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, Changing pressure and volume by changing temperature, One law, summarising empirical laws	
the kinetic theory of ideal gases Revision Notes: assumptions of kinetic theory of gases Summary Diagrams: Constructing a model of a gas	
absolute (Kelvin) temperature as proportional to the average energy per particle, with average energy $\approx kT$ as a useful approximation Revision Notes: internal energy Summary Diagrams: The kinetic energy of a single particle	
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Random walk of molecules in a gas; distance gone in N steps related to $\sqrt{N}$ Revision Notes: Brownian motion, random processes, random variation Summary Diagrams: Bromine diffusing, Random walk	

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 nitrogen molecule	
internal energy Revision Notes: internal energy, thermal properties of materials, specific thermal capacity	

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: Changing pressure and volume by changing temperature, One law, summarising empirical laws	

I can make calculations and estimates involving:

the universal gas law equation $pV = NkT$ where $N = nN_A$ and $Nk = nR$; number of moles n and Avogadro constant N_A	
Revision Notes: ideal gas laws, the mole and Avogadro number	
Summary Diagrams: Boyle's law, density and number of molecules, Changing pressure and volume by changing temperature, One law, summarising empirical laws	
the equation for the kinetic model of a gas: $pV = \frac{1}{3}Nm\overline{c^2}$	
Revision Notes: assumptions of kinetic theory of gases, root mean square speed	
Summary Diagrams: Constructing a model of a gas, Boltzmann constant and gas molecules, The kinetic energy of a single particle, The speed of a nitrogen molecule	
temperature and energy change using $\Delta E = mc\Delta\theta$	
Revision Notes: specific thermal capacity	
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Revision Notes

Ideal gas

An ideal gas is an abstraction from the fact that many real gases have closely similar behaviour, in particular that the ratio pV/nT (where n is the number of moles of gas present) is very nearly the same for all of them at sufficiently low pressure and high temperature. This ratio is called the gas constant R.

An ideal gas obeys the ideal gas law: $pV = NkT$ (where N is the number of molecules of gas and k is the Boltzmann constant). As the pressure is reduced and the temperature raised, real gases approximate more and more closely to this behaviour.

Comparing the two equations above shows that $Nk = nR$. For 1 mole, $n = 1$ and $N = N_A$ the Avagadro constant. Thus $R = N_A k$.

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.

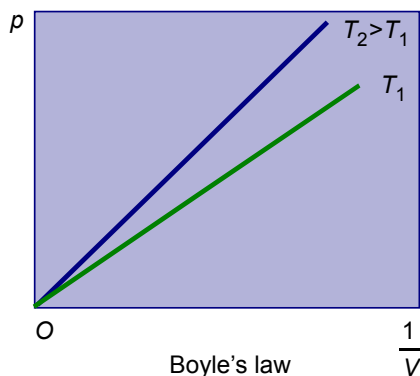The idea of an ideal gas is also valuable because there is a simple model to explain ideal gas behaviour. This is the kinetic theory of gases.
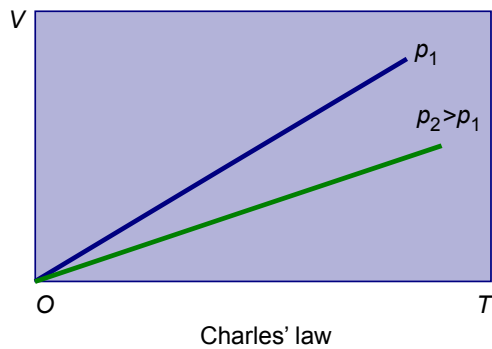
Ideal gas laws

The ideal gas laws are experimental laws relating the pressure p, volume V, temperature T and number n of moles of a gas.
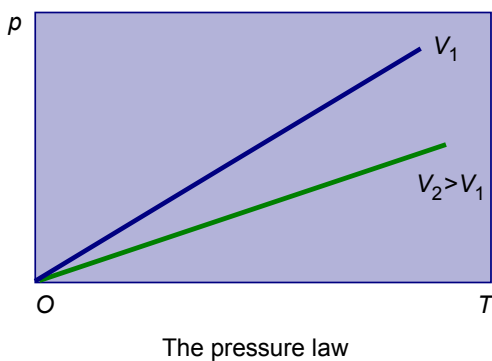
Boyle's law: pV = constant for constant n and T.

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}, calculated from the fact that 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 derived. 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: Constructing a model of a gas for the argument in outline.

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

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

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 $U = \tfrac{3}{2} NkT$,

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

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

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: Transferring 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 (i.e. 1kg) 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 $\tfrac{3}{2} kT$, so to raise the temperature of a gas of N molecules by ΔT requires energy $\tfrac{3}{2} Nk\Delta T$. Thus the thermal capacity per mole, for heating at constant volume, is $\tfrac{3}{2} N_A k$.

Materials differ in molar thermal capacity because their particles are capable of storing 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.

There are two basic means of measuring the amount of energy passed from one part of a system to another. **Work done**, equal to the force acting multiplied by the component of the displacement in the direction of the force.

Energy is also transferred from one place to another by **thermal flow**, in which no work is done, but 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 Diagram: Transferring energy to molecules

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Brownian motion

Brownian motion is the random jittering motion of small particles of matter suspended in a gas or in liquid. Each particle is bombarded haphazardly and unevenly by fast moving molecules.

Brownian motion is seen when smoke particles in air, or fragments of pollen grains in water, are observed using a microscope. These particles are of the order of a micrometre or less in size and are continually bombarded by fast moving air or water molecules too small to see. Because the bombardment is uneven and random, each particle is pushed by the average force of impacts in a direction which changes continuously at random. This unpredictable motion is increased if the temperature of the liquid or gas is increased as the molecules move faster on average so the impacts are greater and more frequent.

Brownian motion

arrangement

microscope view
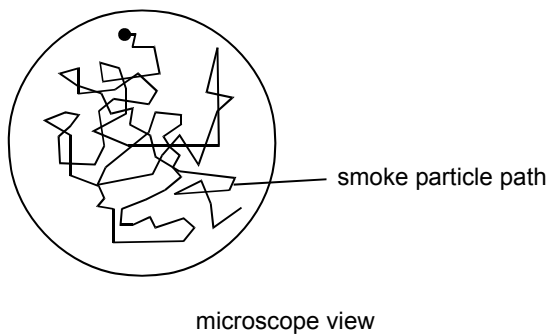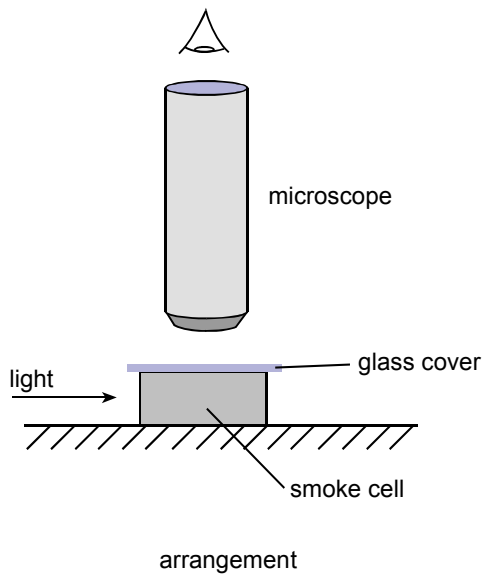
The average distance traveled in N steps is of the order $\sqrt{N}$ steps.

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Random processes

Random processes occur where individual changes or events cannot be predicted in detail, but only on average. Such processes are important in the theory of radioactive decay and in the kinetic theory of gases.

A random process is a change or an event with one or more outcomes, including no change, that can occur with a certain probability in a given time interval.

The statistical outcome of a very large number of random changes or events is very predictable.

Radioactive decay of an unstable isotope
The decay of an unstable nucleus is a random event. Each unstable nucleus is as likely to disintegrate in a given time interval as any other unstable nucleus of the isotope. Thus the probability of the decay of a nucleus in a certain time interval is the same for any nucleus.

Hence, for N unstable nuclei, the number of nuclei δN that disintegrate in a short time interval δt is proportional to N and to δt, that is δN is proportional to $N \, \delta t$.

Introducing a constant of proportionality λ, the decay constant, gives $\delta N = -\lambda N \delta t$, where the minus sign indicates a decrease of the number of nuclei with increase of time.

The decay constant λ is therefore equal to the fraction of nuclei that decay per unit time. That is

$$\lambda = -\frac{\delta N / N}{\delta t}$$

equal to the probability of decay per unit time.

The above equation gives

$$\frac{\delta N}{\delta t} = -\lambda N$$

which becomes

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -\lambda N$$

in the limit $\delta t \rightarrow 0$.

The solution of the differential equation above is

$$N = N_0 e^{-\lambda t}$$

where N_0 is the initial number of unstable nuclei present.

Random walk
A molecule in a gas collides randomly and frequently with other molecules. Thus it changes direction frequently, taking a complicated zig-zag path. The average displacement on such a path is zero. But the root mean square distance travelled is $\sqrt{N}$ x the step length if the total zig-zag path contains N steps.

Typically a gas molecule at ordinary temperatures and pressures makes steps of the order 10^{-7} m between collisions, colliding about 10^9 times each second. Thus in 1000 seconds (a quarter of an hour) it will make $N = 10^{12}$ steps in a zig-zag path of total length 10^5 m. In the same time, the root mean square distance travelled from its starting point will be of the order 10^6 x 10^{-7} m = 0.1 m. This is typical of the distance through which molecules of a gas diffuse in several minutes.

Similarly, the number N of counts that occur in a given time, in a random process such as radioactive decay, will fluctuate. It is likely to vary above or below the value N by an amount equal to $\sqrt{N}$. The fractional variation expected is of the order $(\sqrt{N}) / N$, which equals $1/(\sqrt{N})$ and gets smaller as N increases.

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Random variation
Random variation has to do with small unpredictable variations in quantities, for example electrical noise. Some variations in experimental results may appear to be random.

Random events are such that the occurrence of one such event predicts nothing about the occurrence of another. Truly random variation may be rather rare. It does appear to arise in quantum phenomena, where only the probability of events can be calculated. Random electrical noise is a practical example. However, variations due to a number of minor and unrelated causes often combine to produce a result that appears random. Values vary unsystematically, and in no obvious sequence. Because there are well-established statistical ways of dealing with random variation, variations in measurements are often treated as if they were random, despite lack of evidence that they really are random.

In measurement, when accidental variations with known or suspected causes have been eliminated, systematic error has been allowed for, and no trends in the variations appear, variations of measurements around a central value are often treated as random.

The range within which the value of a quantity may reasonably be believed to lie may be reduced somewhat by making many equivalent measurements, and averaging them. If there are N independent but equivalent measurements, each with an estimated uncertainty, then the uncertainty of the mean of N values is smaller than the uncertainty of a single value by the factor $\sqrt{N}$.

Radioactive decay is a random process. This is why repeated counts using a Geiger tube at a fixed distance from a radioactive source with a long half-life give measurements that vary at random. The probability of arrival of a count within any short period of time is fixed, regardless of the time since the last count arrived. Repeated counts taken over a fixed period of time show a distribution of the number of counts arriving in that time. The distribution is called the Poisson distribution. The most frequent number of counts in a fixed time is simply the long run average of counts in that time. If this average is N counts, the number of counts in the fixed time varies typically by $\pm \sqrt{N}$.

We can expect about 70% of equivalent readings to lie within the range from $N - \sqrt{N}$ to $N + \sqrt{N}$. To reduce the uncertainty in a set of observations to less than 5%, the number of counts should be over 400, corresponding to $\sqrt{N} / N = 0.05$. For an uncertainty of less than 1%, the number of counts should be more than 10 000, corresponding to $\sqrt{N} / N = 0.01$.

Poisson distribution

range $\overline{N} \pm \sqrt{N}$

frequency of counts

$\sqrt{N}$

$\overline{N}$ count N
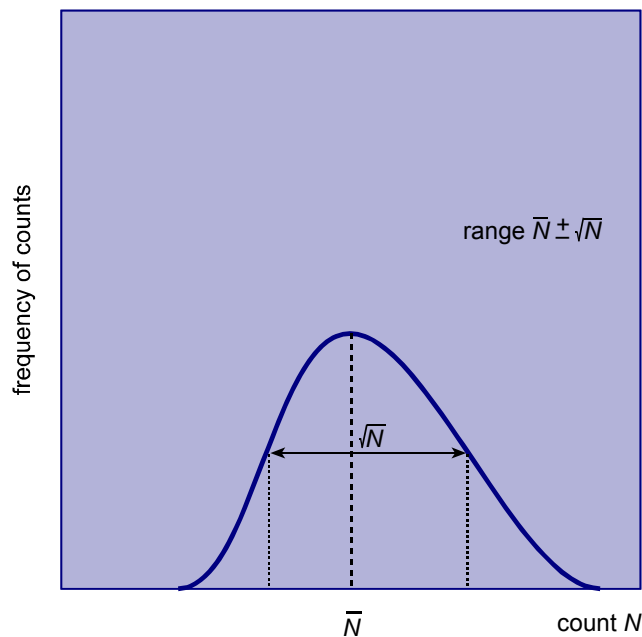
Absolute temperature

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 where three phases of water – liquid, solid and gas – co-exist in equilibrium.

By assigning the exact value of 273.16 K to the triple point of water, the interval between ice point and steam point is 100 K, hence (to 3 significant figures):

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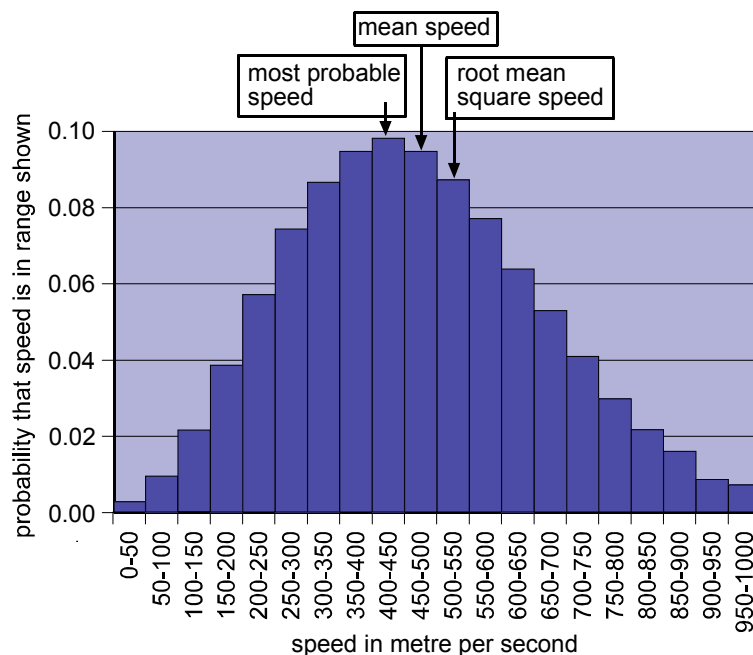
The peak of the distribution, the most probable speed, is at 422 m s^{-1}. The mean speed is a little larger, 476 m s^{-1}.

The kinetic theory predicts the total translational kinetic energy of the molecules:
$\frac{1}{2}mv_1^2 + \frac{1}{2}mv_2^2 + ... \frac{1}{2}mv_N^2 = \frac{3}{2}NkT$

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}.

Thermal properties of materials

The thermal properties of a material describe how it responds to changes in temperature.

The thermal properties of materials include:

1. Specific thermal capacity, which is the energy needed to raise the temperature of unit mass of material by one degree.

2. Specific latent heat for a given change of phase, which is the energy needed to change unit mass of material, without change of temperature, for example from liquid to vapour.

3. Thermal expansion which is the change of length of a solid per unit length per unit change in temperature.

4. Thermal conductivity which is the energy conducted per unit cross-sectional area through a substance per unit temperature gradient normal to the area.

There is energy stored inside a lump of matter. Much of this is the energy of random thermal agitation of its atoms, ions or molecules, including kinetic energy of motion of particles and potential energy arising from forces between them. There may also be energy the particles have because the material is magnetised, for example. The higher the temperature, the greater the energy randomly dispersed amongst the particles. If the energy per particle is large enough, bonds begin to be broken so that, for example the substance may change phase from solid to liquid to vapour, or to atoms may begin to disassociate into ions and electrons.

To raise the temperature of mass m of a substance from T_1 to T_2, the energy needed $\Delta E = m C (T_2 - T_1)$, where C is the specific thermal capacity of the material. The unit of C is J kg^{-1} K^{-1} or J mol^{-1} K^{-1}.

The energy ΔE needed to melt mass m of a substance, without a change in temperature is $\Delta E = mL$, where L is the **specific latent heat** of fusion. There are similar latent heats of evaporation and sublimation when a liquid or solid becomes a vapour. The unit of L is J kg^{-1} or J mol^{-1}.

When the temperature of a solid or a liquid increases, the particles vibrate with increased amplitude. If the vibrations were purely harmonic, their mean positions would not change because the oscillations are symmetrical. But if the vibrations are unsymmetrical (anharmonic) the increased amplitude may lead to a small increase in the average distance between particles. This is why most materials expand on heating, but is also why this expansion is rather small. The increase in length or volume is often approximately proportional to the temperature change.

Thermal conduction is the flow of energy under a difference of temperature.

1. The temperature gradient between any two points is the temperature difference between the two points divided by the distance between them. The unit of temperature gradient is K m^{-1}.

2. Heat transfer takes place along a temperature gradient. For a sample of material of length L and cross-sectional area A, the energy transfer Q in time t along the length of the sample is proportional to the temperature gradient, and is given by the equation

$$\frac{Q}{t} = \frac{kA(T_1 - T_2)}{L}$$

where T_1 is the temperature at the hot end of the sample, T_2 is the temperature at the cooler end and k is the **thermal conductivity** of the sample.

The unit of thermal conductivity k is $W\ m^{-1}\ K^{-1}$.

Temperature gradient
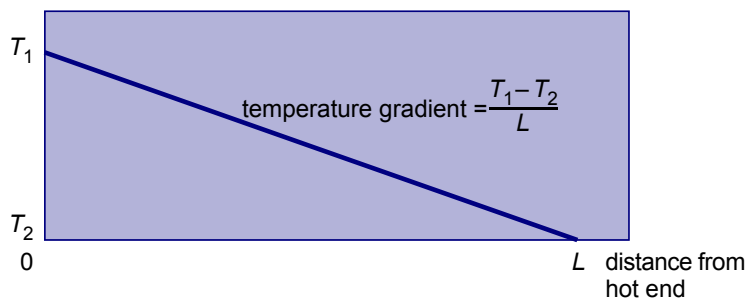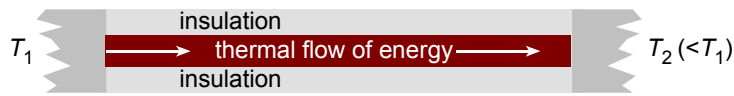
The above equation is analogous to the electrical equation

$$I = \sigma A \frac{V}{L}$$

for the current I through a conductor of uniform cross-sectional area A and length L when a potential difference V is applied across its ends. Thermal conductivity k and electrical conductivity σ are in this way analogous.

Relationships
1. Specific thermal capacity: $\Delta E = m\ C\ (T_2 - T_1)$

2. Specific latent heat: $\Delta E = m\ L.$

3. Thermal expansion: $\Delta L = \alpha\ L\ (T_2 - T_1).$

4. Thermal conductivity:

$$\frac{Q}{t} = \frac{kA(T_1 - T_2)}{L} \quad \text{where } T_1 > T_2.$$

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The mole and Avogadro number
Atoms and molecules are counted in moles where 1 **mole** is defined as the number of atoms present in exactly 12 g of $^{12}_{6}C$ (carbon 12). Carbon-12 is chosen as a reference because it can be separated easily from the other carbon isotopes.

The number of atoms in 12 g of carbon-12 has been measured accurately and is equal to 6.02×10^{23}. This number is referred to as the **Avogadro** constant (symbol N_A). Thus n moles of substance consisting of identical particles contains $n\,N_A$ such particles.

The **molar mass** M of a substance is the mass of N_A particles of the substance. Thus the mass of one particle of the substance of molar mass M is equal to M / N_A.

1 **atomic mass unit** (u) is defined as one-twelfth of the mass of a carbon-12 atom. A carbon-12 atom has a mass which is equal to 2.0×10^{-23} g (= 12 g / N_A).

Hence 1 u = 1/12 $\times$ 12 g / N_A = 1/ N_A in grams = 1.66×10^{-24} g = 1.66×10^{-27} kg.

Because the mass of a proton and of a neutron are both approximately equal to 1 u, the mass number of an isotope is therefore approximately equal to the mass in grams of one mole of the atoms of that isotope. For example, a nucleus of $^{238}_{92}U$ (uranium-238) consists of 238 neutrons and protons and therefore has a mass of approximately 238 u. Hence the mass of N_A uranium 238 atoms is approximately 238 g or 0.238 kg.

The number of atoms or molecules in mass m of an element or compound of molar mass M is equal to the number of moles (m / M) $\times$ the number of particles per mole N_A. This type of calculation is used in radioactivity calculations where the number of atoms in a radioactive isotope has to be determined. For example, the number of atoms in 1 kg of $^{238}_{92}U$ (uranium-238) is (1 / 0.238)N_A.

Relationships
The number of atoms or molecules in mass m of an element or compound of molar mass M is equal to (m / M)N_A.

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Summary Diagrams

Boyle's law, density and number of molecules

Boyle's law and gas density

pressure p

volume V
mass m
density d

Boyle's law:
compress gas to half volume:
double pressure and density

half as much gas in half volume:
same pressure and density

double mass of gas in same volume:
double pressure and density

pressure $2p$

volume $V/2$
mass m
density $2d$

push in
piston

pressure p

volume $V/2$
mass $m/2$
density d

temperature constant in each case

pressure $2p$

volume V
mass $2m$
density $2d$

pump in
more air

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

Boyle's law and number of molecules

Two ways to double gas pressure

N molecules in volume V

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

N molecules in volume V/2

2N molecules in volume V

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

pressure proportional to 1/volume
p 1/V

pressure proportional to number of molecules
p 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 = constant N/V

Boyle's law in two forms

pV = constant N   p = constant   N/V

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

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Changing pressure and volume by changing temperature

Pressure and volume of gases increasing with temperature

Constant volume

pressure *p*

T/ C

heat gas:
pressure
increases

pressure *p*

−273   0
temperature/ C

Constant pressure

volume *V*

T/ C

heat gas:
volume
increases

volume *V*

−273   0
temperature/ C

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 *p*

0   273
temperature/K

pressure proportional to Kelvin temperature
p   T

volume *V*

0   273
temperature/K

volume proportional to Kelvin temperature
V   T

Pressure and volume are proportional to absolute temperature

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One law, summarising empirical laws

One law for all gases

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

pressure p

volume V

compress gas:
pressure p increases
constant temperature T

Amount law $p \propto N$

pressure p

number N

add more molecules:
pressure p increases
constant temperature T

Pressure law $p \propto T$

pressure p

T/K

heat gas:
pressure p increases
constant volume V

Charles' law $V \propto T$

T/K

volume V

heat gas:
volume V increases
constant pressure p

Combine the relationships into one

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

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

combine:
$pV \propto T$

10^5
N m^{-2}

Combine unknown N and k into measurable quantity R

Number of molecules N not known
constant k 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}

For N molecules $pV = NkT$. For n moles, $N = nN_A$ and $pV = nN_A kT = nRT$.
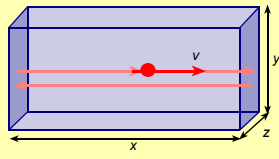
Constructing a model of a gas

Kinetic model of a gas

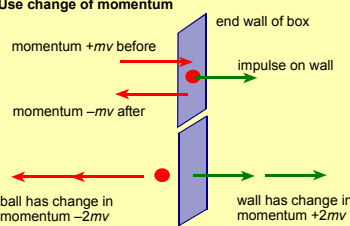**To start: one molecule in a box**

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

collisions per second $= v/2x$

Use change of momentum

end wall of box

momentum $+mv$ before

impulse on wall

momentum $-mv$ after

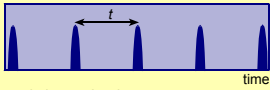ball has change in momentum $-2mv$

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 $= mv^2/x$
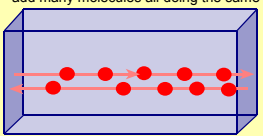
force

time

impulse each time molecule returns

Calculate pressure = force on wall/area of wall

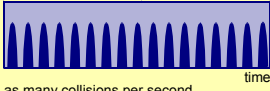force on wall $= mv^2/x$

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

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

pressure p

xyz = volume V

area of wall $= yz$

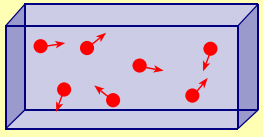add many molecules all doing the same

N molecules

improve model

force

time

N times as many collisions per second
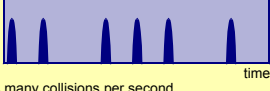
pressure $p = Nmv^2/V$

allow molecules to move in random directions

1/3 of molecules in each direction, on average

improve model

force

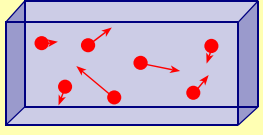time

1/3 as many collisions per second

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

allow molecules to move at random speeds

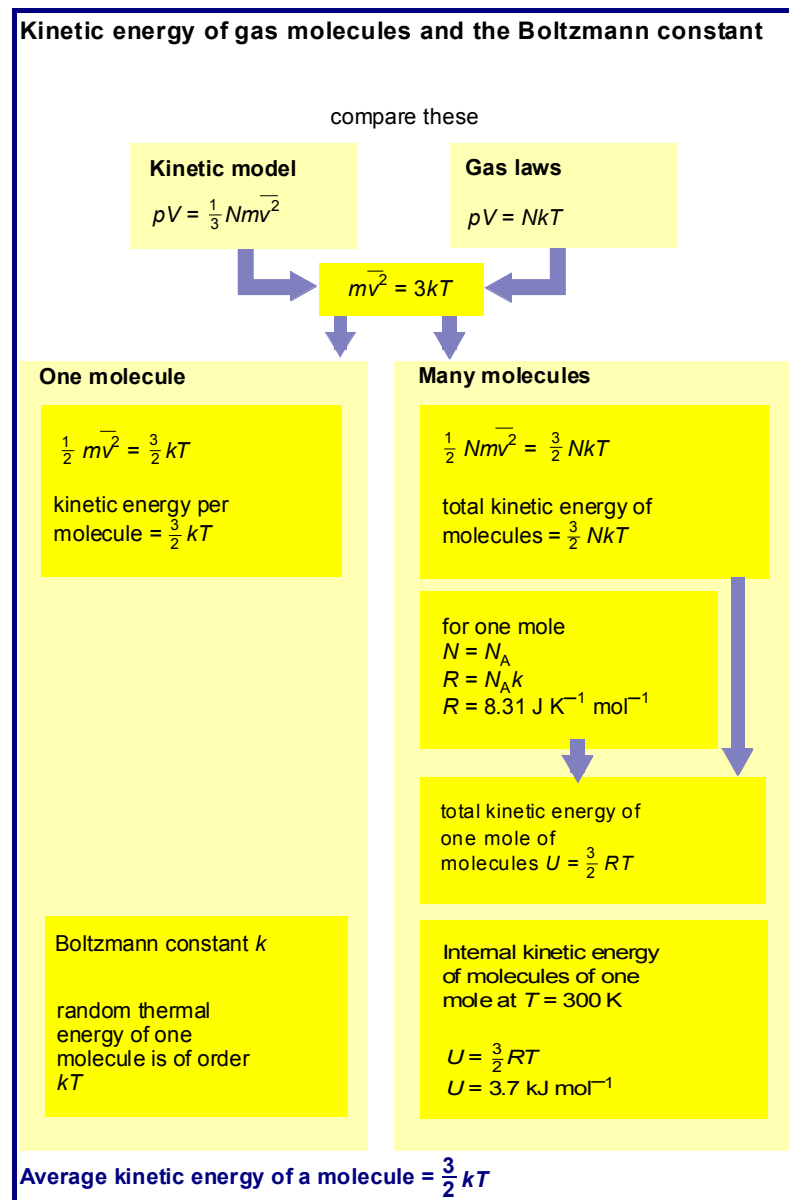take average over v^2

improve model

force

time

average impulse stays the same

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

The kinetic theory of gases predicts that $pV = \frac{1}{3} Nm\overline{v^2}$

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Boltzmann constant and 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 $= \frac{3}{2}kT$

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
$N = N_A$
$R = N_A k$
$R = 8.31 \text{ J K}^{-1}\text{ mol}^{-1}$

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

Boltzmann constant k

random thermal
energy of one
molecule is of order
kT

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

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

Average kinetic energy of a molecule $= \frac{3}{2}kT$

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The kinetic energy of a single particle

Looking at the kinetic energy of a single particle

Starting points

$$E_k = \tfrac{1}{2} mv^2$$

From the kinetic theory	From experimental work with gases

$$P = \tfrac{1}{3}\frac{N m \overline{v^2}}{V}$$

rearrange

	P: pressure of the gas		*P*: pressure of the gas	Note similarities

$$PV = \tfrac{1}{3} N m \overline{v^2}$$

V: volume of the gas
N: number of molecules
m: mass of one molecule
$\overline{v^2}$: mean square velocity

$$PV = nRT$$

V: volume of the gas
n: number of moles
T: temperature of gas
R: universal gas constant

rearrange

$$PV = \tfrac{2N}{3}\left(\tfrac{1}{2} m \overline{v^2}\right)$$

$$PV = \tfrac{2N}{3}\left(\tfrac{1}{2} m \overline{v^2}\right)$$

Something measured about the Universe, turning out to be important

Work with one mole   ÷*N*   ÷*n*

$$PV\,(\text{mol}^{-1}) = \tfrac{2}{3}\,(E_k)$$

$$PV\,(\text{mol}^{-1}) = RT$$

$$\tfrac{2}{3}\,(E_k) = RT$$

rearrange

$$E_k = \tfrac{3}{2} RT$$

This is the energy for one molecule, no matter what it is, depending only on temperature, and a universal constant.

define, *k*, Boltzmann's constant $= \dfrac{R}{N}$

For one molecule

$$E_k = \tfrac{3}{2} kT$$

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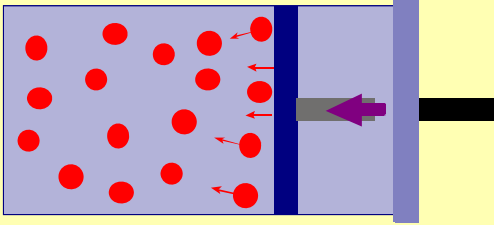$k = 1.38 \times 10^{-23}\ \text{J K}^{-1}$

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Transferring energy to molecules

Transfers of energy to molecules in two ways

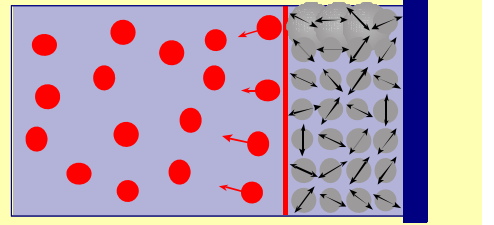**Hit the molecules yourself**

work done = force   distance

molecules speeded up   piston pushed in

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

cool gas or other material   hot wall

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 U

=

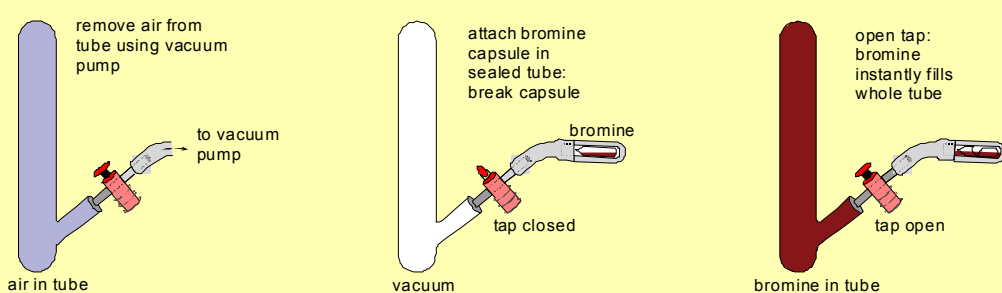work done W *plus*   thermal transfer Q

$$U = W + Q$$

Energy can be given to molecules by heating and by doing work

Bromine diffusing

Evidence for moving molecules

Bromine expanding into a vacuum

remove air from tube using vacuum pump

to vacuum pump

air in tube

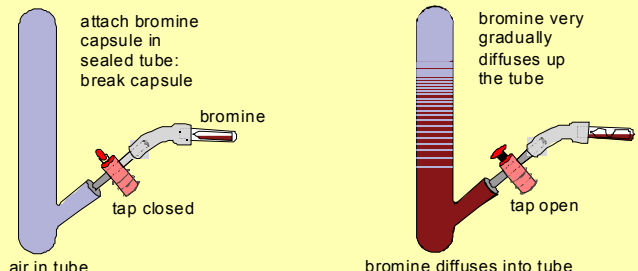attach bromine capsule in sealed tube: break capsule

bromine

tap closed

vacuum

open tap: bromine instantly fills whole tube

tap open

bromine in tube

Bromine diffusing into air

attach bromine capsule in sealed tube: break capsule

bromine

tap closed

air in tube

bromine very gradually diffuses up the tube

tap open

bromine diffuses into tube

Diffusion shows that molecules move. Rapid diffusion into a vacuum demonstrates high molecular speeds

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Random walk

Simplified one-dimensional random walk

Rule: a particle moves one step at a time, with equal probability to the right or left

Notation: let the steps be x_1, x_2, x_3 etc. with each x equal to +1 or –1

Total distance X travelled in N steps

$$X = (x_1 + x_2 + x_3 + ... + x_i + ...x_N)$$

Expected value E(X) of X

$$E(X) = (0)$$

Each step is equally likely to be +1 or –1. Thus, on average, over many random walks, the total distance will add up to zero.

Variation of X around the expected value

Departure r from expected value is:

$$r = X - E(X)$$

Since E(X) = 0

$$E(r^2) = E(X^2)$$

The expected value of r is zero. But the expected value of r^2 is not zero. Since E(X) = 0 the expected value of r^2 is the same as the expected value of x^2

Expected value of r^2

$$E(r^2) = E(X^2)$$

$$= E(x_1 + x_2 + x_3 + ... + x_i + ...x_N)^2$$

The result is simple:
mean square variation

$$E(r^2) = N$$

root mean square variation

$$= \sqrt{N}$$

When mulitiplied out this gives two types of term:

squared terms:

$$x_1^2 + x_2^2 + x_3^2 + ... + x_i^2 + ...x_N^2$$

this contains N terms each equal to +1 expected value = N

$$(+1)^2 = +1$$
$$(-1)^2 = +1$$

mixed terms:

$$x_1 x_2 + x_1 x_3 + ... + x_i x_j + ...$$

this contains N(N–1) terms each equally likely to be +1 or –1

(+1)	(+1) = +1
(+1)	(–1) = –1
(–1)	(+1) = –1
(–1)	(–1) = +1

expected value = 0
compare $(a + b)^2 = a^2 + ab + ba + b^2$

Root mean square distance travelled in random walk = $\sqrt{N}$

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The speed of a nitrogen molecule

Speed of a nitrogen molecule

Assume warm room temperature T = 300 K

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

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

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

kinetic energy of a molecule

from dynamics   from kinetic model

$\frac{1}{2}mv^2$ → $v^2 = \dfrac{3\,kT}{m}$ ← $\frac{3}{2}kT$

mass m of N_2 molecule

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

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

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

calculate speed

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

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

v = 500 m s^{-1} approximately

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

NB: The speed calculated here is the root mean square speed.

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