Revision Guide for Chapter 13

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I can show my understanding of effects, ideas and relationships by describing and explaining cases involving:

the behaviour of ideal gases Revision Notes: Ideal gas; Ideal gas laws; Summary Diagrams: Boyle's law, density and number of molecules; Change of pressure and volume with temperature; Ideal gas laws in pictures	
the kinetic theory of ideal gases Revision Notes: Assumptions of kinetic theory of gases Summary Diagrams: Kinetic theory of ideal gases	
absolute (Kelvin) temperature as proportional to the average energy per particle, with average energy ≈ kT as a useful approximation Revision Notes: Internal energy Summary Diagrams: Kinetic energy of gas molecules	
energy transfer producing a change of temperature (in gases, liquids and solids) Revision Notes: Specific thermal capacity; Conservation of energy; Summary Diagrams: Transfers of energy to molecules	

I can use the following words and phrases accurately when describing effects and observations:

absolute temperature Revision Notes: Absolute temperature	
ideal gas Revision Notes: Ideal gas	
root mean square speed Revision Notes: Root mean square speed Summary Diagrams: The speed of a molecule	
internal energy Revision Notes: Internal energy	

I can sketch, plot and interpret:

graphs showing relationships between p, V and T for an ideal gas Revision Notes: Ideal gas laws; Summary Diagrams: Change of pressure and volume with temperature; Ideal gas laws in pictures	

I can make calculations and estimates involving:

the universal gas law equation $pV = NkT = nRT$ Revision Notes: Ideal gas laws; Summary Diagrams: Boyle's law, density and number of molecules; Change of pressure and volume with temperature; Ideal gas laws in pictures	
the equation for the kinetic model of a gas: $pV = \frac{1}{3}Nm\overline{c^2}$ Revision Notes: Root mean square speed Summary Diagrams: The speed of a molecule; Kinetic theory of ideal gases	
temperature and energy change using $\Delta E = mc\Delta\theta$ Revision Notes: Specific thermal capacity	

Revision Notes

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Ideal gas

An ideal gas is an abstraction from the fact that many real gases have closely similar behaviour, in particular that the ratio $p\,V / n\,T$ is very nearly the same for all of them at sufficiently low pressure and high temperature.

An ideal gas obeys the ideal gas law: $pV = NkT$. As the pressure is reduced and the temperature raised, real gases approximate more and more closely to this behaviour.

Departure from ideal gas behaviour occurs at high pressures because the volume of the molecules is then a significant fraction of the measured volume, thus reducing the effective volume available for the molecules to move in. Departures occur at low temperatures because the molecules then move slowly enough to be significantly affected by attractions between themselves, thus reducing the gas pressure.

The idea of an ideal gas is also valuable because there is a simple model to explain ideal gas behaviour. This is the kinetic theory of gases.

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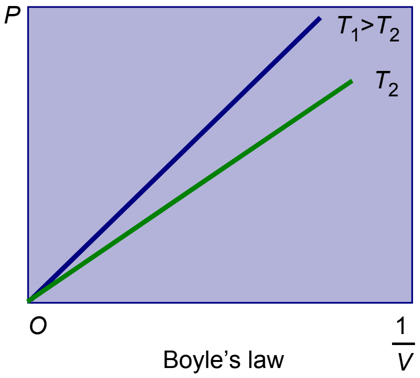
Ideal gas laws

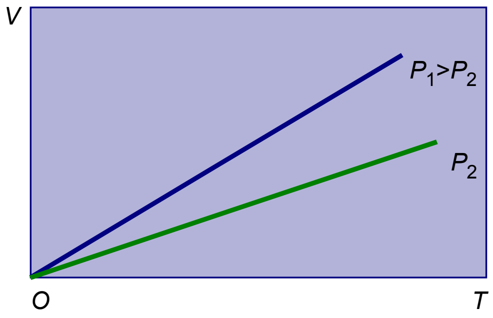
The ideal gas laws are experimental laws relating the pressure p, volume V, temperature T and number n of moles of a gas.

Boyle's law: $p\,V$ = constant for constant n and T.



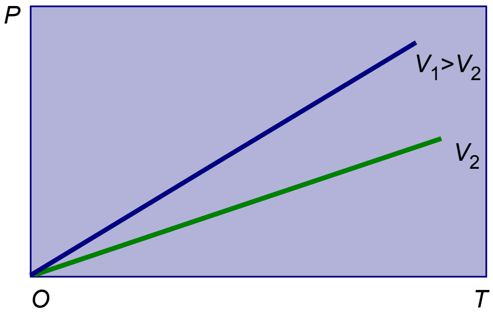
Boyle’s law

Charles' law: V / T = constant for constant p and T.



Charles' law

The **pressure law**: p / T = constant for constant n and V.



The pressure law

These laws can be combined into the general ideal gas law
$pV = NkT$ where N is the number of molecules and k is the Boltzmann constant.

This can also be written as $pV = nRT$ where n is the number of moles, and $R = N_A k$ is the molar gas constant, with N_A the number of molecules per mole (Avogadro number).

The value of R is 8.3 J mol^{-1} K^{-1} because an ideal gas at 273 K and a pressure of 101 kPa has a molar volume V_m = 0.0224 m^3 (or 22.4 litre).

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Assumptions of kinetic theory of gases

The kinetic theory of gases explains the behaviour of a gas as due to the motion of its molecules.

The theory is based on the following assumptions:

1. A gas consists of molecules of negligible size.
2. The molecules collide elastically with each other and the container, on average gaining or losing no energy.
3. The molecules are in continual random motion.
4. There are negligible forces of attraction between the molecules.
5. The duration of an impact is much less than the time between impacts.

Using these assumptions, the ideal gas relationship $pV = NkT$ can be explained. The pressure of a gas is explained as due to the bombardment of the walls of its container by molecules colliding with and rebounding from the walls. See Summary Diagrams: Kinetic theory of ideal gases for the argument in outline.

The kinetic theory gives, for the pressure p of volume V of an ideal gas:

$pV = \frac{1}{3}Nm\langle c^2 \rangle$.

where:

N is the number of molecules

m is the mass of a molecule

$\langle c^2 \rangle$ is the mean of the squares of the molecular speeds

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Internal energy

The internal energy U of a number N of molecules of an ideal monatomic gas is $U = \frac{3}{2}NkT$, where T is the absolute temperature of the gas and k is the Boltzmann constant.

If the temperature of an ideal monatomic gas increases by ΔT, with no change of volume so that no work is done, the internal energy changes by

$\Delta U = \frac{3}{2}Nk\Delta T$

Internal energy is the scientific term that replaces what in everyday speech is called the 'heat' in a body. The term 'heat' is reserved to mean the thermal flow of energy under a temperature difference. See Summary Diagrams: Transfers of energy to molecules

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Specific thermal capacity

The specific thermal capacity of a material is the energy needed to raise the temperature of unit mass of material by 1 K.

The SI unit of specific thermal capacity is J kg^{-1} K^{-1}. The unit of molar thermal capacity is J mol^{-1} K^{-1}.

To change the temperature of mass m of material from T_1 to T_2, the energy transfer to or from the material = $m\,c\,(T_2 - T_1)$, where c is the specific thermal capacity of the material.

In the case of an ideal monatomic gas, the mean energy of a molecule is $\frac{3}{2}kT$, so to raise the temperature of a gas of N molecules by ΔT requires energy $\frac{3}{2}Nk\Delta T$. Thus the thermal capacity per mole, for heating at constant volume, is $\frac{3}{2}N_A k$.

Materials differ in molar thermal capacity because their particles are capable of having energy in several different ways, for example rotation and vibration as well as translation. At high enough temperatures, the energy is shared out equally amongst all these modes.

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Conservation of energy

Imagine a closed boundary drawn around any set of objects, large or small. In a given time, energy may enter across the boundary and energy may leave across the boundary. The Principle of Conservation of Energy states that the change in energy within the boundary is always exactly equal to the difference between that entering and that leaving. Energy is never manufactured or destroyed.

The SI unit of energy is the joule.

The basic means of measuring the amount of energy passed from one part of a system to another is the **work done**, equal to the force acting multiplied by the component in the direction of the force. For this reason, energy is often said to be 'the capacity to do work'.

However, energy is also transferred from one place to another by **thermal flow**, in which no work is done, when energy flows spontaneously across a temperature difference.

Thus internal energy can change in two distinct ways. Work W can be done on the system, and there may be thermal transfer Q of energy.
$\Delta U = W + Q$

This is the First Law of Thermodynamics. See Summary Diagrams: Transfers of energy to molecules

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Absolute temperature

Temperature indicates how hot an object is. Energy flows spontaneously from hotter things to colder things. It is this fact which underlies the everyday notion of 'hotness'.

The Celsius scale of temperature in °C is defined in terms of:

1. Ice point, 0 °C, which is the temperature of pure melting ice.
2. Steam point, 100 °C, which is the temperature of steam at atmospheric pressure.

The absolute scale of temperature, in kelvin (K), is defined in terms of two fixed points:

1. Absolute zero, 0 K, the lowest possible temperature.
2. The triple point of water, approximately 273 K, which is the temperature at which water, water vapour and steam coexist.

By assigning a value of 273 K to the triple point of water, the interval between ice point and steam point is 100 K, hence:

Absolute temperature in K = temperature in °C + 273.

The mean kinetic energy of the particles of a monatomic ideal gas at absolute temperature T is equal to $\frac{3}{2}kT$, where k is the Boltzmann constant. In general, at sufficiently high temperatures, the energy per particle in any material is some small multiple of kT.

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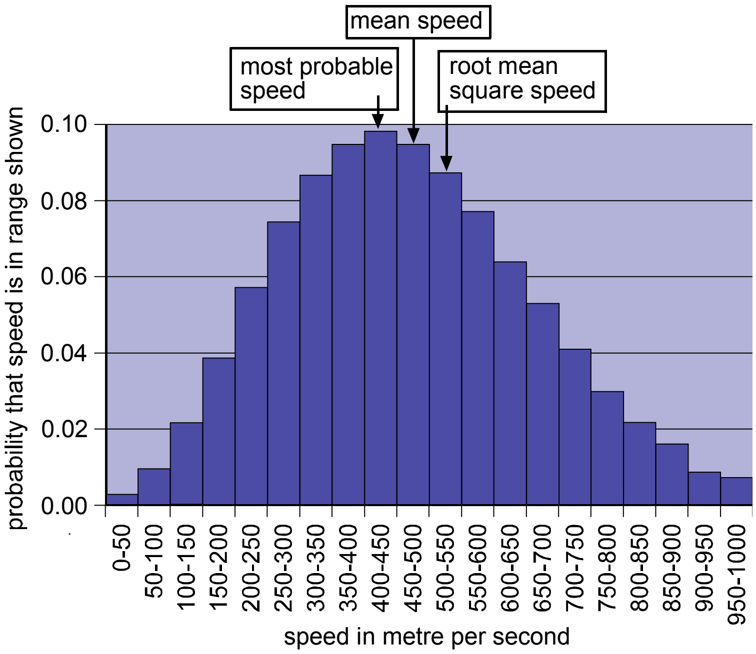
Root mean square speed

The speeds of molecules in a gas vary around an average value. The distribution of speeds of molecules in nitrogen at 300 K is shown below.



The peak of the distribution, the most probable speed, is at 422 m s^{-1}. The mean speed is a little larger, 476 m s^{-1}.

The kinetic theory predicts the total translational kinetic energy of the molecules:

$$\tfrac{1}{2}mv_1^2 + \tfrac{1}{2}mv_2^2 + \ldots . \tfrac{1}{2}mv_N^2 = \tfrac{3}{2}NkT$$

Thus the average of the *squares* of the speeds is equal to $\dfrac{3kT}{m}$

The square root of the mean square speed is called the ‘root mean square speed’. In the case of nitrogen at 300 K it is 517 m s^{-1}.

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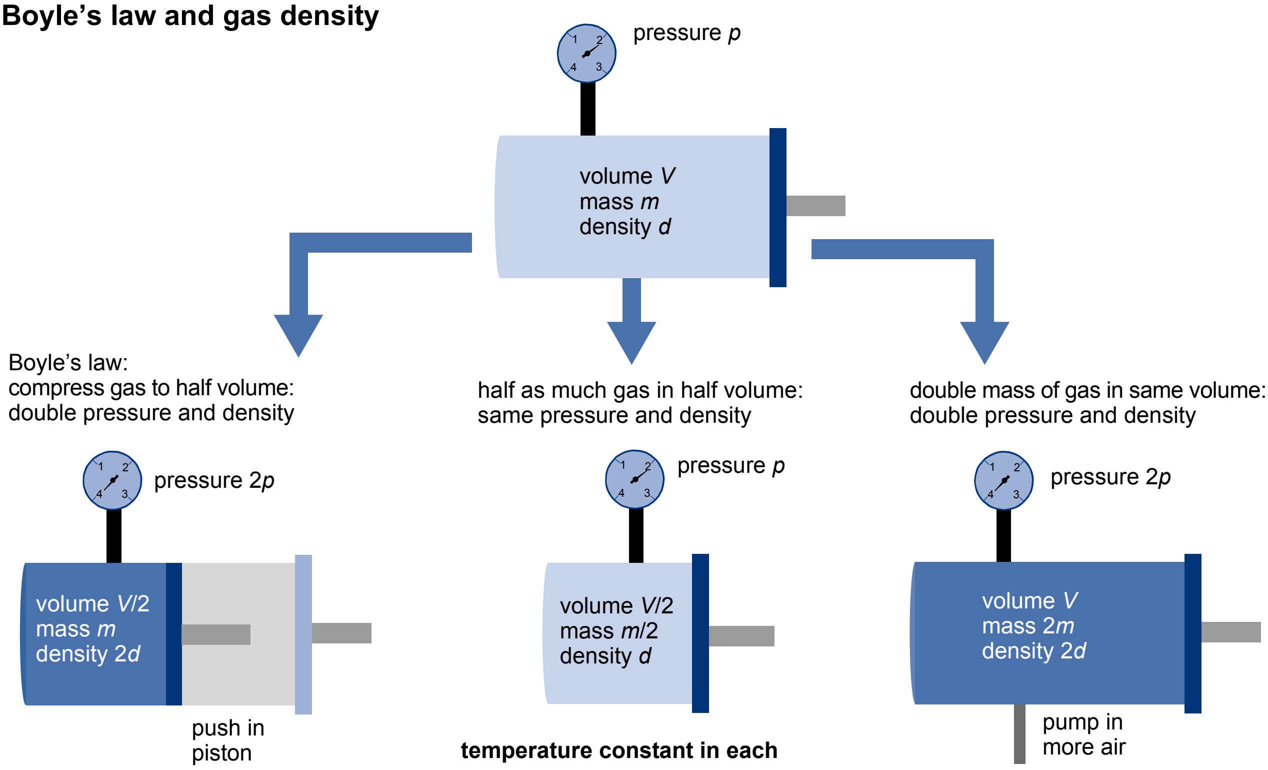
Boyle’s law, density and number of molecules

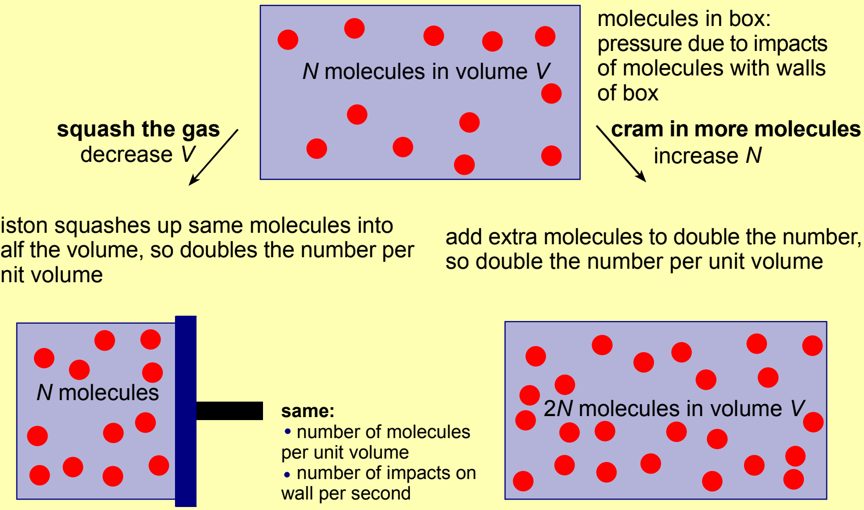
Boyle’s law and gas density



Boyle’s law says that gas pressure is proportional to density

Boyle's law and number of molecules

Two ways to double gas pressure



molecules in box: pressure due to impacts of molecules with walls of box

squash the gas
decrease *V*

cram in more molecules
increase *N*

piston squashes up same molecules into half the volume, so doubles the number per unit volume

add extra molecules to double the number, so double the number per unit volume

same:
- number of molecules per unit volume
- number of impacts on wall per second
- pressure

pressure proportional to 1/volume
$p \propto 1/V$

pressure proportional to number of molecules
$p \propto N$

If.... pressure is proportional to number of impacts on wall per second

and if.... number of impacts on wall per second is proportional to number of molecules per unit volume

Then.... pressure is proportional to number of molecules per unit volume

$p = \text{constant} \times N/V$

Boyle's law in two forms

$$pV = \text{constant} \times N \qquad p = \text{constant} \times N/V$$

Boyle's law says that pressure is proportional to crowding of molecules

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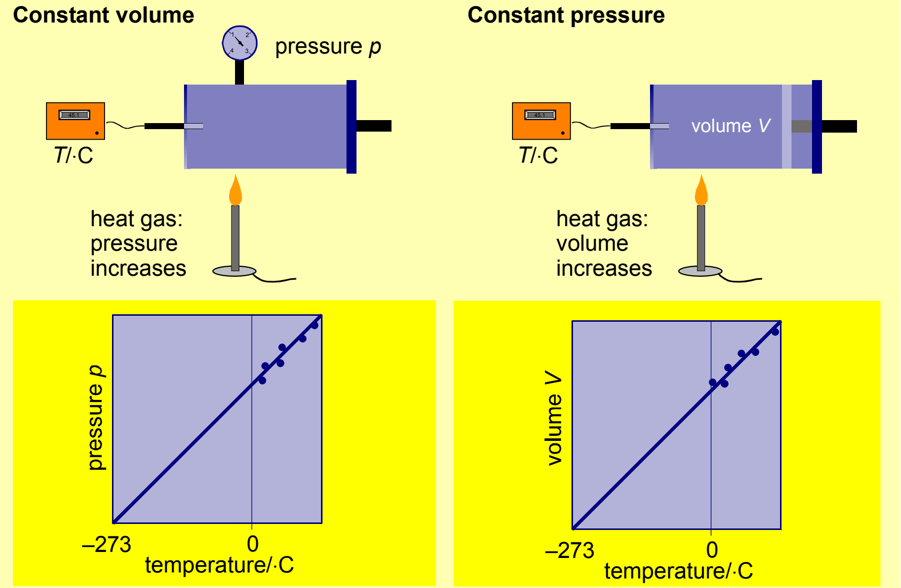
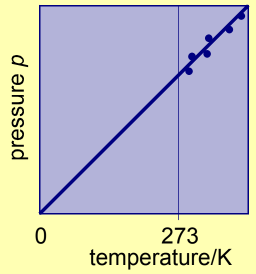
Change of pressure and volume with temperature

Pressure and volume of gases increasing with temperature

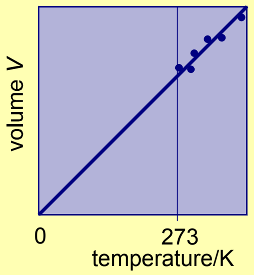


Pressure and volume extrapolate to zero at same temperature –273.16 °C
So define this temperature as zero of Kelvin scale of temperature, symbol T



pressure proportional to Kelvin temperature

$p \propto T$



volume proportional to Kelvin temperature

$V \propto T$

Pressure and volume proportional to absolute temperature

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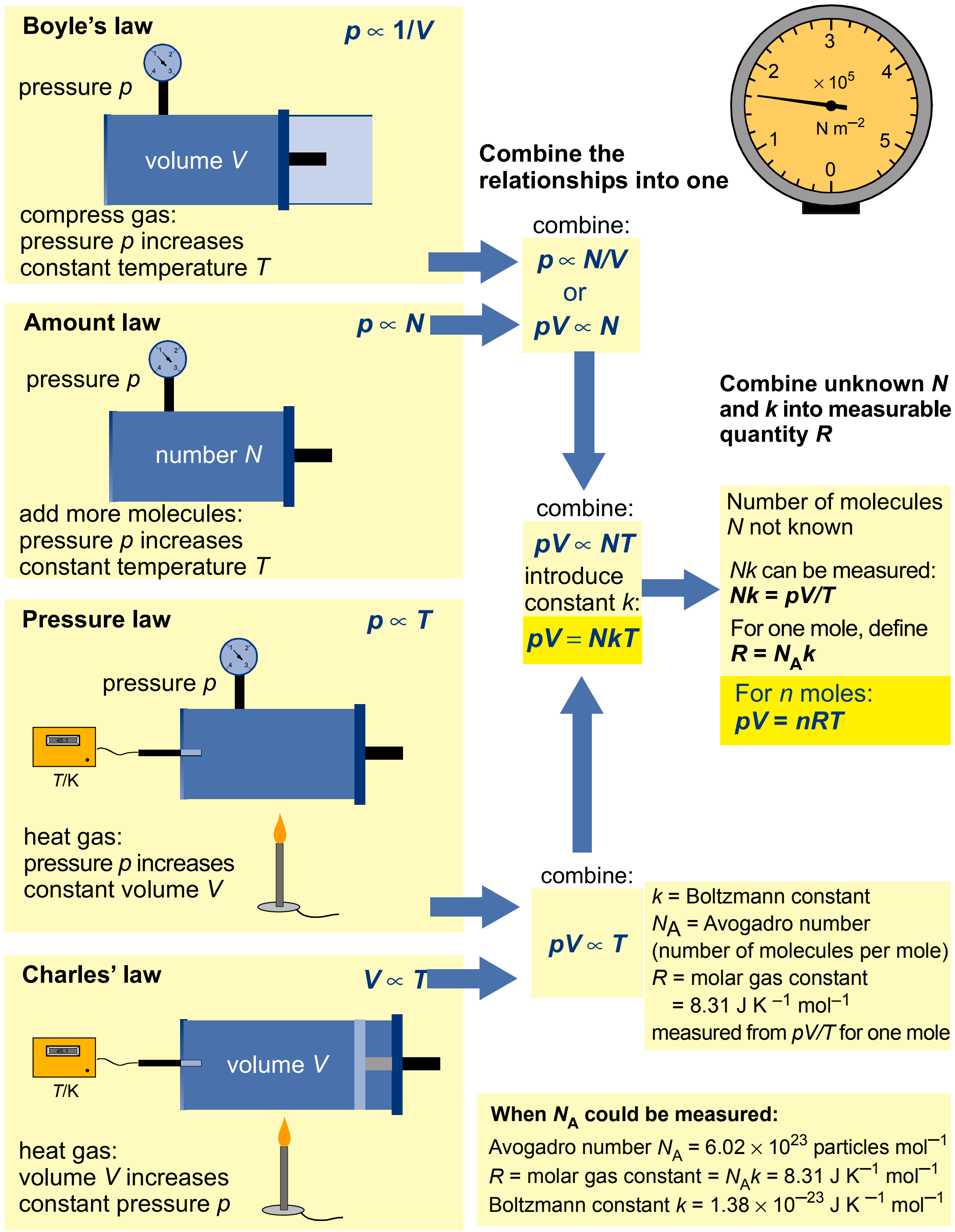
Ideal gas laws in pictures

One law for all gases



Boyle's law $p \propto 1/V$

compress gas:
pressure p increases
constant temperature T

Amount law $p \propto N$

add more molecules:
pressure p increases
constant temperature T

Pressure law $p \propto T$

heat gas:
pressure p increases
constant volume V

Charles' law $V \propto T$

heat gas:
volume V increases
constant pressure p

Combine the relationships into one

combine:
$p \propto N/V$
or
$pV \propto N$

combine:
$pV \propto T$

combine:
$pV \propto NT$
introduce constant k:
$pV = NkT$

Combine unknown N and k into measurable quantity R

Number of molecules N not known

Nk can be measured:
$Nk = pV/T$

For one mole, define
$R = N_A k$

For n moles:
$pV = nRT$

k = Boltzmann constant
N_A = Avogadro number (number of molecules per mole)
R = molar gas constant
= 8.31 J K^{-1} mol^{-1}
measured from pV/T for one mole

When N_A could be measured:

Avogadro number $N_A = 6.02 \times 10^{23}$ particles mol^{-1}
R = molar gas constant = $N_A k$ = 8.31 J K^{-1} mol^{-1}
Boltzmann constant $k = 1.38 \times 10^{-23}$ J K^{-1} mol^{-1}

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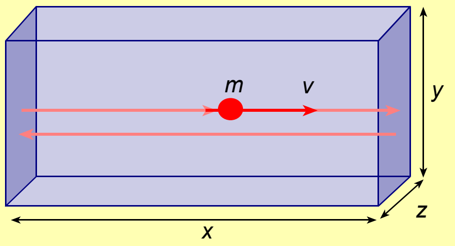
Kinetic theory of ideal gases

Kinetic model of a gas 1

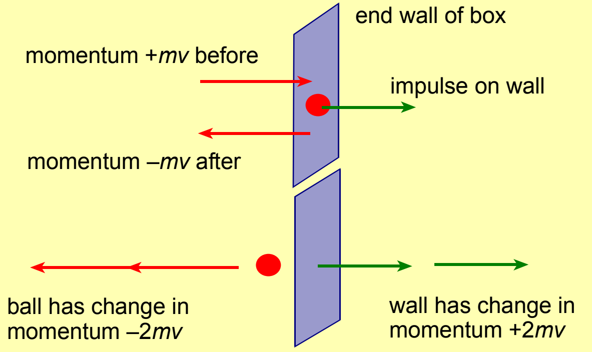
To start: one molecule in a box



round trip time between collisions $\Delta t = 2x/v$

collisions per second = $v/2x$

Use change of momentum


end wall of box

momentum $+mv$ before

impulse on wall

momentum $-mv$ after

ball has change in momentum $-2mv$

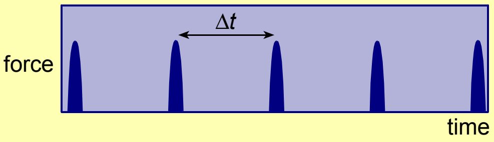
wall has change in momentum $+2mv$

momentum $2mv$ given to wall at each collision

Force = rate of change of momentum

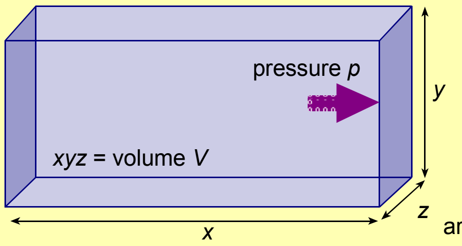
force on wall =
momentum per collision × collisions per second
$2mv$ $v/2x$

force on wall = mv^2/x



impulse each time molecule returns

Kinetic model of a gas 2



area of wall = yz

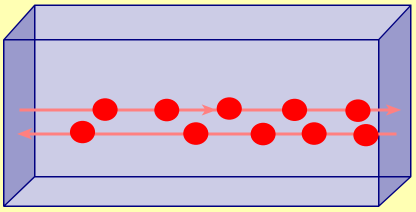
Calculate pressure = force on wall/area of wall

force on wall = mv^2/x

pressure = mv^2/xyz (area = yz)

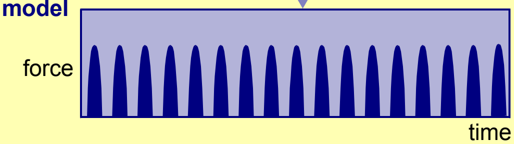
pressure $p = mv^2/V$ ($V = xyz$)

add many molecules all doing the same



N molecules

improve model

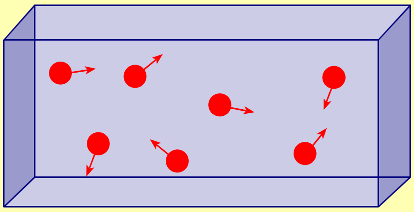


N times as many collisions per second

pressure $p = Nmv^2/V$

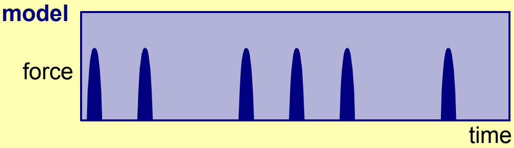
Kinetic model of a gas 3

allow molecules to move in random directions



1/3 of molecules
in each direction,
on average

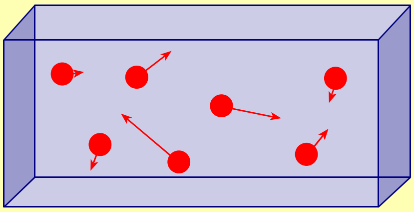
improve model



1/3 as many collisions per second

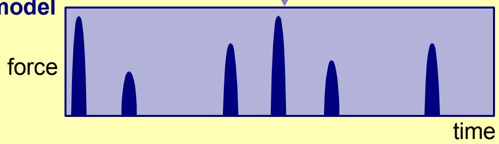
pressure $p = \frac{1}{3}\ Nmv^2/V$

allow molecules to move at random speeds



take average
over v^2

improve model



average impulse stays the same

pressure $p = \frac{1}{3}\ Nm\overline{v^2}/V$

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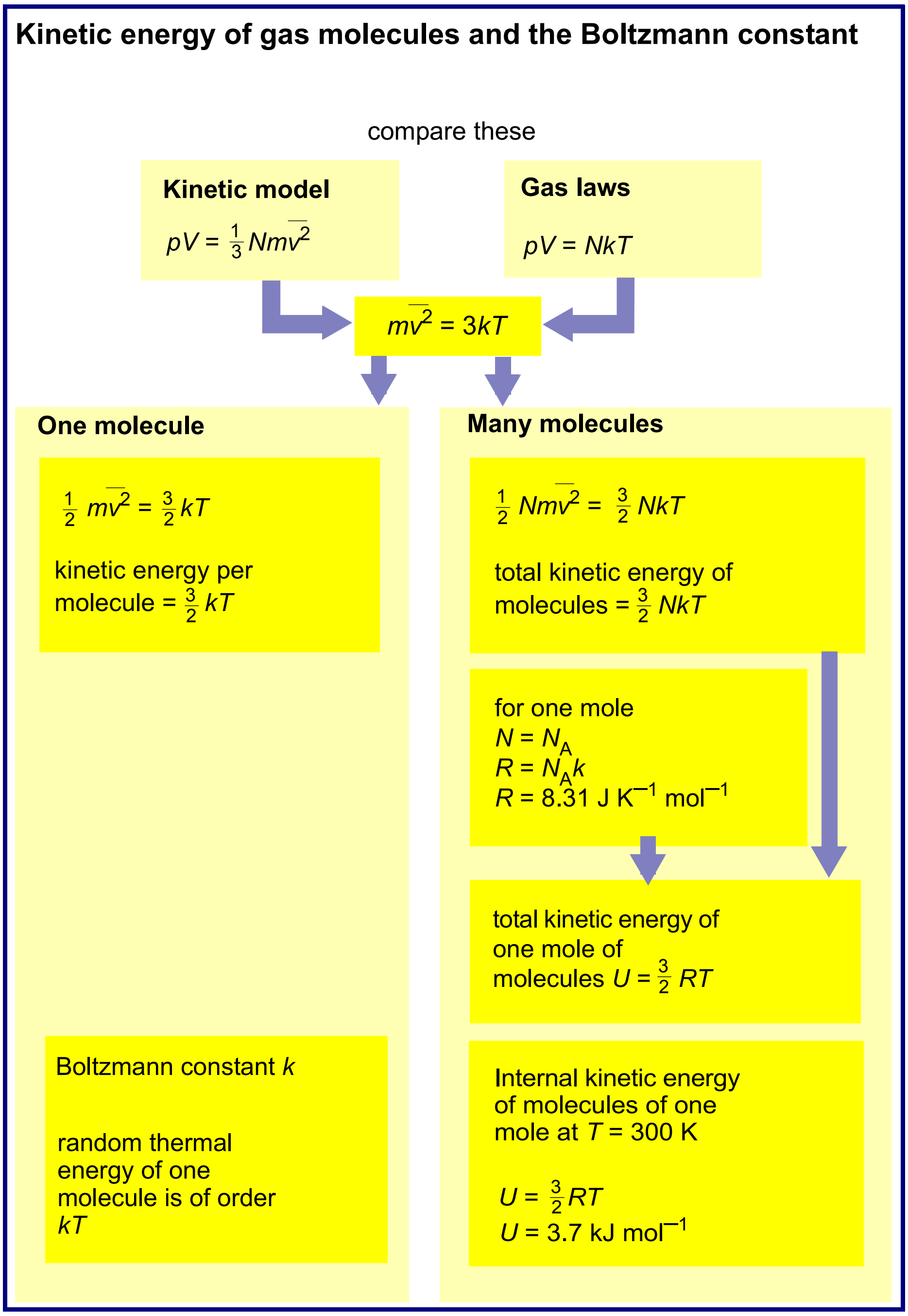
Kinetic energy of gas molecules



Kinetic energy of gas molecules and the Boltzmann constant

compare these

Kinetic model

$pV = \frac{1}{3}Nm\overline{v^2}$

Gas laws

$pV = NkT$

$m\overline{v^2} = 3kT$

One molecule

$\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$

kinetic energy per molecule = $\frac{3}{2}kT$

Boltzmann constant k

random thermal energy of one molecule is of order kT

Many molecules

$\frac{1}{2}Nm\overline{v^2} = \frac{3}{2}NkT$

total kinetic energy of molecules = $\frac{3}{2}NkT$

for one mole
$N = N_A$
$R = N_Ak$
$R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$

total kinetic energy of one mole of molecules $U = \frac{3}{2}RT$

Internal kinetic energy of molecules of one mole at $T = 300$ K

$U = \frac{3}{2}RT$
$U = 3.7\ \text{kJ mol}^{-1}$

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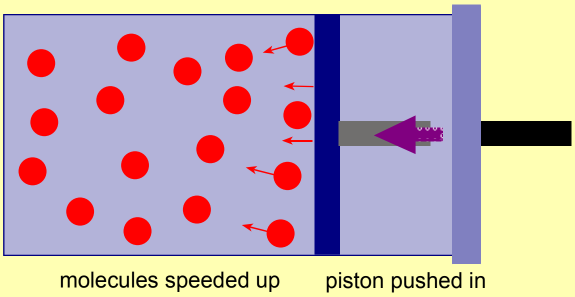
Transfers of energy to molecules

Transfers of energy to molecules in two ways

Hit the molecules yourself

work done = force × distance

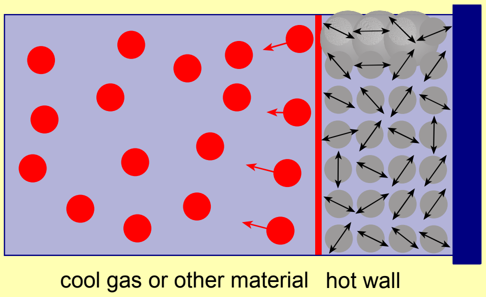


Here the piston strikes molecules and gives extra momentum and so extra kinetic energy.

energy transferred = work W done

Let other molecules hit them

thermal transfer = $mc\,\Delta\theta$



Here the molecules in the hot wall hit other molecules hard and on average give them extra kinetic energy.

energy transferred = energy Q transferred thermally

when both ways are used:

change in internal energy ΔU

=

work done W *plus* thermal transfer Q

$$\Delta U = W + Q$$

Engine designers arrange to transfer energy by way of heating and by way of doing work

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The speed of a molecule

Speed of a nitrogen molecule

Assume warm room temperature $T = 300$ K

mass of 1 mole of $N_2 = 28 \times 10^{-3}$ kg mol^{-1}

Avogadro constant $N_A = 6 \times 10^{23}$ particles mol^{-1}

Boltzmann constant $k = 1.38 \times 10^{-23}$ J K^{-1}

kinetic energy of a molecule

from dynamics

from kinetic model

$$\frac{1}{2}mv^2 \rightarrow v^2 = \frac{3\,kT}{m} \leftarrow \frac{3}{2}kT$$

mass m of N_2 molecule

$$m = \frac{\text{mass of 1 mole of } N_2}{\text{Avogadro constant } N_A}$$

$$m = \frac{28 \times 10^{-3}\ \text{kg mol}^{-1}}{6 \times 10^{23}\ \text{mol}^{-1}}$$

$$m = 4.7 \times 10^{-26}\ \text{kg}$$

calculate speed

$$v^2 = \frac{3 \times 1.4 \times 10^{-23}\ \text{J K}^{-1} \times 300\ \text{K}}{4.7 \times 10^{-26}\ \text{kg}}$$

$$v^2 = 2.7 \times 10^{5}\ \text{J kg}^{-1}\ [\text{same as } (\text{m s}^{-1})^2]$$

$v = 500$ m s^{-1} approximately

Air molecules (mostly nitrogen) at room temperature go as fast as bullets

The speed calculated here is the root mean square speed.

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