Recap from last time

Isothermal – change to a system that takes place at a constant temperature (think thermal -> heat)

Isobaric – change to a system that takes place at a constant pressure (think bar -> pressure)

Isochoric – change to a system that takes place at a constant volume (remember the other two and that this one isn’t them)

Adiabatic – change to a system that takes place without transfer of heat (temperature can change, but heat cannot enter the system!)

Recap from last time

What is the relationship between heat energy, ΔQ, transferred to a system and its corresponding increase in temperature, ΔT?

Heat capacity of the system (J/K)

$$\Delta Q = C\Delta T \rightarrow C = \frac{\mathrm{d}Q}{\mathrm{d}t}$$

Varies depending on the amount of material, so can define

Specific heat capacity (J kg^{-1} K^{-1}) -> $C = mc$
Molar heat capacity (J mol^{-1} K^{-1})

Higher heat capacity, smaller increase in temperature for a given heat

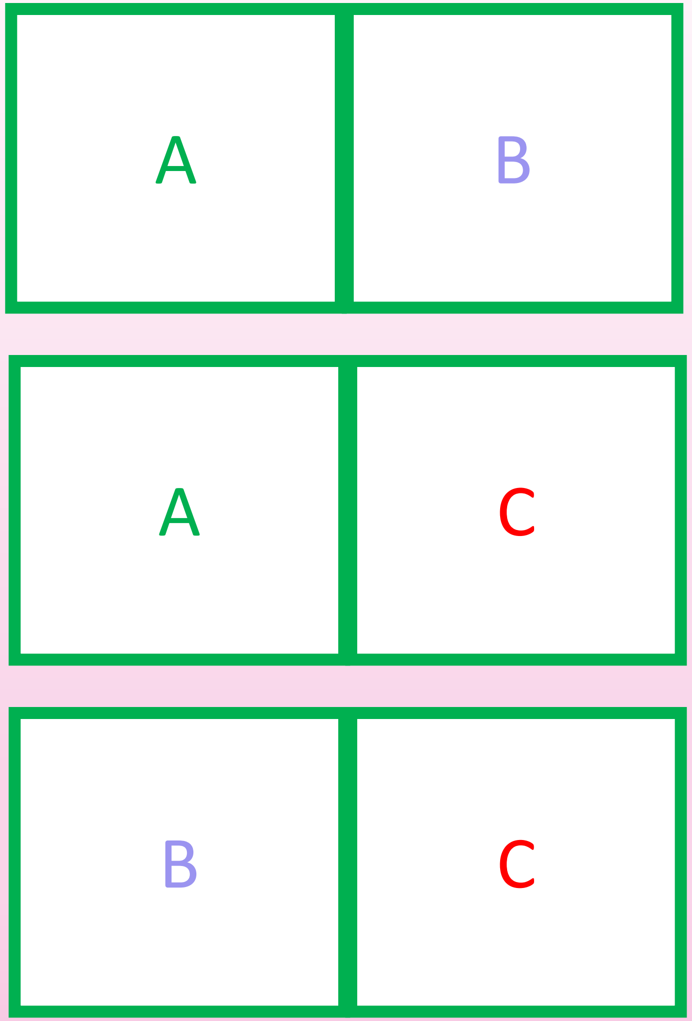
Recap from last time

Take any three systems, A, B and C

If A is in thermal equilibrium with B and is also in thermal equilibrium with C, then B and C must also be in thermal equilibrium

All systems in equilibrium with one another share a common temperature

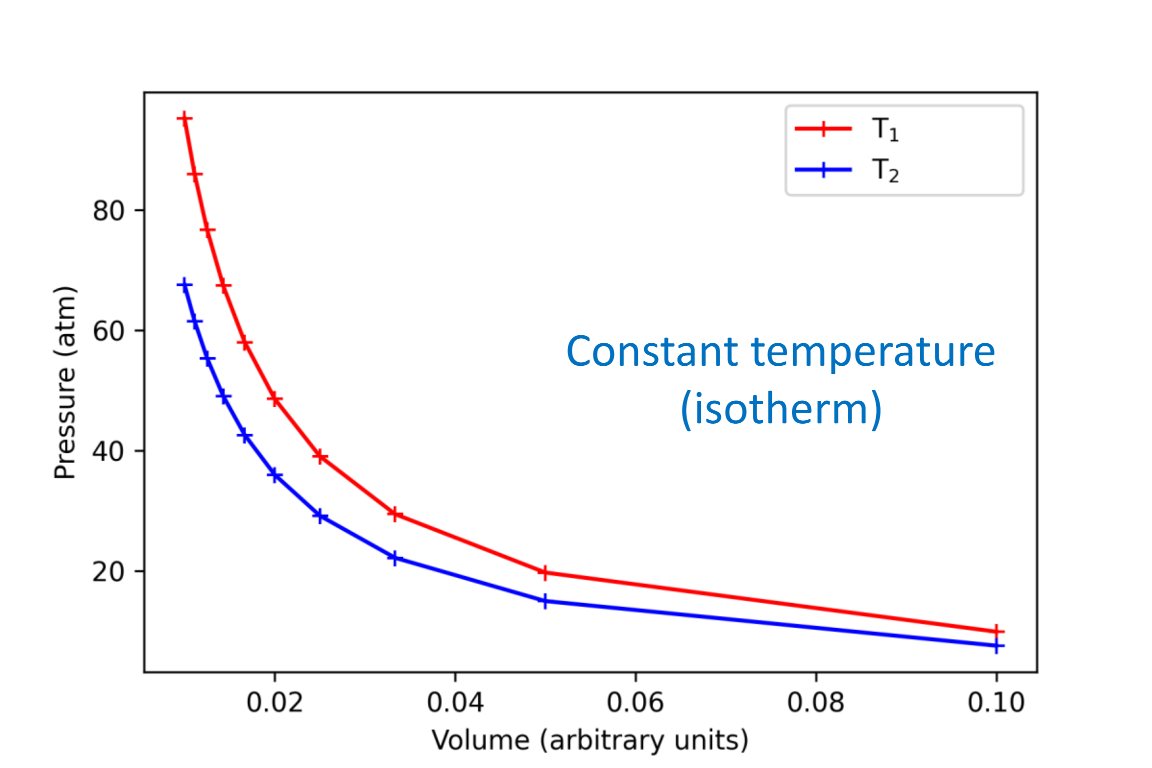
This is the zeroth law of thermodynamics



Boyle's law

"The absolute pressure exerted by a given mass of an ideal gas is inversely proportional to the volume it occupies, if the temperature and amount of gas remains unchanged within a closed system"

$$P \propto \frac{1}{V}$$

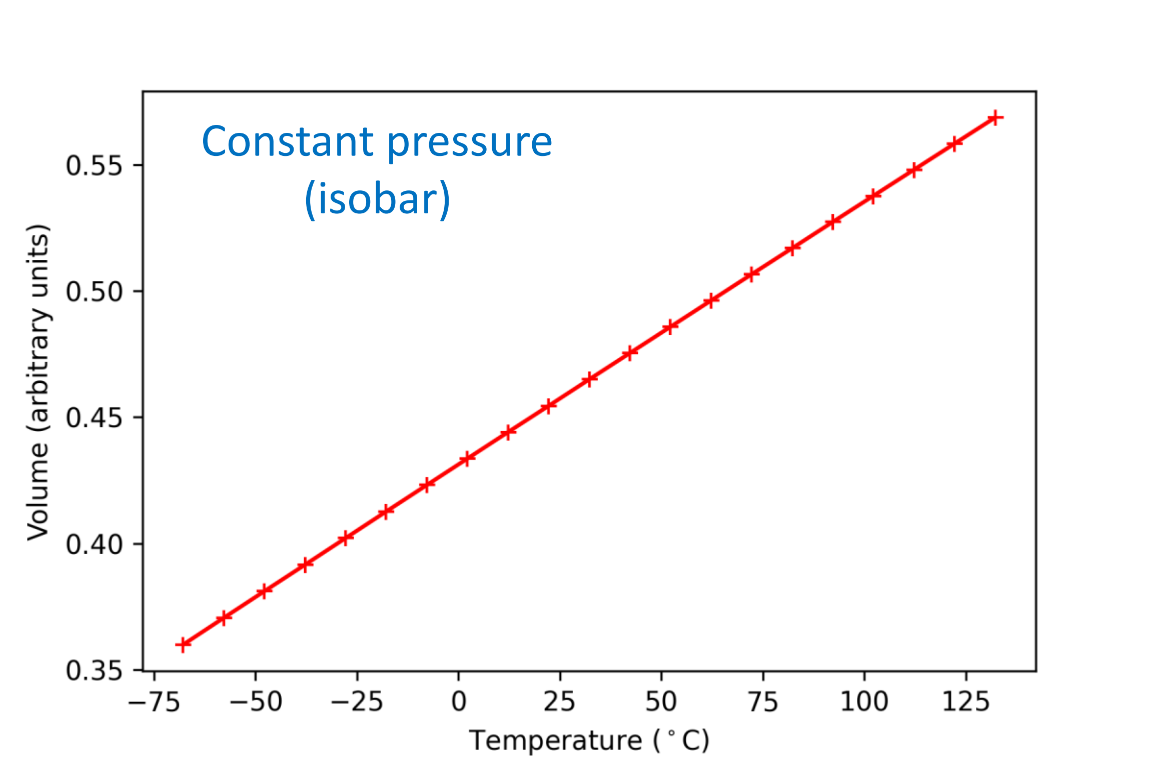


Data for these plots taken from https://nvlpubs.nist.gov/nistpubs/jres/40/jresv40n6p457_A1b.pdf

Charles' law

"When the pressure on a sample of [an ideal gas] is held constant, the Kelvin temperature and volume will be in direct proportion"

$$T \propto V$$



Data for these plots taken from https://nvlpubs.nist.gov/nistpubs/jres/40/jresv40n6p457_A1b.pdf

Equation of state: Ideal gas law

$P \propto \frac{1}{V}$ (for a fixed T) and $T \propto V$ (for a fixed P)

Thus, we can write that $PV = kT$

n: number of moles
R: gas constant
(8.314 J mol^{-1} K^{-1})

$PV = nRT$ (for moles)

N: number of molecules = N_A x n
k_B: Boltzmann's constant
(1.38 x 10^{-23} J K^{-1}) = R/N_A

$PV = Nk_BT$ (for molecules)

Equation of state

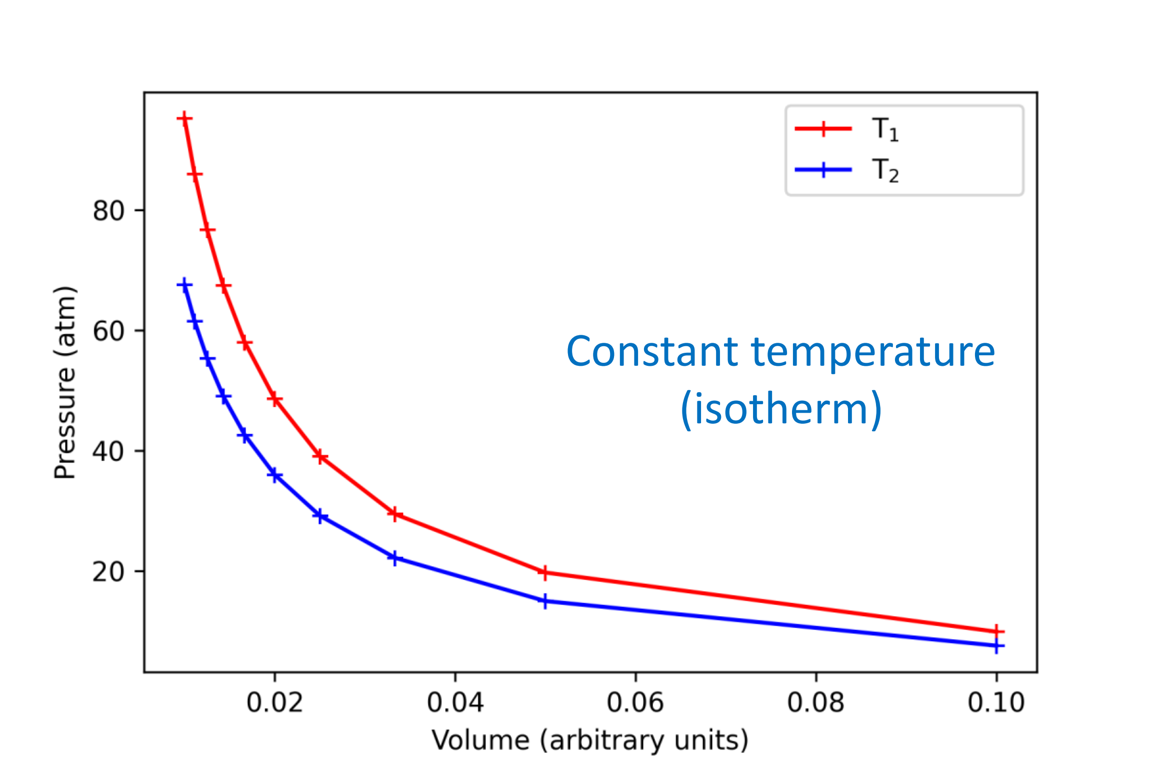
$$PV = nRT$$

An equation of state allows us to describe the macroscopic state of our gas – we usually do this on a PV diagram – a point on this plot represents a specific state

With two of the three variables, we can always determine the third

Q: If the two curves T_1 and T_2 are obtained for the same gas through changing P and V at a fixed T and n, is

1) $T_1 < T_2$?
2) $T_1 = T_2$?
3) $T_1 > T_2$?



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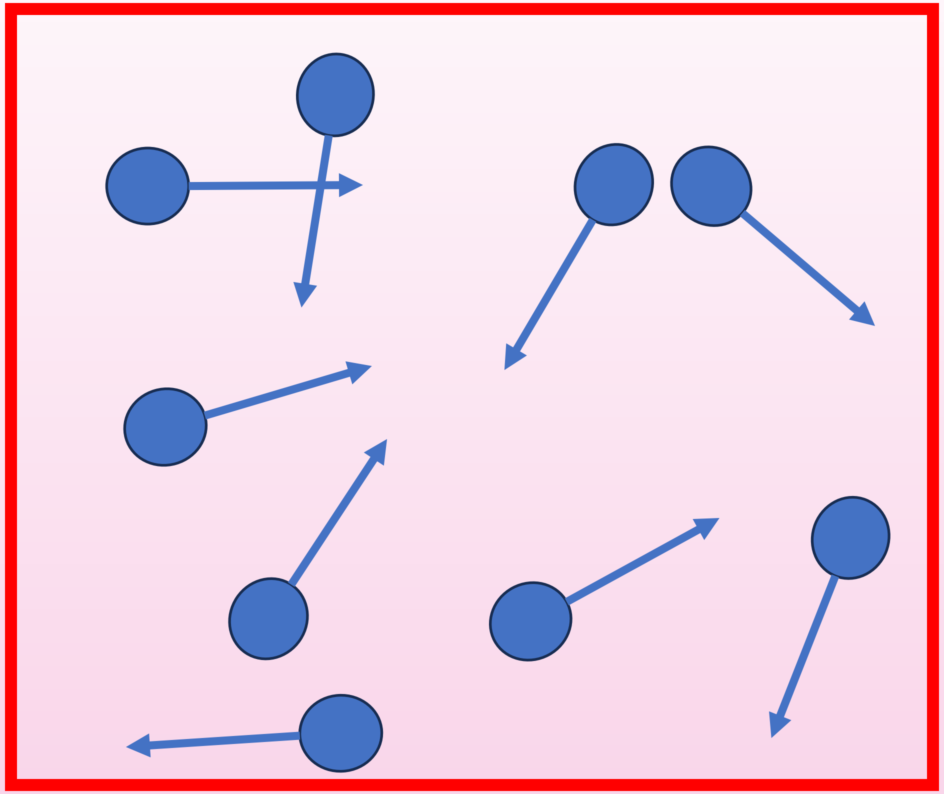
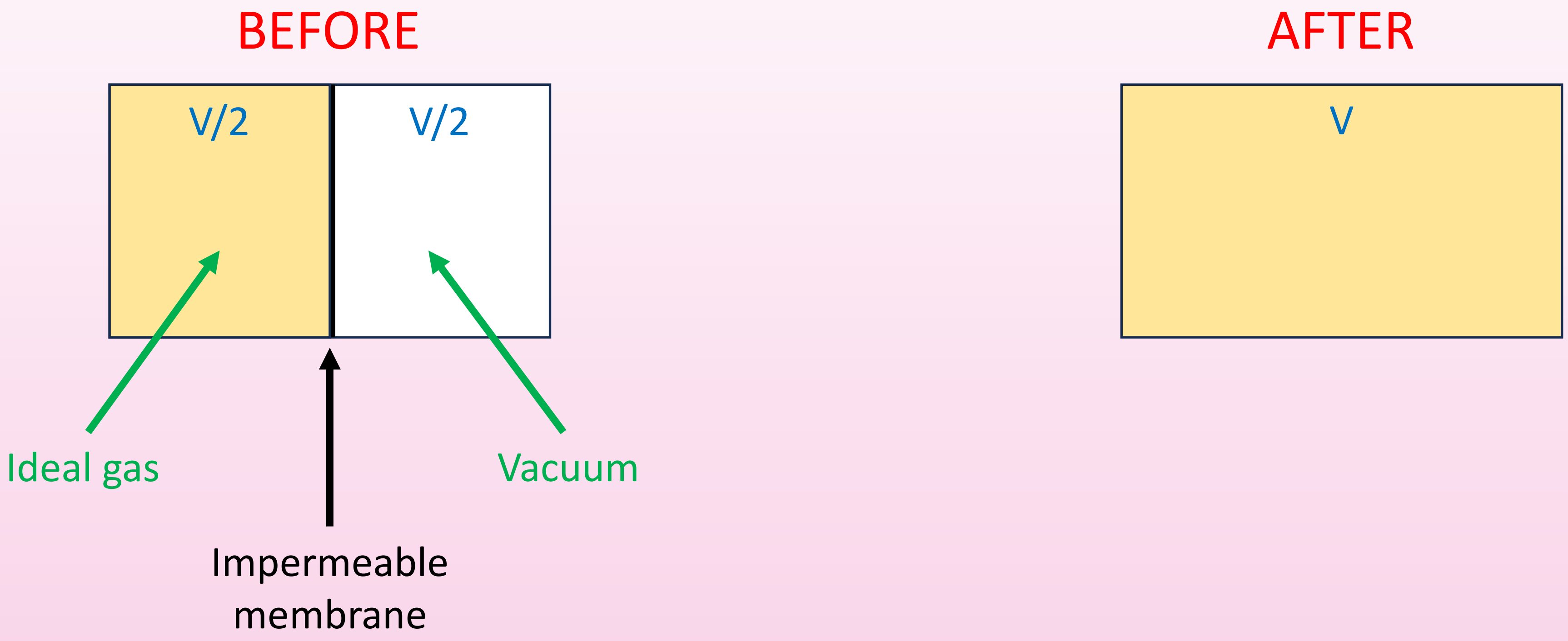
What is an ideal gas?

A collection of molecules (or atoms, for a monatomic gas) that are non-interacting (no inter-atomic forces) that collide elastically

The internal energy of the gas is dependent on the velocities (kinetic energies) of the molecules, and hence on the temperature, and not on pressure and volume



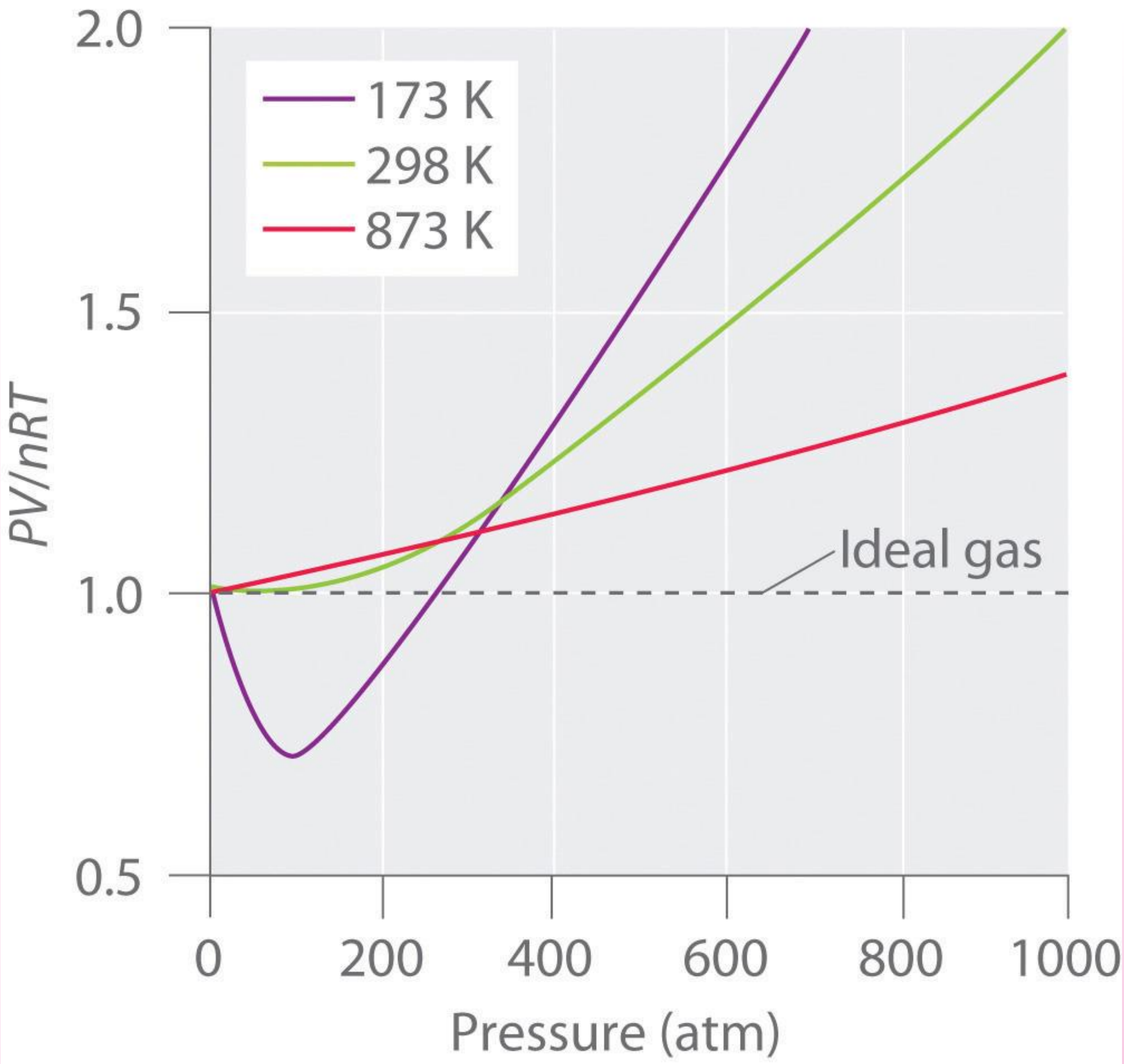
Joule's second law



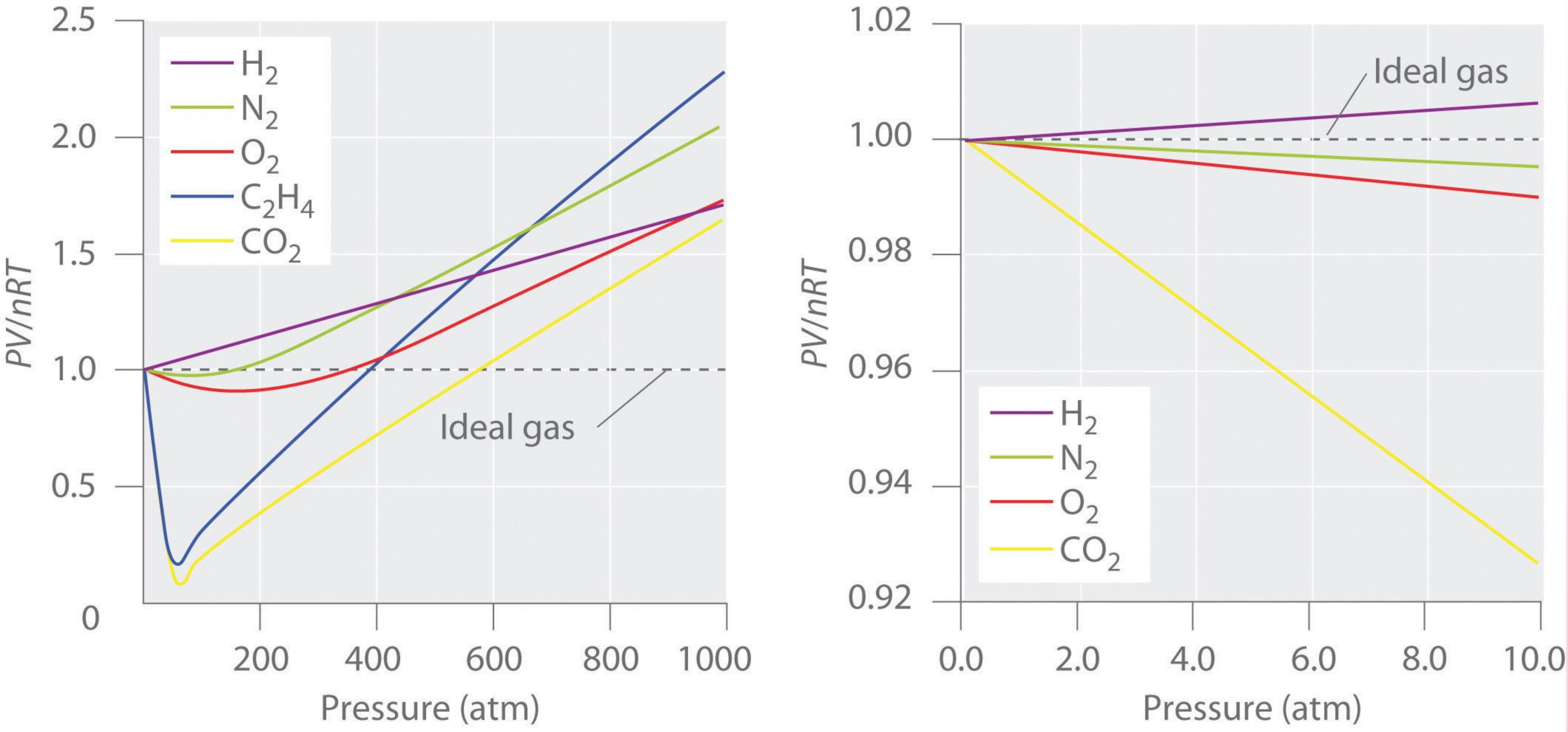
The membrane separating the volumes is removed laterally, so no work is done on the gas

Temperature of the gas did not change in this case!

$\frac{\partial U}{\partial V} = 0$ and so the internal energy only depends on temperature!



https://saylordotorg.github.io/text_general-chemistry-principles-patterns-and-applications-v1.0/section_14/5431a0c57cd814bf3cef509aa88634d1.jpg



(a) ***PV/nRT*** **at high pressures** **(b)** ***PV/nRT*** **at low pressures**

https://saylordotorg.github.io/text_general-chemistry-principles-patterns-and-applications-v1.0/section_14/e524c43ad0c0149af3325f4909df3025.jpg

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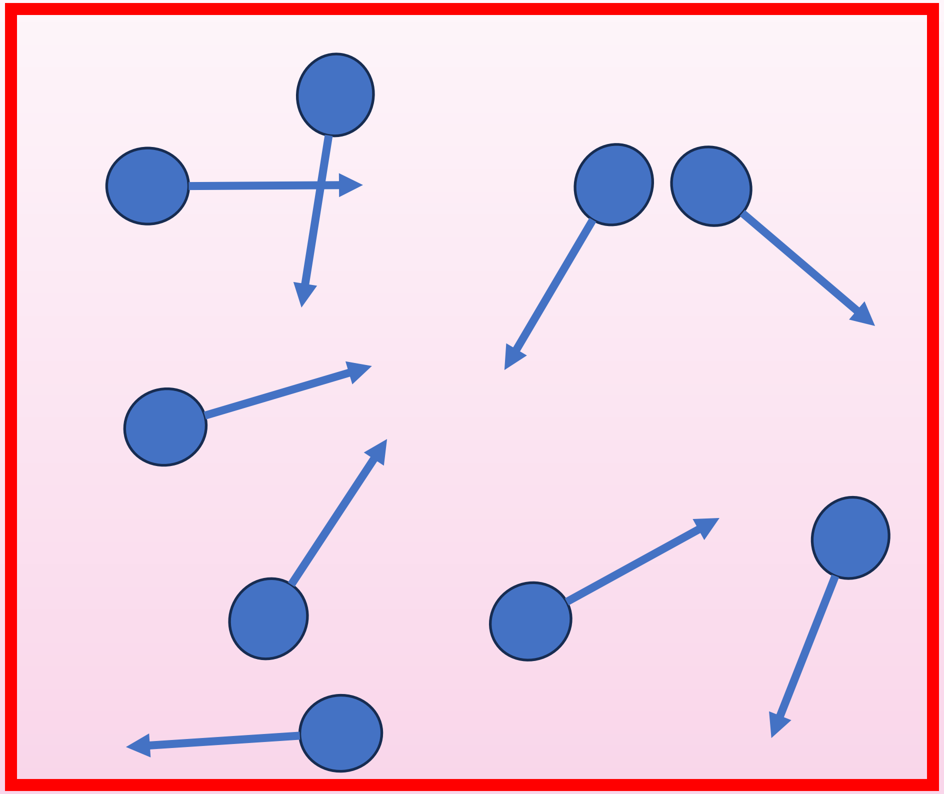


For high KE (and hence T), interatomic forces are negligible

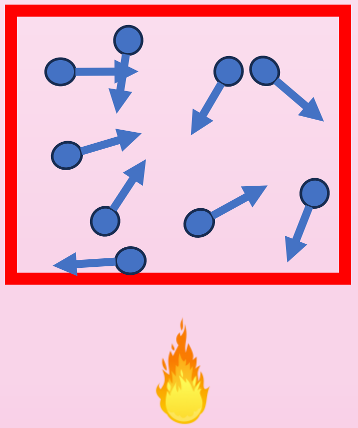
For low pressure, space between molecules increases (and hence interatomic potential decreases – think LJ potential)

We will be dealing with classical (Maxwell-Boltzmann) gases – other examples include Fermi and Bose gases

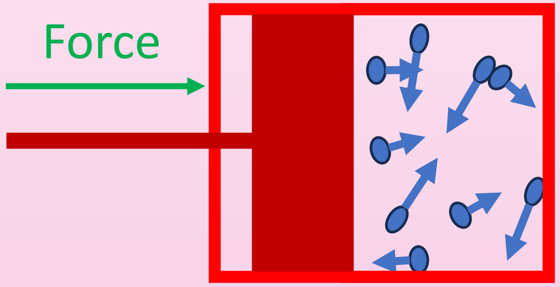
Changing temperature of an ideal gas

How do we go from T_1 to T_2?

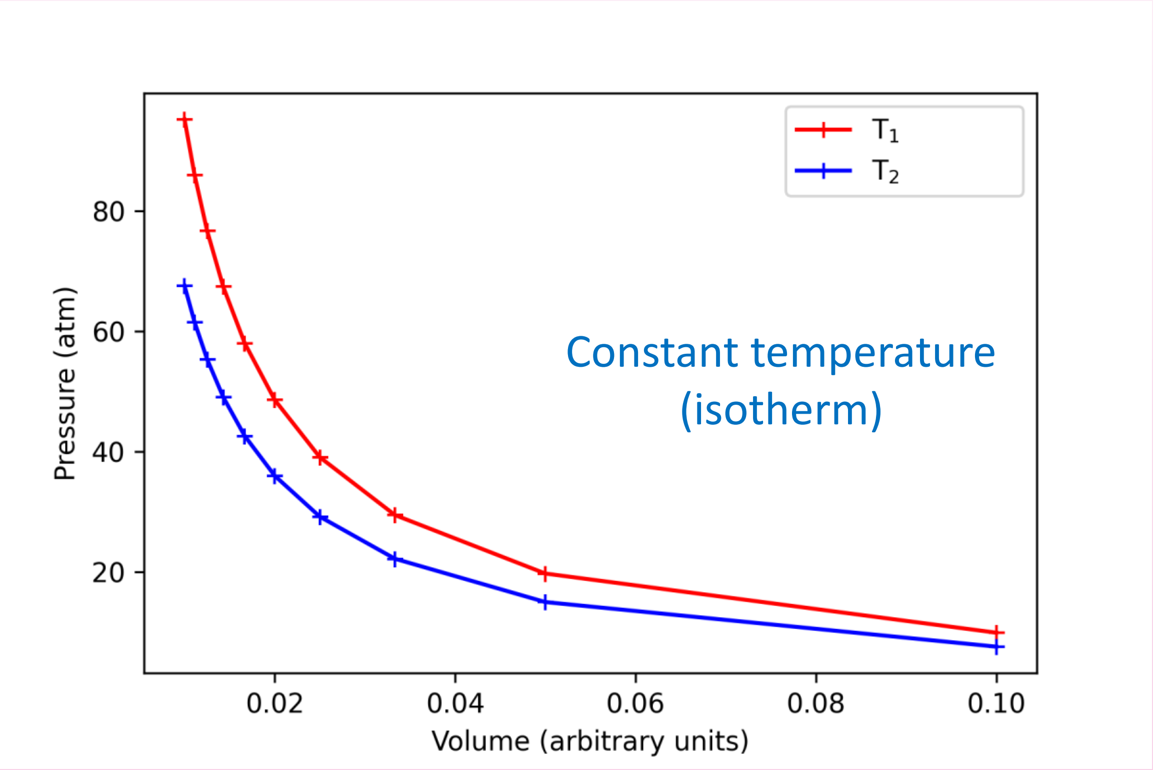
Need to change the internal energy of the gas somehow



1) Transfer heat to the gas



2) Do some work on the gas



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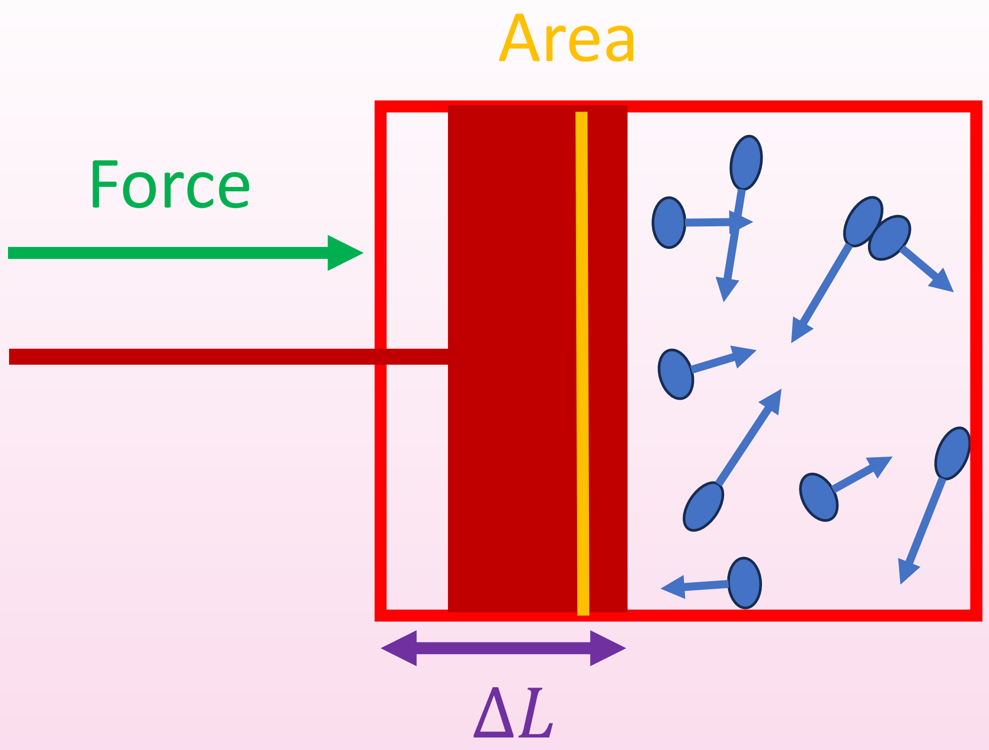
Work done on a gas

Pressure on the gas = force/area

ΔW = force x ΔL

ΔW = pressure x area x ΔL

ΔW = pressure x ΔV



$W_{\mathrm{on}} = \int \mathrm{d}W = \int P\,\mathrm{d}V$ is therefore the work done on the gas

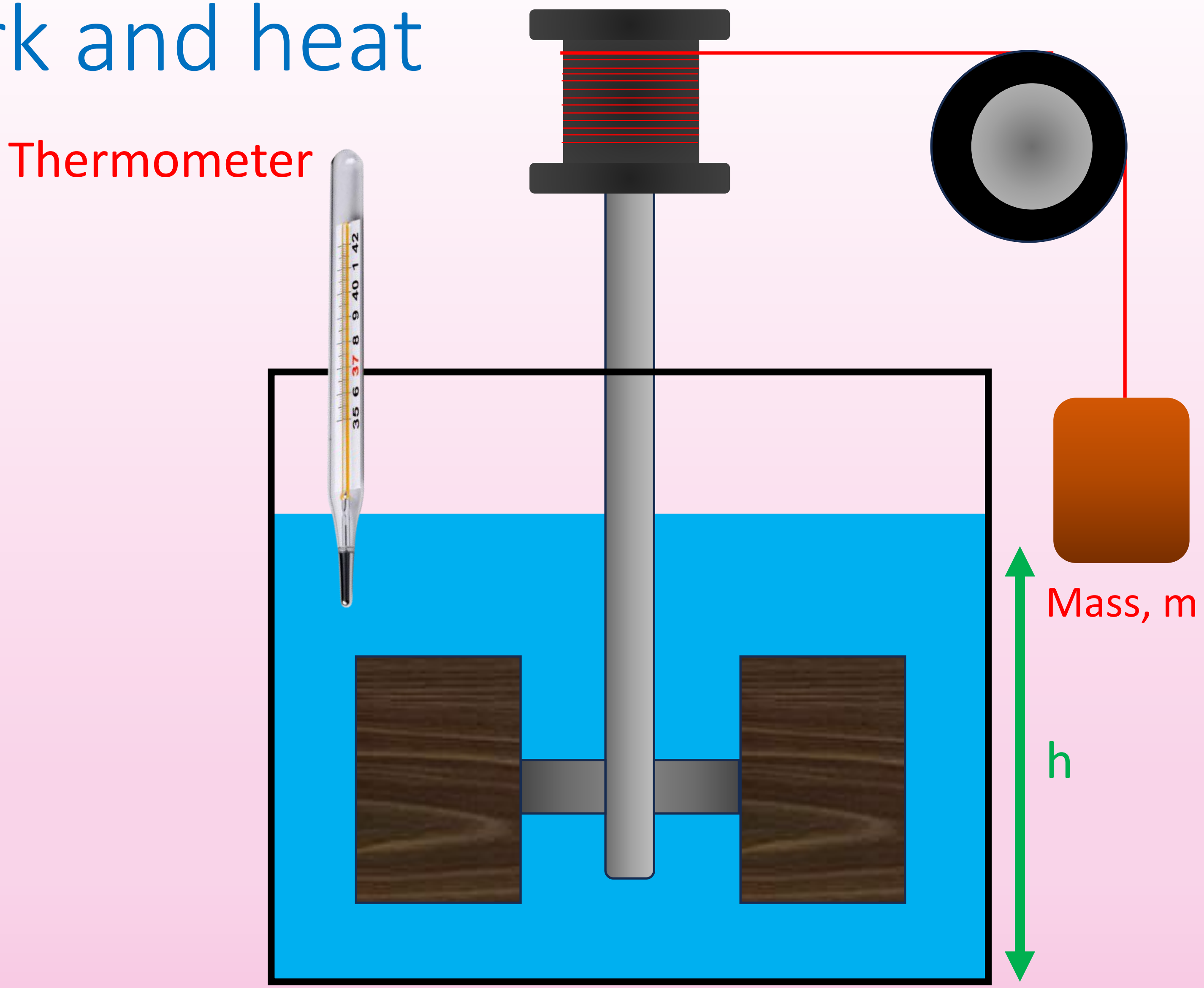
$W_{\mathrm{by}} = -\int P\,\mathrm{d}V$ is the work done by the gas (conservation of energy)

Relationship of work and heat

Mass drops, doing work as potential energy is converted to kinetic energy (mgh)

Paddles are spun by falling mass, raising the temperature of the water

Heat energy and mechanical work must be related



III. *On the Mechanical Equivalent of Heat.* *By* JAMES PRESCOTT JOULE, *F.C.S., Sec. Lit. and Phil. Society, Manchester, Cor. Mem. R.A., Turin, &c. Communicated by* MICHAEL FARADAY, *D.C.L., F.R.S., Foreign Associate of the Academy of Sciences, Paris, &c. &c. &c.*

Received June 6,—Read June 21, 1849.

https://www.jstor.org/stable/108427?seq=2

probable that the above number is slightly in excess. I will therefore conclude by considering it as demonstrated by the experiments contained in this paper,—

1st. *That the quantity of heat produced by the friction of bodies, whether solid or liquid, is always proportional to the quantity of force expended.* And,

2nd. *That the quantity of heat capable of increasing the temperature of a pound of water* (*weighed* in vacuo, *and taken at between* 55° *and* 60°) *by* 1° FAHR., *requires for its evolution the expenditure of a mechanical force represented by the fall of* 772 *lbs. through the space of one foot.*

Oak Field, near Manchester,
June 4th, 1849.

The 1st law of thermodynamics

From Joule's experiments (and logic), it is clear that the change in internal energy of a system, ΔU, is increases with increasing heat transferred into the system, Q_{in}, as well as work done on the system, W_{on}

$$\boxed{\Delta U = Q_{in} + W_{\mathrm{on}}}$$

We can also use this to define internal energy of a system...

Just an expression showing conservation of energy!

Summary

Discussed what an ideal gas is (a non-interacting collection of molecules that collide elastically) and how we can describe it (using any two of the state variables P, V and T)

Learnt that the internal energy of an ideal gas is entirely dependent on the temperature (average kinetic energy of its constituent molecules)

Found that $\Delta U = Q_{in} + W_{\mathrm{on}}$, and that in this house we obey the laws of thermodynamics