KINETIC THEORY

This brief paper on kinetic theory deals with three topics: the hypotheses on which the theory is founded, the calculation of pressure and absolute temperature of an ideal gas and the principal consequences of the theory. The level of this treatise is accessible by people who know algebra, since calculus is only marginally employed, but to understand the matter thoroughly some knowledge of Physics is required, such as the meaning of absolute temperature, energy, average value of a quantity etc; however, several quantities and physical constants involved in the development of the theory are introduced at the right moment.

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Hypotheses of kinetic theory – a qualitative discussion of the premises of the theory with references to facts and considerations confirming each hypothesis.

Calculation of the pressure - a statistical formula for the pressure of an ideal gas is given by starting from the hypotheses of the theory through the analysis of the molecular collisions.

Absolute temperature is a measure of molecular energy - by comparing the formula of the pressure and the state equation of an ideal gas it is proved that absolute temperature is a measure of the average kinetic energy of the molecules.

Polyatomic gases – extension of the theory to polyatomic ideal gases.

Results of kinetic theory – this part examines the implications of kinetic theory:
extension of the theory to **real gases** and **solids**;
calculation of the **root mean square of the molecular velocity** for an ideal gas;
Graham's and **Dalton's laws**;
internal energy of ideal gases and solids;
molar heats of ideal gases at constant volume and of monatomic solids;
calculation of exponent γ in adiabatic processes.

The development of Thermodynamics in the first decades of 19th century took place by integrating sets of experimental observations and theoretical premises which leaded to the modern *heat theory*, expressed by the first and the second law of Thermodynamics. Although First Law completely expresses the equivalence of work and heat by stating that heat is a form of energy, it has an essentially empirical nature, since this law doesn't offer any further explication of heat-work equivalence. This blank, due to lack of a complete theory on the behaviour of the molecules, is filled just by kinetic theory.

The conceptual meaning of kinetic theory consists of the providing a *mechanical and statistical interpretation of Thermodynamics*, by calculating pressure *P* and absolute temperature *T* as average values of mechanical quantities (like mass, velocity, energy etc.). By calculating the pressure of a *perfect* (or *ideal*) *gas* [1]; and comparing the result with the state equation it's possible to express absolute temperature as a function of molecular motion.

Hypotheses of kinetic theory

Kinetic theory is based on a set of hypotheses on the microscopic structure of matter founded on empirical observations. Some hypotheses apply to matter in general (also to liquid and solid phases), the others only to perfect gases.

1. Matter is composed of minimal units ("molecules") which can be considered as massive but dimensionless material points. In reality molecules have a complex structure, but according to the base version of the theory they are devoid of structure and volume. This means that molecules are animated only by translational movements, so ignoring rotations and vibrations. Although physically incorrect, this hypothesis enables us to build an easily treatable model; the corrections necessary to take into account all the degrees of freedom of the molecules and their total volume will be introduced later.

2. Molecules are animated by a continuous random motion (said *motion of thermal agitation*). This applies also to states of matter such as liquid and solid phases which apparently seem – especially this last one – to consist of motionless particles; according to the theory in the solid phase molecules could only perform oscillations around fixed equilibrium positions. Molecular motion is evident in the case of gases and solutions, since these substances tend to diffuse, that is to fill the whole available volume. Also the pressure of a gas filled in a container is due to the tendency to take up the whole space available, so one can easily deduce that pressure originates from the molecules knocks on the internal walls of the container and that it depends on molecular motion, that is on mass and average speed of the molecules.

This hypothesis is confirmed by *Brownian motion*, so named after botanist R. Brown who observed it in 1827. Brown discovered that pollen particles (which are extremely light) in suspension in a water drop seem to be animated by an unceasing random motion which can be described as a succession of extremely short segments. Also particles of different kind but with very little mass and dimensions manifest this behaviour when floating in a fluid. The explication consists in admitting that in the fluids molecules themselves move continuously and randomly and transfer their movement to the pollen particles by knocking on them.

3. The laws of Classical Mechanics apply also to molecular motion. This hypothesis is necessary for proceeding in calculation and can be verified only "*a posteriori*", i.e. by comparing the results predicted by the theory with the available experimental data.

The following hypotheses apply only to *ideal gases*. Let's remember that a gas behaves in "perfect" or "ideal" way, that's it satisfies the state equation with a good approximation, when it's very

rarefied and therefore pressure is very low and temperature sufficiently high, that is rather higher than condensation point.

4. Molecules don't collide on and don't interact each other (it is a simplification; in a more correct theory one has to consider weak intermolecular forces, known as *Van der Waals' forces*), so they persist in linear uniform motion until collide against the walls of the container. This hypothesis is equivalent to admitting that the dimensions of the molecules are extremely small with respect to the average distance between each other, so the less dense a gas is, the nearer to reality it is.

The empirical grounding of this hypothesis is the possibility to strongly compress a gas, especially if it's very rarefied. By increasing pressure it's possible to compress a gas till a very little fraction of the initial volume (for instance, 1/10,000) unless condensation occurs; this means that the total volume of all the molecules of a gas (called *covolume*) is very small with respect to the volume of the container. In practise, the volume of one single molecule is negligible, because it's the ratio between covolume and number of molecules contained in a given gas amount; in one mole there are about $6.022 \cdot 10^{23}$ particles. Therefore the space apparently fitted with an ideal gas is almost completely empty and can be strongly reduced by increasing pressure.

5. *The collisions of the molecules against internal walls of the container are elastic.*

Perhaps this is the more problematic hypothesis, but it's necessary to admit it because otherwise the pressure of a gas at constant volume and temperature could not remain constant over time, as common experience teaches us. In fact, collisions occurring at macroscopic scale never are perfectly elastic, while can be totally inelastic; actually every single collision implies a though minimal energy dispersion in the form of heat. Therefore we are considering the hypothesis more difficult to accept while making reference to phenomena occurring at macroscopic scale. But just coherence of theory with observations compels us to admit that collisions are elastic at microscopic scale, because otherwise we should come to conclusions contrary to experience itself.

Bearing in mind that by definition a collision is elastic if kinetic energy $\frac{1}{2}mv^2$ is conserved, let's suppose *ex absurdo* that the speed of the molecules slows down at every collision against the walls of the container. It follows that also intensity and frequency (number of collisions per second) of the collisions diminish quickly with time. But pressure of a gas is a growing function of both these factors and also it should tend to zero. A balloon fitted with a gas at constant temperature should soon become floppy itself.

Therefore we have to admit that molecular knocks against the walls of the container should be elastic; this conclusion must be extended to eventual collisions between molecules, but as we have seen these can be neglected in the case of very rarefied gases.

Elasticity of collisions implies that molecules don't undergo permanent deformations after collisions, coherently with the hypothesis according to which molecules are devoid of structure: in fact, we are reasoning as they were stiff, extremely little balls.

Calculation of the pressure

Let's start calculating the pressure P exerted by an ideal gas. In principle, the shape of the container should have no importance, because it's expected that pressure depends only on mass and velocity of the molecules; however, in order to proceed with calculation it's better to consider a parallelepiped with faces perpendicular to axes x, y and z respectively. In particular, let's indicate with d the distance between the two faces perpendicular to x-axis and with S the area of their surface.

Since pressure is the ratio between the normal force acting on a surface and the area of this surface, we have to calculate the force acting on the walls of the container, with particular reference to a

face perpendicular to the *x*-axis. By assuming N are the molecules, total force (i.e. the sum of the forces of collision exerted by all the molecules) F will be given by

$$F = Nf$$

in which f is the intensity of the force that a molecule exerts during a collision. Since a force of collision depends on velocity of the single molecule (which isn't the same for all), it's better to substitute f with its average value on all the molecules $<f>$ and interpret F as total average force, whose value, because of the extremely high number of particles, is constant over time unless thermodynamic variables change. Therefore we can write

$$F = N <f>$$

Besides we have to consider that molecules have different velocities. Since velocity is a vector, denoting by v_x, v_y and v_z the three components of $\vec{v}$, by Pythagoras' theorem in the space we have $v^2 = v_x^2 + v_y^2 + v_z^2$. We are interested to average values calculated on all the molecules; since in a chaotic motion there aren't privileged directions of motion, the mean values of v_x, v_y and v_z will be equal on the whole set of the molecules, thus we'll have $<v_x^2> = <v_y^2> = <v_z^2>$ [$<X>$ = mean value of X]. The mean value $<v^2>$ of the square of v will be the sum of three terms equal each other, so we get

$$<v^2> = 3 <v_x^2> .$$

Moreover in order to simplify the calculation let's suppose that all the molecules have same mass m (this is a simplification; consider m as a mean value [2]).

To calculate f we have to apply the second law of Dynamics in the form

$$\vec{f} = \frac{\Delta \vec{q}}{\Delta t}$$

in which $\Delta \vec{q}$ is the variation of linear momentum of a single molecule due to one collision.
We have to employ the hypothesis according to which collisions are elastic. Let's treat molecules as very little, rigid spheres which when touching the walls of the container undergo a force $\vec{f}$ normal to the wall and directed toward inside. Kinetic energy is conserved and *absolute* values of v_x, v_y and v_z don't vary. Since acceleration also is normal to the hit surface, only v_x varies by changing sign. Hence the variation of linear momentum Δq is equal to the only component Δq_x :

$$\Delta q = \Delta q_x = mv_{x\,2} - mv_{x\,1}$$

where m is the mass of the molecule and 1 and 2 refer respectively to the instants immediately previous and following the collision. Since $v_{x\,1} = -v_{x\,2}$ by neglecting the sign we get

$$\Delta q = 2\,mv_x$$
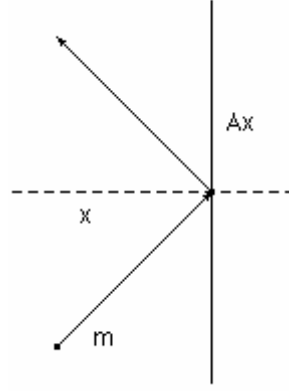
Elastic collision against a wall: the molecule "m" is reflected by the wall and forms equal angles of incidence and reflection.

To find the force f we have to divide Δq per the time Δt between two consecutive collisions against the same wall. Time is distance per speed; in our case the space is the double of the distance d between the walls perpendicular to the x-axis (the molecule, after a collision against a wall, will undergo some knocks on the others before returning to the same wall; the distance covered along the x-axis is 2d), and speed is v_x.
Therefore for a single molecule with velocity v_x we get

$$\Delta t \ = \ \frac{2d}{v_x}$$

$$f \ = \ \frac{2mv_x}{\frac{2d}{v_x}} \ = \ \frac{mv_x^2}{d}$$

We have to consider the mean value $<f>$, therefore substitute v_x^2 with $<v_x^2>$. By multiplying $<f>$ by the number N of all the molecules we get the total force F exerted by an ideal gas on a wall:

$$F \ = \ \frac{Nm<v_x^2>}{d}$$

To calculate the pressure P it's enough to divide F per the area S of the wall, so we have $d \cdot S = V$ (volume of the container) at the denominator. One reaches the same result by considering the other faces and the y and z axes: pressure doesn't depend on the axis that we have choose to execute the calculations, as one can rightly expect since pressure must be uniform in all the directions. Therefore

$$P \ = \ N\frac{m<v_i^2>}{V}$$

in which the index i can be x, y or z. Since $<v^2> \ = \ 3<v_i^2>$ we have

$$P \ = \ \frac{1}{3} \cdot N\frac{m<v^2>}{V}$$

This formula contains mechanical quantities (m and v) and has statistical character, because implies the average value of the square of velocity on all the molecules.

Absolute temperature is a measure of molecular energy

Now we can pass to the *meaning of absolute temperature according to kinetic theory*. From the state equation of an ideal gas

$$P\,V\ =\ n\,R\,T$$

in which n are the moles and R is the ideal gas constant we can express P in function of the others variables:

$$P\ =\ \frac{nRT}{V}$$

By making equal the two expressions of the pressure we get

$$\frac{1}{3}\cdot N\,\frac{m<v^2>}{V}\ =\ \frac{nRT}{V}$$

The total number of the molecules N is equal to number of moles n times Avogadro's number [3] N_A (i.e. the number of molecules in one mole); finally, we obtain the following mechanical and statistical expression for absolute temperature:

$$T\ =\ \frac{N_A}{3R}\,m<v^2>$$

This formula confirms the founding idea of the whole kinetic theory, according to which absolute temperature is a statistical measure of chaotic molecular motion.
To generalize this formula to non-homogeneous gas mixtures we have to substitute $m<v^2>$ with $<mv^2>$.
It's better to find a relation between temperature and average molecular kinetic energy $<E_c>$. Since $<mv^2>\ =\ 2<E_c>$ we get

$$T\ =\ \frac{2}{3}\frac{N_A}{R}\cdot<E_c>\qquad\Rightarrow\qquad<E_c>\ =\ \frac{3}{2}\frac{R}{N_A}T.$$

The ratio between the gas constant R and the Avogadro's constant N_A is *Boltzmann's constant* "k", a very important quantity in Thermodynamics, equal to about $1{,}38\cdot10^{-23}\ \dfrac{J}{K}$.

Finally we get

$$<E_c>\ =\ \frac{3}{2}kT$$

So, according to the simplest version of kinetic theory, *mean kinetic energy of one molecule of an ideal gas is proportional to absolute temperature of the gas*. This equation applies also to gas mixtures.

Though not specified in the formulas, *velocity and mean velocity-squared are always relative to the container, which is supposed in rest*. The uniform linear motion of all molecules doesn't influence temperature, which depends only by random motion. This principle applies also to liquids: systematic motions like rotations with same angular velocity don't imply increase of temperature.

Polyatomic gases

The final equation

$$<E_c> \quad = \quad \frac{3}{2}kT$$

applies only to a perfect gas by ignoring rotations and vibrations of the molecules. Actually, molecules are often composed of two or more atoms; therefore one has to consider also those motions. Since to ignore rotations and vibrations means to consider only the translational motion, it follows that the previous equation gives us the mean value of the only translational kinetic energy, which is the total kinetic energy only in the case of a monatomic molecule. To extend the theory to a polyatomic ideal gas we have to apply the *principle of energy equipartition*, according to which average energy is distributed uniformly among all the *degrees of freedom* of the molecule; the "degrees of freedom" are all the independent coordinates defining position and orientation of one object. For a material point the degrees of freedom are the position coordinates, e.g. the three Cartesian coordinates $x\,y\,z$ in a given frame of reference. Therefore mean kinetic energy associated with one degree of freedom is

$$<E_{c\,1}> \quad = \quad \frac{1}{2}kT$$

that we can consider as the fundamental relation between energy and temperature.

The degrees of freedom of a diatomic molecule are five (three are translational and two rotational), since one of the two atoms – while admitting that the chemical bond is rigid – can rotate around the another, so its relative position is identified by two angles ϑ and φ ; for a 3-atomic or polyatomic molecule the rotational degrees are three (the third atom can rotate around the axis connecting the first two at fixed distances from each of them). While ignoring vibrational degrees, mean kinetic energies of diatomic and 3-atomic molecules will be respectively $\frac{5}{2}kT$ and $3kT$.

Results of kinetic theory

Real gases – Kinetic theory can apply to real gases, liquids and solids by admitting that attractive and repulsive forces act between the molecules. In the case of a real gas one has to consider also the *gas covolume*, that is the sum of the volumes of all the molecules, so the state equation of a perfect gas $PV = nRT$ must be replaced with equations more complex as the *Van der Waals'* one [4].

Solids - In the case of solids it's supposed molecules are oscillating around fixed equilibrium positions, so mean total energy of a molecule is the sum of potential energy and kinetic energy. By supposing that, on the average, potential energy is equal to kinetic energy, the total energy of one molecule of a substance at the solid state is the double of the kinetic energy. By considering monatomic solids such as metals the average total energy of one molecule is

$$<E> \quad = \quad 3kT$$

Root mean square velocity of the molecules – Let's consider a chemically homogeneous perfect gas (that is, all the molecules have same mass). We can calculate the *root mean square velocity* (v_{rms}) of the molecules, i.e. the square root of the average value of the *translational* velocity of the molecules:

$$v_{rms} \quad = \quad \sqrt{<v^2>} \quad = \quad \sqrt{\frac{v_1^2 + v_2^2 + ... + v_N^2}{N}}$$

where N is the number of molecules, and v_i refers to translational velocity of the i-th particle. Starting from

$$\frac{1}{2}m<v^2> \;=\; \frac{3}{2}kT$$

we have

$$<v^2> \;=\; \frac{3kT}{m} \quad \Rightarrow \quad v_{rsm} \;=\; \sqrt{\frac{3kT}{m}}$$

From this microscopic formula we can get an expression containing macroscopic quantities by multiplying numerator and denominator by the number N of molecules. Since $kN = n\,(k{\cdot}N_A) = nR$ where n is the number of moles , and $mN = n\,(mN_A) = nM$ where M is the molar mass, we get

$$v_{rms} \;=\; \sqrt{\frac{3RT}{M}}$$

or also, since for one mole $RT = PV$ and $\dfrac{V}{M} = \dfrac{1}{\rho}$ where ρ is the density,

$$v_{rms} \;=\; \sqrt{\frac{3P}{\rho}}$$

which is the formula we looked for.

Graham's law of diffusion – according to this experimental law, *average velocities of the molecules of two gases at the same pressure are inversely proportional to the square root of the respective densities*, that is

$$\frac{v_a}{v_b} \;=\; \sqrt{\frac{\rho_b}{\rho_a}}$$

where ρ is the density (ratio between mass and volume) and a and b denote the two gases. It means that, pressure being equal, lighter gases diffuse more rapidly.
It's a consequence of the law of the root mean square velocity calculated above, since in Statistics it's proved that $v_{rms} = \sqrt{\dfrac{3\pi}{8}}\,v_m$, where v_m is average speed. So the ratios between r.m.s. velocities and between average velocities are equal. By admitting that pressures are equal, we have

$$\frac{v_a}{v_b} \;=\; \frac{(v_{rms})_a}{(v_{rms})_b} \;=\; \sqrt{\frac{\rho_b}{\rho_a}}$$

Sometimes physicists refers to Graham's law as the law according to which velocity of diffusion of a gas is inversely proportional to the square root of the molar mass *at a given temperature*, as we can see by the formula

$$v_{rms} \;=\; \sqrt{\frac{3RT}{M}}$$

Dalton's law of partials pressures – This law affirms that [*total*] *pressure of a mixture of ideal gases is the sum of the partial pressures exerted by each [chemically homogeneous] gas*.
Let's start from

$$P \;=\; \frac{1}{3}\cdot N\frac{<mv^2>}{V}$$

valid also for a mixture with N molecules.

If the gas we denote by the index "k" contains N_k molecules of mass m_k and average velocity squared $<v^2>_k$, we can write

$$<mv^2> \;=\; \frac{\sum_k N_k m_k <v^2>_k}{N} \quad\Rightarrow\quad P \;=\; \sum_k \frac{1}{3}\frac{N_k m_k <v^2>_k}{V} \;=\; \sum_k P_k$$

which is just Dalton's law.

One can get this law directly by state equation: for each gas of the mixture $P_k \;=\; \dfrac{n_k RT}{V}$ and for the whole mixture

$PV \;=\; nRT$. Now, $\displaystyle\sum_k P_k \;=\; \frac{RT}{V}\sum_k n_k$ with $\displaystyle\sum_k n_k \;=\; n \;\Rightarrow\; \sum_k P_k \;=\; \frac{nRT}{V} \;=\; P$.

Internal energy of an ideal gas – It's well known that internal energy U of an ideal gas is a function only of its temperature. Kinetic theory implies just that; indeed internal energy of a perfect gas is equal to total kinetic energy of the molecules of the gas, therefore

$$U \;=\; N<E_c> \;=\; \frac{m}{2}NkT$$

where m is the number of degrees of freedom and k the Boltzmann's constant. Since $N = n N_A$, where n are the moles and N_A is Avogadro's number, and $N_A k = R$ where R is the constant of the ideal gases, we get

$$U \;=\; \frac{m}{2}RT$$

This formula is the equivalent, at macroscopic level, of the formula

$$<E_c> \;=\; \frac{m}{2}kT$$

valid for molecules with m degrees of freedom.

Internal energy of a monatomic solid (metals, etc.) – On the basis of the same method we applied to an ideal gas, the internal energy of one mole of monatomic solid substance is

$$U \;=\; 3RT$$

(remember that the particles of solids oscillate about their equilibrium positions, so their total energy is the sum of kinetic energy and potential energy, which on the average are equal over time).

Molar heats – Premised that *molar heat* of a substance is the heat capacity of one mole of this substance, we have

$$\Delta Q \;=\; n C_M \Delta T.$$

in which ΔQ is the heat transferred into one mole of a substance not undergoing a phase transition. In the case of ideal gases at constant volume $\Delta Q \;=\; \Delta U$ since the whole heat absorbed by the gas is converted into internal energy. By denoting with C_V the molar heat at constant volume we get

$$C_V \Delta T \;=\; \Delta U \;=\; \frac{m}{2}R\Delta T$$

and finally

$$C_V \;=\; \frac{m}{2}R$$

In the case of monatomic solids (metals etc.) the molar heat is given by

$$C_M \ = \ 3\,R$$

(3 R = ca. 6 $\dfrac{cal}{mol \cdot K}$), in agreement with the experimental *Dulong-Petit's law* (which is correct only if the temperature is higher than a critical threshold depending on the chemical composition of the substance).

Calculation of the exponent in adiabatic transformations - The equation of an adiabatic process for an ideal gas is

$$PV^\gamma \ = \ K$$

where γ is an exponent depending on the molecular structure of the gas and K is a constant.
From the first principle written in differential form, put $dQ = 0$, we get

$$dU + PdV \ = \ 0 \quad \Rightarrow \quad \frac{m}{2}RdT + RT\frac{dV}{V} \ = \ 0 \quad \Rightarrow \quad \frac{dT}{T} \ = \ -\frac{2}{m}\cdot\frac{dV}{V} \quad \Rightarrow \quad T \ = \ V^{-\frac{2}{m}}$$

By substituting into the state equation $PV \ = \ nRT$ we get

$$PV \ = \ nRV^{-\frac{2}{m}} \quad \Rightarrow \quad PV^{\frac{m+2}{m}} \ = \ nR \ , \ \text{from which we deduce} \ \gamma \ = \ \frac{m+2}{m} \ .$$

Notes

1. A gas is said *perfect* or *ideal* if its behaviour agrees by a good approximation with Boyle's and Gay-Lussac's laws, which occurs if its temperature is much higher than its point of condensation and if the gas is very rarefied.
The state equation of perfect gases $P V \ = \ n R T$ puts in relation pressure, volume, absolute temperature and number of moles. The constant of ideal gases is $R \ = \ $ca 8.31 $\dfrac{J}{mol \cdot K}$.

2. Even if a gas were chemically pure, nevertheless its molecules should not have same mass, since elements have several isotopes.

3. The number of molecules in one mole is always equal to Avogadro's number (or Avogadro's constant), that is ca $6.02 \cdot 10^{23}$ for any substance. Hence mole, not mass, must be considered as measurement unit of the "amount of matter or substance".

4. According to Van der Waals's equation, pressure P is given by

$$P \ = \ \frac{nRT}{V - nb} \ - \ \frac{an^2}{V^2}$$

where n are the moles and a and b are positive constants characteristics of each gas. In particular, b is covolume of one mole.

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