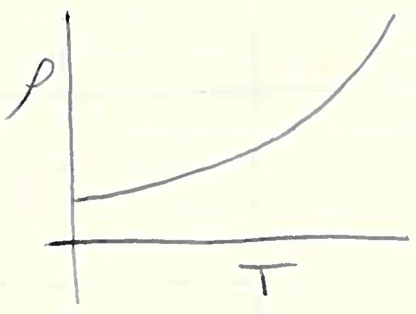
Two bodies not in equilibrium, X & Y with temperatures $T_X > T_Y$, if placed in direct contact, will eventually reach equilibrium with both at temperature T and $(T_X > T > T_Y)$.

This happens via <u>heat transfer</u> from the hotter to the colder body.

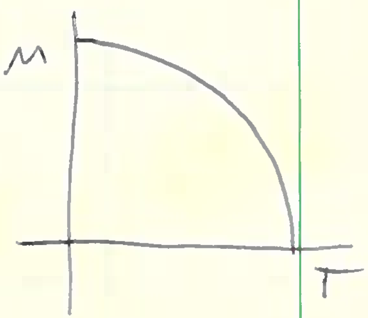
Physical properties of materials depend on temperature



Volume of gas at constant p

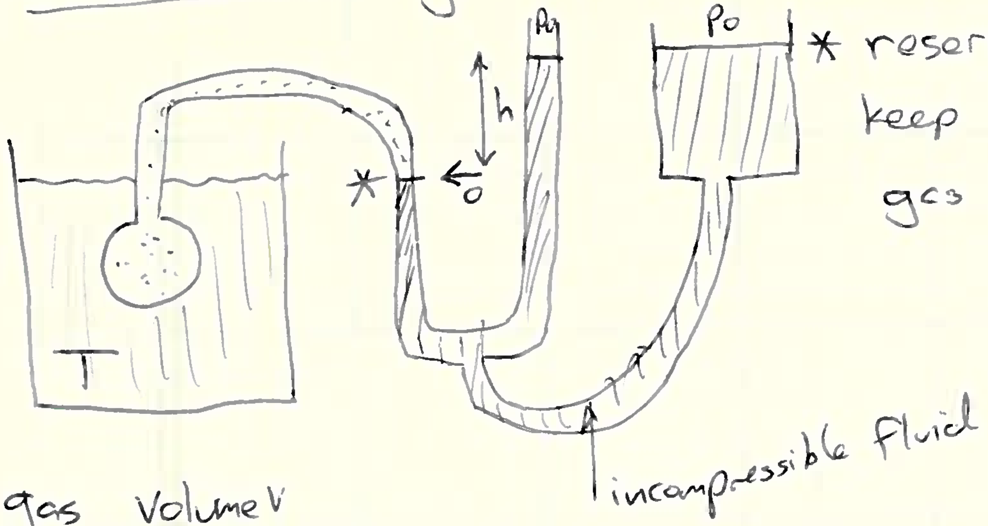


resistivity of Cu



Magnetization of Fe

Constant-Volume gas thermometer



* reservoir – adjust to keep volume of gas fixed.

gas volume V
pressure p
temp T

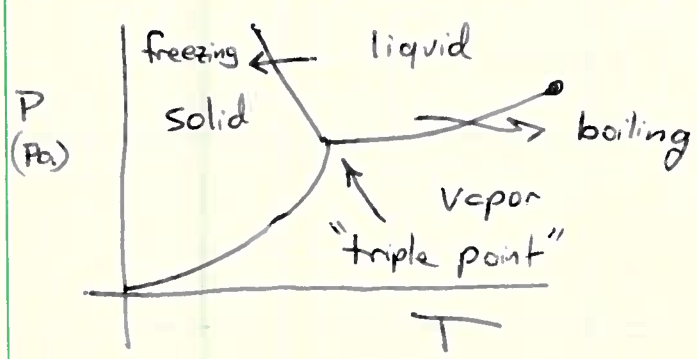
$$p - p_0 = \rho g h$$

$$\frac{T}{T_R} = \frac{p}{p_R}$$

p_R : reference pressure
T_R : reference temperature

(need to take all pressures (densities) very small to get a T/T_R which is independent of details about what kind of gas is used).

Reference temperature : triple point of water



$T_3 = 273.16\ K$

$P_3 = 0.00602\ atm$

uniquely determined

Overkill. Use this tedious way to measure temperature as a way to calibrate other simpler thermometers, such as the familiar mercury thermometer, which is based on the expansion of Hg as T increases

Some temperatures in Kelvins

boiling pt. of H_2O at $p = 1\,atm$: $T = 373.125\,K$

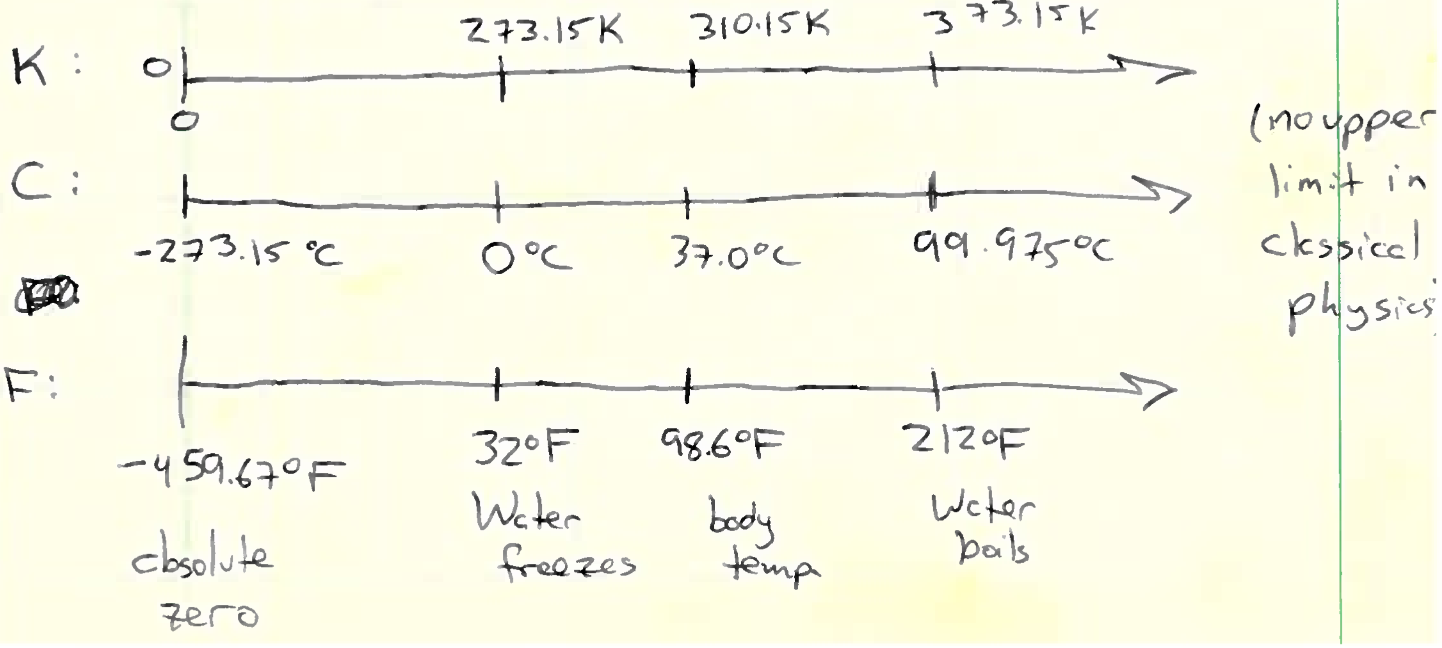
[temperature of universe - glow left over from big bang (or whatever)] → $T = 3\,K$.

[coldest possible temperature] → $T = 0\,K$

Other temperature scales : Celsius (= centigrade) & Fahrenheit :

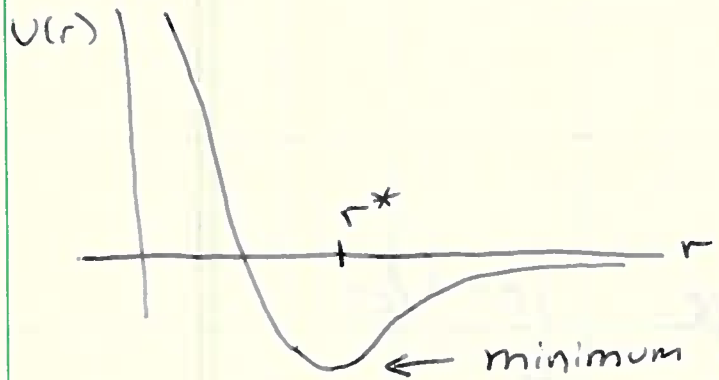
Celsius : $T_C = T_K - 273.15$

Fahrenheit: $T_F = \frac{9}{5} T_C + 32$



Thermal expansion: Objects generally expand with increasing temperature.

Microscopic picture: potential energy for a pair of atoms or molecules vs separation r



← minimum energy = groundstate

At T=0, atoms sit at optimal distance r* apart (up to "quantum jiggling"). Heating up → adds thermal energy → atoms jiggle more away from r* → average separation increases → whole object expands.

So usually hotter objects are less dense. Why hot air rises (eg hot air balloon).

Counterexample: water & ice - ice floats i.e. less dense even though colder. Different from other liquids. As discussed in book, this peculiarity of water is essential for life to exist on earth.

Coefficients of linear expansion.

Increase temperature of rod by $\Delta T \rightarrow$ length increases by $\Delta L = \alpha L \Delta T$

↑ "coeff of linear expansion"

Can integrate $\frac{dL}{L} = \alpha dT$

to get $\boxed{L = L_0 e^{\alpha T}}$. For $\alpha T \ll 1$

this gives $\boxed{L \approx L_0 (1 + \alpha T)}$ $+ O(\alpha T)^2$

Substance	α $(10^{-6}/C^\circ)$	
Aluminum	23	← expands more since α larger
Brass	19	
Steel	11	
Diamond	1.2	← expands less since α smaller

note: $\alpha T \ll 1$ for large range of temperatures.
(Objects would melt usually far before $\alpha T \sim 1$.)

<u>Area expansion</u>: $A \sim L^2$ so $A = A_0 e^{2\alpha T}$
$\approx A_0 (1 + 2\alpha T)$.

<u>Volume expansion</u>: $V \sim L^3$ so $V = V_0 e^{3\alpha T}$
$\approx V_0 (1 + 3\alpha T)$

<u>Heat</u> Internal energy stored in jiggling and potential energy of atoms & molecules. Transferred from hotter body to colder — eventually brings temperatures to be the same.

Heat & work describe process of bringing system from one state to another — depends on path. $\boxed{\text{Heat = transfer of energy}}$

Measure heat in same units as energy : joule.

<u>Heat capacity</u> :
$$Q = C\,(T_f - T_i)$$
↑ const. of "heat capacity

<u>Specific heat</u>:
$$Q = c\,m\,(T_f - T_i)$$
specific heat = heat capacity / unit mass

useful since heat capacity ~ mass of object

Some specific heats :

lead	128	J/kg K
water	4190	J/kg K

i.e. it takes 128 joules of heat to raise 1 kg of lead by 1 Kelvin of temperature

To raise 1 kg of water by 1 K temperature takes 4190 J.

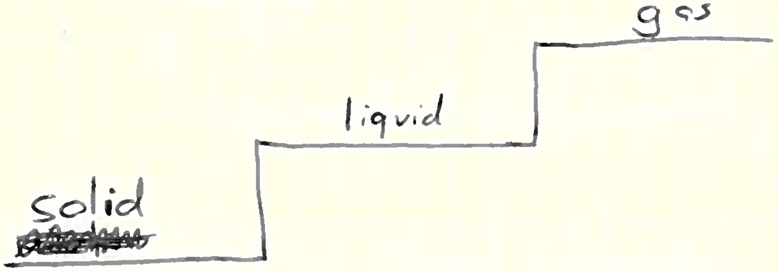
Molar specific heat : $(1 \text{ mol} = 6.02 \times 10^{23})$
joules required to raise 1 mol of an element by a temperature of 1K.
About the same ~ 25 J/mol K for most elements. ⟹ Atoms of all kinds absorb heat in same way.

Heats of transformation : Amount of heat / unit mass required for a sample to undergo a given phase transformation – such as liquid → gas "heat of vaporization" or ~~liquid → solid~~ solid → liquid "heat of fusion."

$$Q = L\, m.$$ L : heat of transformatio

heat ↑ ↑ mass

picture :



have to add heat to bring up to next level – get back heat when dropping down level.
Water from liquid → gas $L_V = 2256$ kJ/k

from solid → liquid $L_F = 333$ kJ/kg.

E.g. when we sweat – skin gives off water which evaporates, absorbing body heat, cooling us off.