

descent being due to the heat generated by their friction against the earth's atmosphere; and there is reason to believe that bodies of this kind compose the immense circumsolar nebula called the zodiacal light, and also, possibly, the solar corona which becomes visible in total eclipses. It is probable that these small bodies, being retarded by the resistance of an ethereal medium, which is too rare to interfere sensibly with the motion of such large bodies as the planets, are gradually sucked into the sun, and thus furnish some contribution towards the maintenance of solar heat. But the perturbations of the inferior planets and comets furnish an approximate indication of the quantity of matter circulating within the orbit of Mercury, and this quantity is found to be such that the heat which it could produce would only be equivalent to a few centuries of solar radiation.

Helmholtz has suggested that the smallness of the sun's density—only $\frac{1}{4}$ of that of the earth—may be due to the expanded condition consequent on the possession of a very high temperature, and that this high temperature may be kept up by a gradual contraction. Contraction involves approach towards the sun's centre, and therefore the performance of work by solar gravitation. By assuming that the work thus done yields an equivalent of heat, he brings out the result that, if the sun were of uniform density throughout, the heat developed by a contraction amounting to only one ten-thousandth of the solar diameter, would be as much as is emitted by the sun in 2100 years.

235. Sources of Energy available to Man.—Man cannot produce energy; he can only apply to his purposes the stores of energy which he finds ready to his hand. With some unimportant exceptions, these can all be traced to three sources:—

I. The solar rays.

II. The energy of the earth's rotation.

III. The energy of the relative motions of the moon, earth, and sun, combined with the potential energy of their mutual gravitation.

The fires which drive our steam-engines owe their energy, as we have seen, to the solar rays. The animals which work for us derive their energy from the food which they eat, and thus, indirectly, from the solar rays. Our water-mills are driven by the descent of water, which has fallen as rain from the clouds, to which it was raised in the form of vapour by means of heat derived from the solar rays.

The wind which propels our sailing-vessels, and turns our wind-

mills, is due to the joint action of heat derived from the sun, and the earth's rotation.

The tides, which are sometimes employed for driving mills, are due to sources II. and III. combined.

The work which man obtains, by his own appliances, from the winds and tides, is altogether insignificant when compared with the work done by these agents without his intervention, this work being chiefly spent in friction. It is certain that all the work which they do, involves the loss of so much energy from the original sources; a loss which is astronomically insignificant for such a period as a century, but may produce, and probably has produced, very sensible effects in long ages. In the case of tidal friction, great part of the loss must fall upon the energy of the earth's rotation; but the case is very different with winds. Neglecting the comparatively insignificant effect of aerial tides, due to the gravitation of the moon and sun, wind-friction cannot in the slightest degree affect the rate of the earth's rotation, for it is impossible for any action exerted between parts of a system to alter the angular momentum¹ of the system. The effect of easterly winds in checking the earth's rotation must therefore be exactly balanced by the effect of westerly winds in accelerating it. In applying this principle, it is to be remembered that the couple exerted by the wind is jointly proportional to the force of friction resolved in an easterly or westerly direction, and to the distance from the earth's axis.

236. Dissipation of Energy.—From the principles laid down in the present chapter it appears that, although mechanical work can be entirely spent in producing its equivalent of heat, heat cannot be entirely spent in producing mechanical work. Along with the conversion of heat into mechanical effect, there is always the transference of another and usually much larger quantity of heat from a body at a higher to another at a lower temperature. In conduction and radiation heat passes by a more direct process from a warmer to a colder body, usually without yielding any work at all. In these cases, though there is no loss of energy, there is a running to waste as far as regards convertibility; for a body must be hotter than neighbouring bodies, in order that its heat may be available for yielding work. This process of running down to less available forms has been variously styled *diffusion*, *degradation*, and *dissipation* of

¹ The angular momentum is measured by the product of the moment of inertia (see Part I.) and the angular velocity.

energy, and it is not by any means confined to heat. We can assert of energy in general that it often runs down from a higher to a lower grade (that is to a form less available for yielding work), and that, if a quantity of energy is ever raised from a lower to a higher grade, it is only in virtue of the degradation of another quantity, in such sort that there is never a gain, and is generally a loss, of available energy.

This general tendency in nature was first pointed out by Lord Kelvin. It obviously leads to the conclusion that the earth is gradually approaching a condition in which it will no longer be habitable by man as at present constituted.

237. *Kinetic Theory of Gases.*—According to the theory of the constitution of gases which is now generally accepted and is called by the above name, a simple gas consists of a number of very small and exactly equal particles, called atoms or molecules, moving about with various velocities and continually coming into collision with one another and with the sides of the containing vessel. The total volume of the particles themselves is very small compared with the space in which they move, and consequently the time during which a particle is in collision with other particles is a very small part of its whole time.

Each particle is highly elastic. Its shape can be changed by the application of external forces; but it springs back when left to itself and executes vibrations, which we may compare to those of a tuning-fork or a bell. These are the cause of the peculiar features which are detected in the light of an incandescent gas when analysed by the spectroscope. It can also, like any other free body, have a rotatory or spinning motion. The kinetic energy of a particle is accordingly composed of three parts, one due to its vibration, another to its rotation, and a third to its translation. This third part, which is usually greater than the other two, is called the *energy of agitation*. The other two are included together under the name of *internal energy*, which may be defined as the energy of the relative motion of different parts of the same molecule.

In addition to these, we may have movement of the gas as a whole, which is what is meant when in ordinary language we speak of a gas in motion as distinguished from a gas at rest. In this sense, the velocity at any point of a gas is another name for the velocity of the centre of gravity of a small group of molecules surrounding the point. In what follows we leave such velocity out of account.

238. The ratio of the energy of agitation to the internal energy, though it may vary at a given instant from molecule to molecule, or may vary for the same particle from instant to instant, has a definite and permanent value for the aggregate of all the particles—a value independent of changes of pressure or temperature, but not the same for all gases. The symbol β is employed to denote the ratio of the whole kinetic energy of a gas to the energy of agitation, and the value of β for several of the more permanent gases is 1.634.

The heat of a gas is another name for its kinetic energy, that is, for $\Sigma \frac{1}{2} \beta m v^2$, or $\frac{1}{2} \beta m \Sigma v^2$, v denoting the velocity of a molecule, m its mass, and Σ indicating summation for all the molecules. To reduce the expression for this heat to ordinary thermal units we must divide by Joule's equivalent.

The absolute temperature of a given gas is proportional to the average kinetic energy of its molecules, that is, to the average value of $\frac{1}{2} \beta m v^2$, or, omitting constants, to the average value of v^2 . We shall denote the average value of v^2 by V^2 . Its square root V is called the *velocity of mean square*.

In a mixture of two simple gases the value of V^2 is not the same for them both, but varies inversely as m ; in other words, mV^2 has the same value for both constituents. Accordingly, in comparing one gas with another mV^2 is taken as the proportional measure of absolute temperature.

239. The equality of the values of mV^2 for the two components of a mixture is not an arbitrary assumption, but a deduction obtained by a very elaborate mathematical investigation from the supposition of two sets of perfectly elastic balls flying about promiscuously amongst each other.

This and other similar calculations which form an important part of the kinetic theory of gases are conducted by what is called the *statistical method*. Large numbers give steadiness to statistics, and the number of molecules in a cubic centimetre of gas is more than a million of millions of millions. As long as a cubic centimetre of gas remains at the same pressure and temperature the statistics of the velocities of its molecules remain permanent. The velocity of each particle changes in the most irregular manner, but the number of its molecules that have velocities lying between given limits (which may be very close together) never changes by more than an infinitesimal part of itself.

Calculation shows that when we attend not merely to the actual velocities but to their components in a given direction, the statistics of such component velocities will be independent of the direction assumed, even when gravity is taken into account.

240. The pressure of a gas against the walls of the containing vessel is due to the impacts of its particles against the walls. To compute its amount, let u denote the component velocity of a molecule normal to one of the sides supposed plane, u being regarded as positive when the molecule is approaching the side and negative when receding. Let u_1 be a particular positive value of u , and let the number of molecules in unit volume that have approximately this velocity be n_1 . The number of molecules of velocity u_1 that impinge on unit area of the side in unit time will be the number that occupy a volume u_1 , and will therefore be $n_1 u_1$.

Their momentum before striking is their mass mn_1u_1 multiplied by their velocity u_1 , and is therefore $mn_1u_1^2$. This is reversed by the collision, so that the change of momentum is $2mn_1u_1^2$. This, being the change of momentum produced in unit time by the reaction of unit area of the wall, is equal to the pressure on unit area due to the impacts of those molecules which we have been considering. But the number of molecules whose normal velocity is u_1 is, by symmetry, the same as the number whose normal velocity is $-u_1$, hence $2mn_1u_1^2$ is the sum of such terms as mu^2 for all the molecules for which the value of u^2 is u_1^2 .

Thus the total pressure on unit area is the sum of such terms as mu^2 for all the particles in unit volume; that is, calling the pressure p ,

$$p = \Sigma mu^2 = m \Sigma u^2. \quad (1)$$

But, from the symmetry of the constitution of a gas, Σu^2 has the same value for all directions of u . Combining this principle with the principle that the square of a velocity is the sum of the squares of its three rectangular components, we easily deduce $\Sigma u^2 = \frac{1}{3} \Sigma v^2$.

Let N denote the whole number of molecules in unit volume, and ρ the density of the gas, which is Nm , then we have:

$$\Sigma u^2 = \frac{1}{3} \Sigma v^2 = \frac{1}{3} NV^2, \quad (2)$$

$$p = m \Sigma u^2 = \frac{1}{3} Nm V^2 = \frac{1}{3} \rho V^2. \quad (3)$$

241. This last result enables us to compute the value of V for any known gas, for it gives

$$V^2 = \frac{3p}{\rho}. \quad (4)$$

Thus in C.G.S. measure we have for hydrogen (see pp. 305, 306), $p = 1.0136 \times 10^6$, $\rho = .00008957$, whence $V = 184,300$ cm. per sec. This is about one nautical mile per second.

The value of V for any gas bears a constant ratio to the velocity of sound in the gas, namely, the ratio $\sqrt{\frac{3}{\kappa}}$, where κ denotes the ratio of the two specific heats.

Since the energy of agitation in unit volume is $\frac{1}{2} \rho V^2$, and p is $\frac{1}{3} \rho V^2$, these quantities have the same dimensions and are as 3 to 2.

The equation $p = \frac{1}{3} \rho V^2$ shows that when V^2 (and therefore the absolute temperature) is given, p varies as ρ . This is Boyle's law.

Again, it shows that when ρ is given, p varies as V^2 , that is, as the absolute temperature; and that, when p is given, ρ varies inversely as V^2 ; that is, the volume varies directly as the absolute temperature.

Further, from the equation $p = \frac{1}{3} Nm V^2$ we deduce that when two gases have the same pressure p and the same temperature (measured by mV^2), they have the same number of particles N in unit volume, and their densities (since $\rho = Nm$) are directly as m the mass of a single particle of each; that is, the densities (at the same pressure and temperature) are directly as the atomic weights. This is known as Avogadro's law.

242. In questions relating to specific heat it is convenient to make the unit of heat equal to the unit of energy, so that the quantity of heat in a mass Σm will be not only proportional but equal to $\frac{1}{2} \beta \Sigma mv^2$, or to $\frac{1}{2} \beta V^2 \Sigma m$, and to employ a unit of temperature such that absolute temperature shall be not only proportional but equal to mV^2 . Then, denoting absolute temperature by θ , and quantity of heat or energy in unit volume by E , we have

$$V^2 = \frac{\theta}{m} \quad (5) \quad E = \frac{1}{2} \beta V^2 \Sigma m = \frac{1}{2} \beta V^2 \rho = \frac{1}{2} \beta \frac{\rho}{m} \theta = \frac{1}{2} \beta N \theta. \quad (6)$$

N denoting, as before, the number of molecules in unit volume.

The thermal capacity at constant volume, for unit volume of the gas, is defined as $\frac{dE}{d\theta}$, and is $\frac{1}{2} \beta N$, it being assumed that β is constant. Since N is the same for all gases at the same temperature and pressure, the thermal capacity per unit volume is the same for all gases that have the same value of β .

The specific heat at constant volume is the thermal capacity of the volume $\frac{1}{\rho}$, and is therefore $\frac{1}{2} \beta N \frac{1}{\rho}$ or $\frac{1}{2} \frac{\beta}{m}$. Hence the specific heat

is inversely as the atomic weight, as asserted by the law of Dulong and Petit.

Again we have

$$p = \frac{1}{3} \rho V^2 = \frac{1}{3} \rho_m = \frac{1}{3} N \theta, \quad (7)$$

$$\frac{p}{\rho \theta} = \frac{1}{3m} = \frac{p \times \text{volume of unit mass}}{\theta}. \quad (8)$$

The work done by the gas (initially at unit volume) in expanding against constant pressure p when θ is increased by unity is $p \times$ increase of volume $= p \frac{1}{\theta} = \frac{p}{3m}$. If the original volume be $\frac{1}{\rho}$ (in which case the mass will be unity) the work in expanding will be $\frac{1}{3m}$. Hence, the ratio of the specific heat at constant pressure to that at constant volume is

$$\kappa = \frac{\frac{1}{3m} + \frac{\beta}{2m}}{\frac{\beta}{3m}} = \frac{2}{3\beta} + 1, \quad (9)$$

giving

$$\beta = \frac{2}{3(\kappa - 1)}. \quad (10)$$

If we assume $\kappa = 1.408$, we find $\beta = 1.634$.

243. The rate at which a gas escapes through a porous partition will be jointly as the number of molecules in unit volume and the mean value of the velocity resolved normal to the partition; or in our notation it will be jointly as N and the mean value of u . This latter, though not identical with the square root of the mean value of u^2 , that is, with the square root of $\frac{1}{3} V^2$, can be shown to be in a fixed ratio to it. Hence the rate of diffusion will be proportional to NV . At given temperature and pressure, N is the same for all gases, hence the rate of diffusion will be directly as V , that is inversely as \sqrt{m} , or inversely as the square root of the density Nm .

244. Van der Waals' Formula for correcting Boyle's Law.—In the calculation by which we have obtained the formula $p = \frac{1}{3} \rho V^2$, the molecules were treated as indefinitely small. Increased size of the molecules (for given V , m , and n) would involve more frequent collision and therefore increased pressure. Calculation shows that the value of p as corrected for the finite size of the molecules is

$$\frac{1}{3} \frac{\rho V^2}{1 - b\rho}, \text{ or } \frac{1}{3} V^2 / \left(\frac{1}{\rho} - b \right),$$

b being a small quantity which is constant for a given gas.

Again, the theory of capillarity as applied to liquids teaches that the mutual attraction of the molecules which compose the surface-layer of a liquid pulls the surface-layer inwards upon the rest of the liquid, and that the pressure at the outer boundary of the surface-layer is therefore less than the pressure at and within its inner boundary. The same reasoning which leads to this result in the case of liquids is applicable on a diminished scale to gases. Accordingly p and V are smallest at the boundary of a gas, and gradually increase for a very small distance inwards. The formula $p = \frac{1}{3} \rho V^2$ or the corrected formula $p = \frac{1}{3} V^2 / \left(\frac{1}{\rho} - b \right)$, is applicable to the gas as a whole, but will not be true if we employ the value of V^2 for the gas as a whole in combination with the value of p at the boundary. In practical measurement of p it is the pressure at the boundary that is measured. This will be less than $\frac{1}{3} V^2 / \left(\frac{1}{\rho} - b \right)$ by the pressure due to the skin attraction, which is easily shown to be proportional to ρ^2 , and may be denoted by $a\rho^2$, a being constant for a given gas. Hence if we make p stand for the pressure at the bounding surface of the gas, we have

$$p + a\rho^2 = \frac{1}{3} V^2 / \left(\frac{1}{\rho} - b \right), \text{ or} \\ (p + a\rho^2) \left(\frac{1}{\rho} - b \right) = \frac{1}{3} V^2. \quad (11)$$

This investigation is due to Van der Waals, who writes the first member of (11) in the form $(p + \frac{a}{v^2})(v - b)$, v denoting the volume of unit mass of the gas. According to his theory it is this product, and not the simple product pv , that is constant at given temperature.

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b being a small quantity which is constant for a given gas.

Again, the theory of capillarity as applied to liquids teaches that the mutual attraction of the molecules which compose the surface-layer of a liquid pulls the surface-layer inwards upon the rest of the liquid, and that the pressure at the outer boundary of the surface-layer is therefore less than the pressure at and within its inner boundary. The same reasoning which leads to this result in the case of liquids is applicable on a diminished scale to gases. Accordingly p and V are smallest at the boundary of a gas, and gradually increase for a very small distance inwards. The formula $p = \frac{1}{3} \rho V^2$ or the corrected formula $p = \frac{1}{3} V^2 / \left(\frac{1}{\rho} - b \right)$, is applicable to the gas as a whole, but will not be true if we employ the value of V^2 for the gas as a whole in combination with the value of p at the boundary. In practical measurement of p it is the pressure at the boundary that is measured. This will be less than $\frac{1}{3} V^2 / \left(\frac{1}{\rho} - b \right)$ by the pressure due to the skin attraction, which is easily shown to be proportional to ρ^2 , and may be denoted by $a\rho^2$, a being constant for a given gas. Hence if we make p stand for the pressure at the bounding surface of the gas, we have

$$p + a\rho^2 = \frac{1}{3} V^2 / \left(\frac{1}{\rho} - b \right), \text{ or} \\ (p + a\rho^2) \left(\frac{1}{\rho} - b \right) = \frac{1}{3} V^2. \quad (11)$$

This investigation is due to Van der Waals, who writes the first member of (11) in the form $(p + \frac{a}{v^2})(v - b)$, v denoting the volume of unit mass of the gas. According to his theory it is this product, and not the simple product pv , that is constant at given temperature.