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The Nature of the Motion which we call Heat*

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SUMMARY

Krönig has recently proposed that the molecules of a gas do not oscillate about definite positions of equilibrium, but that they move with constant velocity in straight lines until they strike against other molecules, or against the surface of the container. I share this view, but believe that rotary as well as rectilineal motions are present, since the *vis viva* of the translatory motion alone is too small to represent the whole heat present in the gas. I assert that the translatory motion of the molecules will also be in a constant ratio to the motions of the constituents of the molecules among themselves, because the transfer of *vis viva* from translatory to internal motions, and conversely, by collisions, must eventually reach an equilibrium.

The molecular conditions that must be satisfied in order that a gas may behave as an *ideal* gas are indicated. Types of molecular motion occurring in the solid, liquid, and gaseous states are described, and a qualitative theory of evaporation is given.

In order to explain the relations of volumes of gases combining by chemical reactions, it is assumed that in simple gases two or more atoms are combined to form one molecule.

By considering collisions of molecules of mass m against the wall of a container of volume v, assuming that all n molecules move with velocity u, Clausius shows that the pressure of the gas is equal to $(mnu^2/3v)$. The absolute temperature is proportional to $(\frac{1}{2}nmu^2)$. The actual velocities of gas molecules can be calculated in this way; for example, at the temperature of melting ice, the velocity of an oxygen molecule is, on the average, 461 metres per second.

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The ratio of the *vis viva* of translatory motion to the total *vis viva* is found to be equal to $3(\gamma' - \gamma)/2\gamma$, where γ is the specific heat of the gas at constant volume (for unit volume) and γ' is specific heat at constant pressure. For air, $\gamma'/\gamma = 1{\cdot}421$, and hence this ratio is 0·6315.

1. Before writing my first memoir on heat, which was published in 1850,† and in which heat is assumed to be a motion, I had already formed for myself a distinct conception of the nature of this motion, and had even employed the same in several investigations and calculations. In my former memoirs I intentionally avoided mentioning this conception, because I wished to separate the conclusions which are deducible from certain general principles from those which presuppose a particular kind of motion, and because I hoped to be able at some future time to devote a separate memoir to my notion of this motion and to the special conclusions which flow therefrom. The execution of this project, however, has been retarded longer than I at first expected, inasmuch as the difficulties of the subject, as well as other occupations, have hitherto prevented me from giving to its development that degree of completeness which I deemed necessary for publication.

A memoir has lately been published by Krönig, under the title *Grundzüge einer Theorie der Gase*,‡ in which I have recognized some of my own views. Seeing that Krönig has arrived at these views just as independently as I have, and has published them before me, all claim to priority on my part is of course out of the question; nevertheless, the subject having once been mooted in this memoir, I feel myself induced to publish those parts of my own views which I have not yet found in it. For the present, I shall confine myself to a brief indication of a few principal points, and reserve a more complete analysis for another time.††

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2. Krönig assumes that the molecules of gas do not oscillate about definite positions of equilibrium, but that they move with constant velocity in straight lines until they strike against other molecules, or against some surface which is to them impermeable. I share this view completely, and I also believe that the expansive force of the gas arises from this motion. On the other hand, I am of opinion that this is not the only motion present.

In the first place, the hypothesis of a rotatory as well as a progressive motion of the molecules at once suggests itself; for at every impact of two bodies, unless the same happens to be central and rectilineal, a rotatory as well as a translatory motion ensues.

I am also of opinion that vibrations take place within the several masses in a state of progressive motion. Such vibrations are conceivable in several ways. Even if we limit ourselves to the consideration of the atomic masses solely, and regard these as absolutely rigid, it is still possible that a molecule, which consists of several atoms, may not also constitute an absolutely rigid mass, but that within it the several atoms are to a certain extent moveable, and thus capable of oscillating with respect to each other.

I may also remark, that by thus ascribing a movement to the atomic masses themselves, we do not exclude the hypothesis that each atomic mass may be provided with a quantity of finer matter, which, without separating from the atom, may still be moveable in its vicinity.

By means of a mathematical investigation given at the end of the present memoir, it may be proved that the *vis viva* of the translatory motion alone is too small to represent the whole heat present in the gas; so that without entering into the probability of the same, we are thus compelled to assume one or more motions of another kind.

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have not been able to procure the memoir of Joule in question, and therefore I am ignorant how far he has pursued the subject, and whether his views coincide with mine in all points. It is to be regretted that Joule did not publish his memoir in a more widely circulated periodical. (See the Bibliography for Joule's paper; this note by Clausius induced Joule to send his paper to *Philosophical Magazine*, requesting that it be reprinted, but observing that "The *Memoirs of the Literary and Philosophical Society of Manchester* are at present regularly forwarded to the principal scientific societies of Europe and America.")

According to this calculation, the excess of the whole *vis viva* over that of the translatory motion alone is particularly important in gases of a complicated chemical constitution, in which each molecule consists of a great number of atoms.

3. In one and the same gas the translatory motion of the whole molecules will always have a constant relation to the several motions which, in addition to the above, the constituents of the molecules likewise possess. For brevity I will call the latter the *motions of the constituents*.

Conceive a number of molecules whose constituents are in active motion, but which have no translatory motion. It is evident the latter will commence as soon as two molecules in contact strike against each other in consequence of the motion of their constituents. The translatory motion thus originated will of course occasion a corresponding loss of *vis viva* in the motion of the constituents. On the other hand, if the constituents of a number of molecules in a state of translatory motion were motionless, they could not long remain so, in consequence of the collisions between the molecules themselves, and between them and fixed sides or walls. It is only when all possible motions have reached a certain relation towards one another, which relation will depend upon the constitution of the molecules, that they will cease mutually to increase or diminish each other.

When two molecules whose constituents are in motion come into collision they will not rebound, like two elastic balls, according to the ordinary laws of elasticity; for their velocities and directions after collision will depend, not only upon the motion which the whole molecules had before impact, but also upon the motion of those constituents which are nearest each other at the moment of collision. After the equalization of the several motions, however, when the translatory motion is, on the whole, neither increased nor diminished by the motions of the constituents, we may, in our investigation of the total action of a great number of molecules, neglect the irregularities occurring at the several collisions, and assume that, in reference to the translatory motion, the molecules follow the common laws of elasticity.

4. The explanation of the expansive force of gases and its dependence upon volume and temperature, as given by Krönig, suffers no essential modification through the introduction of other motions.

The pressure of the gas against a fixed surface is caused by the molecules in great number continually striking against and rebounding from the same. The force which must thence arise is, in the first place, by equal velocity of motion inversely proportional to the volume of the given quantity of gas; and secondly, by equal volume proportional to the *vis viva* of the translatory motion: the other motions do not here immediately come into consideration.

On the other hand, from Gay-Lussac's law we know that, under constant volume, the pressure of a perfect gas increases in the same ratio as the temperature calculated from − 273° C., which we call the absolute temperature. Hence, according to the above, it follows that the absolute temperature is proportional to the *vis viva* of the translatory motion of the molecules. But as, according to a former remark, the several motions in one and the same gas bear a constant relation to each other, it is evident that the *vis viva* of the translatory motion forms an aliquot part of the total *vis viva*, so that the absolute temperature is also proportional to the whole *vis viva* in the gas.

These considerations, together with others connected therewith to be given hereafter, induced me, in my memoir "On the Moving Force of Heat," to express the opinion that the specific heat of gases was constant; which opinion was in opposition to the experiments then known.† The quantity of heat which must be imparted to a gas, under constant volume, in order to raise its temperature is to be considered as the increase of the *vis viva* in the gas, inasmuch as in this case no work is done whereby heat could be consumed. The specific heat *under constant volume*, therefore, is in a perfect gas the magnitude which Rankine calls the *true* specific heat. Now the assertion that the true specific heat of a gas is constant, is simply equivalent to the assertion that *the total* vis viva *in the gas has a constant ratio to the* vis viva *of the translatory motion which serves us as a measure of the temperature*. With respect to the specific heat under constant pressure, I have proved in the memoir before cited, and by means of a hypothesis proceeding from the same considerations, that it differs only by a constant magnitude from the true specific heat.

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† Poggendorff's *Annalen*, vol. lxxix, p. 393. *Phil. Mag.*, vol. ii, pp. 1, 102.

5. The foregoing is true for permanent gases only, and even for these only approximatively. In general, the small deviations which present themselves can be easily accounted for.

In order that Mariotte's and Gay-Lussac's laws, as well as others in connexion with the same, may be strictly fulfilled, the gas must satisfy the following conditions with respect to its molecular condition:—

(1) The space actually filled by the molecules of the gas must be infinitesimal in comparison to the whole space occupied by the gas itself.

(2) The duration of an impact, that is to say, the time required to produce the actually occurring change in the motion of a molecule when it strikes another molecule or a fixed surface, must be infinitesimal in comparison to the interval of time between two successive collisions.

(3) The influence of the molecular forces must be infinitesimal. Two conditions are herein involved. In the first place, it is requisite that the force with which all the molecules at their mean distances attract each other, vanish when compared with the expansive force due to the motion. But the molecules are not always at their mean distances asunder; on the contrary, during their motion a molecule is often brought into close proximity to another, or to a fixed surface consisting of active molecules, and in such moments the molecular forces will of course commence their activity. The second condition requires, therefore, that those parts of the path described by a molecule under the influence of the molecular forces, when the latter are capable of altering appreciably the direction or velocity of the molecule's motion, should vanish when compared with those parts of its path with respect to which the influence of these forces may be regarded as zero.

If these conditions are not fulfilled, deviations in several ways from the simple laws of gases necessarily arise; and these deviations become more important the less the molecular condition of the gas fulfils the conditions in question.

On becoming acquainted with the celebrated investigations of Regnault on the deviations of gases from Mariotte's and Gay-Lussac's laws, I attempted, by means of the principles above intimated, to deduce some conclusions with respect to the molecular

condition of several gases from the nature of the deviations which Regnault detected in the same. A description of this method, however, would be too prolix; and even the results, in consequence of the many difficulties encountered in actual calculation, are too uncertain to merit being here adduced.

Whenever, therefore, in the sequel a gas is spoken of, we shall, as before, conceive it to be one which *perfectly* fulfils the above conditions, and which Regnault calls an *ideal* gas, inasmuch as all known gases present but an approximation to this condition.

6. After these considerations on the *gaseous* condition, the question at once arises in what manner the *solid* and *liquid* conditions differ from the gaseous. Although a definition of these states of aggregation, in order to be satisfactory in all its details, would require a more complete knowledge than we at present possess of the condition of the individual molecules, yet it appears to me that several fundamental distinctions may be advanced with tolerable probability.

A motion of the molecules takes place in all three states of aggregation.

In the *solid* state, the motion is such that the molecules move about certain positions of equilibrium without ever forsaking the same, unless acted upon by foreign forces. In solid bodies, therefore, the motion may be characterized as a vibrating one, which may, however, be of a very complicated kind. In the first place, the constituents of a molecule may vibrate among themselves; and secondly, the molecule may vibrate as a whole: again, the latter vibrations may consist in oscillations to and fro of the centre of gravity, as well as in rotatory oscillations around this centre of gravity. In cases where external forces act on the body, as in concussions, the molecules may also be permanently displaced.

In the *liquid* state the molecules have no longer any definite position of equilibrium. They can turn completely around their centres of gravity; and the latter, too, may be moved completely out of its place. The separating action of the motion is not, however, sufficiently strong, in comparison to the mutual attraction between the molecules, to be able to separate the latter entirely. Although a molecule no longer adheres to definite neighbouring molecules, still it does not spontaneously forsake the latter, but only under the

united actions of forces proceeding from other molecules, with respect to which it then occupies the same position as it formerly did with respect to its neighbouring molecules. In liquids, therefore, an oscillatory, a rotatory, and a translatory motion of the molecules takes place, but in such a manner that these molecules are not thereby separated from each other, but, even in the absence of external forces, remain within a certain volume.

Lastly, in the *gaseous* state the motion of the molecules entirely transports them beyond the spheres of their mutual attraction, causing them to recede in right lines according to the ordinary laws of motion. If two such molecules come into collision during their motion, they will in general fly asunder again with the same vehemence with which they moved towards each other; and this will the more readily occur, since a molecule will be attracted with much less force by another single molecule than by all the molecules which in the liquid or solid state surround it.

7. The phænomenon of *evaporation* appearing peculiarly interesting to me, I have attempted to account for the same in the following manner.

It has been stated above, that in liquids a molecule, during its motion, either remains within the sphere of attraction of its neighbouring molecules, or only leaves the same in order to take up a corresponding position with respect to other neighbouring molecules. This applies only to the mean value of the motions, however; and as the latter are quite irregular, we must assume that the velocities of the several molecules deviate within wide limits on both sides of this mean value.

Taking next the surface of a liquid into consideration, I assume that, amongst the varied motions to and fro, it happens that under the influence of a favourable cooperation of the translatory, oscillatory, and rotatory motions, a molecule separates itself with such violence from its neighbouring molecules that it has already receded from the sphere of their action before losing all its velocity under the influence of their attracting forces, and thus that it continues its flight into the space above the liquid.

Conceive this space to be enclosed, and at the commencement empty; it will gradually become more and more filled with these expelled molecules, which will now deport themselves in the space

exactly as a gas, and consequently in their motion strike against the enclosing surfaces. The liquid itself, however, will form one of these surfaces; and when a molecule strikes against the same, it will not in general be driven back, but rather retained, and, as it were, absorbed in consequence of the renewed attraction of the other molecules into whose vicinity it has been driven. A state of equilibrium will ensue when the number of molecules in the superincumbent space is such, that on the average as many molecules strike against, and are retained by the surface of the liquid in a given time, as there are molecules expelled from it in the same time. The resulting state of equilibrium, therefore, is not a state of rest or a cessation of evaporation, but a state in which evaporation and condensation continually take place and compensate each other in consequence of their equal intensity.

The density of the vapour necessary for this compensation depends upon the number of molecules expelled from the surface of the liquid in the unit of time; and this number is again evidently dependent upon the activity of the motion within the liquid, that is to say, upon its temperature. I have not yet succeeded in deducing from these considerations the law according to which the pressure of vapour must increase with the temperature.

The preceding remarks on the deportment of the surface of the liquid towards the superincumbent vapour, apply in a similar manner to the other surfaces which enclose the space filled with vapour. The vapour is in the first place condensed on these surfaces, and the liquid thus produced then suffers evaporation, so that here also a state must be attained in which condensation and evaporation become equal. The requisite quantity of condensed vapour on these surfaces depends upon the density of the vapour in the enclosed space, upon the temperature of the vapour and of the enclosing surfaces, and upon the force with which the molecules of vapour are attracted towards these surfaces. In this respect a maximum will occur when the enclosing surfaces are completely moistened with the condensed liquid; and as soon as this takes place, these surfaces deport themselves exactly like a single surface of the same liquid.

8. The reason why the presence of another gas above the liquid cannot impede the evaporation of the same may now be immediately explained.

The pressure of the gas on the liquid arises solely from the fact, that here and there single molecules of gas strike against the surface of the liquid. In other respects, however, inasmuch as the molecules of gas themselves actually fill but a very small part of the superincumbent space, the latter must be considered as empty, and as offering a free passage to the molecules of the liquid. In general these molecules will only come into collision with those of the gas at comparatively great distances from the surface, and the former will then deport themselves towards the latter as would the molecules of any other admixed gas. We must conclude, therefore, that the liquid also expels its molecules into the space filled with gas; and that in this case also the quantity of vapour thus mixed with the gas continues to increase until, on the whole, as many molecules of vapour strike against and are absorbed by the surface of the liquid as the latter itself expels; and the number of molecules of vapour to the unit of volume requisite hereto, is the same whether the space does or does not contain additional molecules of gas.

The pressure of the gas, however, exercises a different influence on the interior of the liquid. Here also, or at places where the mass of liquid is bounded by a side of the vessel, it may happen that the molecules separate from each other with such force that for a moment the continuity of the mass is broken. The small vacuum thus produced, however, is surrounded on all sides by masses which do not admit of the passage of the moved molecules; and hence this vacuum will only then become magnified into a bubble of vapour, and be able to continue as such, when the number of molecules expelled from its enclosing liquid walls is sufficient to produce an internal vapour-pressure capable of holding in equilibrium the pressure which acts externally and tends to compress the bubble again. Hence the expansive force of the enclosed vapour must be greater, the greater the pressure to which the liquid is exposed, and thus is explained the relation which exists between the pressure and the temperature of the boiling-point.

The relations will be more complicated when the gas above the liquid is itself condensable, and forms a liquid which mixes with the given one, for then of course the tendency of the two kinds of matter to mix enters as a new force. I shall not here enter into these phænomena.

As in liquids, so also in solids the possibility of an evaporation

may be comprehended; nevertheless it does not follow from this that, on the contrary, an evaporation *must* take place on the surface of all bodies. It is, in fact, readily conceivable that the mutual cohension of the molecules of a body may be so great, that, so long as the temperature does not exceed a certain limit, even the most favourable combination of the several molecular motions is not able to overcome this cohesion.

9. The explanation of the *generation* and *consumption* of heat accompanying changes of the state of aggregation and of the volume of a body, follows immediately, according to the above principles, from the consideration of the positive and negative work done by the active forces.

In the first place, let us consider the *interior* work.

When the molecules of a body change their relative positions, the change may be either in the same direction as that according to which the forces resident in the molecules tend to move the latter, or in a direction opposite to this. In the first case, a certain velocity is imparted by the forces to the molecules during their passage from one position to the other, and the *vis viva* of this velocity is immediately transformed into heat; in the second case, and disregarding for the present the action of extraordinary foreign forces, it is in virtue of heat that the molecules move in directions opposed to the interior forces, and the retardation which these molecules thereby suffer through the action of the opposing forces appears as a diminution of the motion of heat.

In the passage from the solid to the liquid state the molecules do not, indeed, recede beyond the spheres of their mutual action; but, according to the above hypothesis, they pass from a definite and, with respect to the molecular forces, suitable position, to other irregular positions, in doing which the forces which tend to retain the molecules in the former position have to be overcome.

In evaporation, the complete separation which takes place between the several molecules and the remaining mass evidently again necessitates the overcoming of opposing forces.

With respect to gaseous bodies, it is evident from what has been above remarked concerning the requisites of a perfect gaseous state, that as soon as a gas has once attained this state, molecular attractions have no longer to be overcome during its further expansion, so

that during the changes of volume of an ideal gas no interior work has to be performed.

10. Besides the interior, we have in the next place to consider the *exterior* work, and the corresponding change in the quantity of heat.

In the first place, with respect to the changes in the heat of a permanent gas subjected to pressure or expanding by overcoming a counter-pressure, Krönig has already remarked at the conclusion of his memoir, that when one of the sides against which the molecules of gas strike is itself in motion, these molecules will not rebound with velocities equal to those they possessed when moving towards the side. If the side approaches the molecules, the velocity of the molecules on leaving the same is in general greater than before, if it recedes less. By means of special mathematical considerations, it may without difficulty be proved that the increase or decrease of the *vis viva* thereby produced must exactly correspond to the external work done by the expansive force of the gas; nevertheless it is not even necessary to give a special proof of this theorem, since the same is an immediate consequence of the general law of equivalence between *vis viva* and work.

If the side moves so slowly that the pressure of the gas against the moving side is just as great as against a stationary one, then, in determining the work, the velocity of the side no longer enters into consideration, but merely the whole path described by the same. On the contrary, if the velocity of the side is so great that in the vicinity of the same a sensible compression or rarefaction of the gas thereby ensues, then the pressure actually exercised by the gas during the motion must always be brought into calculation.

When an overflow takes place between two vessels filled with gases of different densities, or between a full and an empty vessel, on the whole no work will be performed, and therefore no change in the total quantity of heat can occur. It is not here asserted that no change in the quantity of heat takes place in either of the two vessels considered separately, for a mass of gas whose molecules move principally in a definite direction deports itself towards adjoining gaseous masses in the same manner as a moved side; and when the moved gaseous mass strikes against stationary walls, just as much motion of heat makes its appearance as *vis viva* is lost by the common translatory motion of the whole mass.

Just as in the changes of volume of gaseous bodies, so also in other cases the external work must be taken into consideration; as, for instance, the work which during the evaporation is employed to overcome external resistance, and thus to make room for the vapour as it is generated. In solid and liquid bodies which only suffer small changes of volume, the external work is also for the most part only small; nevertheless here also cases occur in which its influence becomes considerable.

11. Lastly, I must mention a phænomenon the explanation of which appears to me to be of great importance, viz. *when two gases combine with each other, or when a gas combines with another body, and the combination is also gaseous, the volume of the compound gas bears a simple ratio to the volumes of the single constituents, at least when the latter are gaseous.*

Krönig has already proved that the pressure exerted by a gas on the unit of its enclosing surface must be proportional to the number of molecules contained in the unit of volume, and to the *vis viva* of the several molecules arising from their translatory motion, the only one which Krönig considers.

If we apply this to simple gases, and assume that, when pressure and temperature are the same, equal volumes contain the same number of atoms—a hypothesis which for other reasons is very probable,—it follows that, in reference to their translatory motion, the atoms of different gases must have the same *vis viva*.

We will next examine in what manner this theorem remains true when applied to the molecules of compound gases.

12. In the first place, let us compare compound gases amongst themselves, *e.g.* two gases to form which the constituents have combined in ratios of volume respectively equal to 1 : 1 and 1 : 2. Nitric acid and nitrous acid may serve as examples.

With respect to these two gases, we know that quantities containing the same amount of oxygen occupy the same volume. Hence here, too, equal volumes contain the same number of molecules, although in the one gas each molecule consists of two, and in the other of three atoms; and we must further conclude, that even these differently constituted molecules have the same *vis viva* with respect to their translatory motion.

In most other compound gases we are led to the same conclusion; and in cases which do not submit themselves to this rule, it does not appear to me impossible that the discrepancy may be accounted for in one or both of two ways: either the gas was not sufficiently removed from its points of condensation when its volume was determined, or the chemical formula hitherto employed does not properly represent the manner in which the atoms are combined to form molecules.

On comparing compound and simple gases, however, an unmistakeable deviation from the foregoing rule shows itself, inasmuch as the space corresponding to an atom of the simple gas does not correspond to a molecule of the compound one. When two simple gases combine in equal volumes, it is well known that no change of volume takes place, whilst according to the above rule the volume ought to be diminished in the ratio of 2 : 1. Again, when a volume of one gas combines with two or three volumes of another, the combination is found to occupy two volumes, whereas according to rule it ought only to occupy one volume, and so on.

13. On seeking to explain these curious anomalies, and especially to find a common law governing the relations of volume in gases, I was led to adopt the following view as being most plausible. I beg to offer the same to the scientific public as a hypothesis which is at least worthy of further examination.

I assume that the force which determines chemical combination, and which probably consists in a kind of polarity of the atoms, is already active in simple substances, and that *in these likewise two or more atoms are combined to form one molecule.*

For instance, let equal volumes of oxygen and nitrogen be given. A mixture of these gases contains a certain number of molecules, which consist either of two atoms of oxygen or of two atoms of nitrogen. Conceive the mixture to pass into a chemical compound, and the latter then contains just as many molecules, which are merely constituted in a different manner, inasmuch as each consists of an atom of oxygen and an atom of nitrogen. Hence there is no reason why a change of volume should take place. If, on the other hand, one volume of oxygen and two of nitrogen are given, then in the mixture each molecule consists of two, and in the compound of three atoms. The chemical combination, therefore, has caused the number of

molecules to diminish in the ratio of 3 : 2, and consequently the volume ought to diminish in the same ratio.

It is well known that some simple substances do not, in the gaseous form, occupy the volume which their atomic weights and the volumes of their combinations would lead us to anticipate, but another, and in most cases a smaller volume, which bears to the former a simple ratio. A special investigation of these substances would here be out of place, more especially as two of them, sulphur and phosphorus, deport themselves in other respects in so remarkable a manner, in consequence of the variety of conditions they are capable of assuming, that we may reasonably expect further discoveries from chemistry with respect to these bodies; and then, perhaps, besides other irregularities, those of the volumes of their vapours will be explained. Nevertheless I may here recall one circumstance which in some cases may possibly facilitate this explanation. I refer to the fact, that the above hypothesis, according to which the molecules of simple substances each consist of *two* atoms, may not be the only possible one.

On comparing with each other all cases of simple and compound gases, we must not expect to find immediately a perfect agreement throughout. I am of opinion, however, that, under the present uncertainty with respect to the inner constitution of several bodies, and particularly of those which possess a complicated chemical composition, too great weight out not to be laid upon individual anomalies; and I deem it probable, that, by means of the above hypothesis respecting the molecules of simple substances, all relations of volume in gases may be referred back to the theorem, *that the several molecules of all gases possess equal* vis viva *in reference to their translatory motion.*

14. Proceeding to treat the subject mathematically, we will first deduce the expression which shows in what manner the pressure of the gas on the sides of the vessel depends upon the motion of its molecules.

As the shape of the vessel is indifferent, we will select that which is most convenient for our purpose. We will assume the vessel to be very flat, and that two of its sides consist of parallel planes so close to one another that their distance asunder is infinitesimal when compared with the other dimensions of the vessel. Hence we need not

consider the cases where the molecules strike against one of the narrow strips of sides, and we may assume that each moves in a right line until it either strikes against another molecule or against one of the large parallel sides. In fact, to take the small sides into consideration would change nothing in the final result, and would only make the development more prolix.

Let us consider one only of the two large sides; during the unit of time it is struck a certain number of times by molecules moving in all possible directions compatible with an approach towards the surface. We must first determine the number of such shocks, and how many correspond on the average to each direction.

15. Hereafter we shall always assume the gas to be an *ideal* one; in other words, we shall disregard the irregularities proceeding from an imperfect gaseous state, so that in determining the pressure we may, with Krönig, introduce certain simplifications in place of considering the motion exactly as it takes place.

The whole number of shocks received by the side remains unchanged when we assume that the molecules do not disturb each other in their motion, but that each pursues its rectilineal path until it arrives at the side.

Further, although it is not actually necessary that a molecule should obey the ordinary laws of elasticity with respect to elastic spheres and a perfectly plane side, in other words, that when striking the side, the angle and velocity of incidence should equal those of reflexion, yet, according to the laws of probability, we may assume that there are as many molecules whose angles of reflexion fall within a certain interval, *e.g.* between 60° and 61°, as there are molecules whose angles of incidence have the same limits, and that, on the whole, the velocities of the molecules are not changed by the side. No difference will be produced in the final result, therefore, if we assume that for each molecule the angle and velocity of reflexion are equal to those of incidence. According to this, each molecule would move to and fro between the large parallel sides, in the same directions as those chosen by a ray of light between two plane mirrors, until at length it would come in contact with one of the small sides; from this it would be reflected, and then commence a similar series of journeys to and fro, and so forth.

Lastly, there is no doubt that actually the greatest possible variety

exists amongst the velocities of the several molecules. In our considerations, however, we may ascribe a certain mean velocity to all molecules. It will be evident from the following formulæ, that, in order to maintain an equal pressure, this mean velocity must be so chosen that with it the total *vis viva* of all the molecules may be the same as that corresponding to their actual velocities.

16. According to these assumptions, it is evident, that, during the unit of time, each molecule will strike the side under consideration just as often as during that time it can, by following its peculiar direction, travel from the side in question to the other and back again. Let h be the distance between the large parallel sides, and ϑ the acute angle between the normal and the direction of motion; then $h/\cos\vartheta$ is the length of the path from one side to the other, and

$$\frac{u \,.\, \cos\vartheta}{2h} \tag{1}$$

the number of impulses given to the side, u being the velocity of the molecule.

With respect to the directions of the several molecules, we must assume that on the average each direction is equally represented. From this it follows, that the number of molecules moving in directions which form with the normal angles included between ϑ and $\vartheta + d\vartheta$, has to the whole number of molecules the same ratio that the surface of the spherical zone, whose limiting circles correspond to the angles ϑ and $d\vartheta$, has to the surface of the hemisphere, that it, the ratio

$$2\pi \sin\vartheta d\vartheta : 2\pi.$$

Hence if n represents the whole number of molecules, the number which corresponds to the angular interval between ϑ and $\vartheta + d\vartheta$ will be

$$n \sin\vartheta d\vartheta,$$

and the number of shocks imparted by them will be

$$\frac{nu}{2h} \cos\vartheta \sin\vartheta d\vartheta. \tag{2}$$

17. In order to determine the intensity of a shock, the whole velocity must be resolved into two components, one parallel and the other perpendicular to the side. Of these components, the first will not be affected by the shock, and will not enter into consideration in determining its intensity; the second, however, whose magnitude is represented by $u \cos \vartheta$, will be changed by the shock into an equal velocity in the opposite direction. The action of the side upon the molecule, therefore, consists in depriving it in one direction of the velocity $u \cos \vartheta$, calculated according to the normal, and of imparting to it an equal velocity in an opposite direction; in other words, of imparting to it a velocity of $2u \,.\, \cos \vartheta$ in the latter direction. Hence the quantity of motion imparted to the molecule will be

$$2mu \,.\, \cos \vartheta, \tag{3}$$

where m is the mass of the molecule.

Applying this to all molecules which correspond to the interval between ϑ and $\vartheta + d\vartheta$, we obtain during the unit of time,

$$\frac{nu}{2h} \cos \vartheta \sin \vartheta d\vartheta$$

times the same action, hence the quantity of motion imparted to these molecules during the unit of time is

$$\frac{nmu^2}{h} \cos^2 \vartheta \,.\, \sin \vartheta \,.\, d\vartheta. \tag{4}$$

Integrating this expression between the limits $\vartheta = 0$ and $\vartheta = \pi/2$, we find the motion imparted by the side to all the molecules which strike against it during the unit of time to be

$$\frac{nmu^2}{3h}. \tag{5}$$

Let us now conceive the side to be capable of moving freely; then in order that it may not recede before the shocks of the molecules, it must be acted upon on the other side by a counter force, which latter may in fact be regarded as continuous, in consequence of the great number of shocks and the feebleness of each. The intensity of this

force must be such as to enable it, during the unit of time, to generate the quantity of motion represented by the above expression. Since all forces, however, are measured by the quantity of motion they can produce in the unit of time, the above expression at once represents this force as well as the pressure exerted by the gas, the latter being equilibrated by the former.

If α be the superficial area of the side and p the pressure on the unit of surface, then

$$p = \frac{mnu^2}{3\alpha h}.$$

The product αh here involved gives the volume of the vessel or gas; hence representing the same by v, we have

$$p = \frac{mnu^2}{3v}. \tag{6}$$

The same formula would have been obtained if, with Krönig, we had, for the sake of simplification, assumed that one third of the whole molecules move perpendicularly to the side under consideration, and the two remaining thirds in two other directions parallel to the side. Nevertheless I preferred deducing the formula for the pressure without using this simplifying hypothesis.

If we write the last equation in the form

$$\tfrac{3}{2}\,pv = \frac{nmu^2}{2}, \tag{6a}$$

the right-hand side then denotes *the* vis viva *of the translatory motion of the molecules.*† But, according to Mariotte's and Gay-Lussac's laws,

$$pv = T \,.\, \text{const.},$$

† In accordance with a practice lately become general, and with what I have myself done in former memoirs, I call the *semi*-product of the mass into the square of the velocity the *vis viva*, because it is only with this definition of the notion that we can, without the addition of a coefficient, equate the expressions representing a quantity of work and the increase or decrease of *vis viva* which corresponds to the same.

where T is the absolute temperature; hence

$$\frac{nmu^2}{2} = T \,.\, \text{const.};$$

and, as before stated, the *vis viva* of the translatory motion is proportional to the absolute temperature.

18. We may now make an interesting application of the above equations by determining the velocity u with which the several molecules of gas move.

The product nm represents the mass of the whole given quantity of gas, whose weight we will call q. Then g being the force of gravity,

$$nm = \frac{q}{g};$$

and from equation (6) we deduce

$$u^2 = \frac{3gpv}{q}. \tag{7}$$

Adopting the metre as unit of length, and the kilogramme as unit of weight, let us suppose a kilogramme of gas under the pressure of 1 atmosphere—10333 kilogrammes on the square metre—to be given. Then

$$g = 9^{\text{m}}\cdot 80896,$$
$$p = 10333,$$
$$q = 1.$$

To determine v, we know that, according to Regnault, a kilogramme of atmospheric air under the pressure of 1 atmosphere, and at the temperature of melting ice, occupies 0·7733 cubic metre. Hence ρ being the specific gravity of the gas under consideration, its volume at the temperature of melting ice will be

$$\frac{0\cdot 7733}{\rho};$$

and at the absolute temperature T, assuming 273° to be the absolute temperature of melting ice, it will be

$$\frac{0\cdot 7733}{\rho} \cdot \frac{T}{273}.$$

Hence we deduce

$$u^2 = 3 \,.\, 9{\cdot}80896 \,.\, 10333 \,.\, 0{\cdot}7733 \,.\, \frac{T}{273 \,.\, \rho}$$

$$= 235130 \,\frac{T}{273 \,.\, \rho},$$

and consequently

$$u = 485^{\mathrm{m}} \sqrt{\frac{T}{273 \,.\, \rho}} \,. \tag{8}$$

As particular cases, we obtain the following numbers corresponding to the temperature of melting ice:—

for oxygen . . . . 461$^{\mathrm{m}}$,

for nitrogen . . . . 492$^{\mathrm{m}}$,

for hydrogen . . 1844$^{\mathrm{m}}$.

These numbers are the mean velocities which, for the totality of molecules, give the same *vis viva* as would their actual velocities. At the same time, however, it is possible that the actual velocities of the several molecules differ materially from their mean value.

19. By means of the equations above established, we will lastly examine *what relation exists between the* vis viva *of the translatory motion and the whole* vis viva, *or heat, in the gas.*

In doing so we will conceive the quantity of heat to be measured, not by the ordinary unit of heat, but by the mechanical unit of *vis viva*, or what is equivalent, by the unit of work. To this end we have only to divide the quantity of heat measured in the ordinary manner by the thermal equivalent of the unit of work, which as before I will denote by A. Let H be the quantity of heat thus determined.

Further, let c be the specific heat of the gas under constant volume, in other words, the true specific heat; then the increase of the quantity of heat in the quantity q of gas corresponding to an elevation of temperature dT is

$$dH = \frac{qc}{A}\, dT.$$

Integrating this equation, we have

$$H = \frac{qc}{A} T. \tag{9}$$

No constant need be added, since, as before remarked, the heat in the gas is proportional to the *vis viva* of the translatory motion, and hence also to the absolute temperature.

The expression on the right of this equation may be replaced by another which is very convenient for our present investigation.

The quantity of heat which must be imparted to the quantity of gas q in order to elevate its temperature by dT and its volume by dv is expressed thus,

$$\frac{qc}{A} dT + pdv,$$

wherein the first term represents the increase of the heat contained in the gas, and the second the quantity of heat consumed by work. If we assume the gas to be heated under constant pressure, the relation between dT and dv is thereby defined. For we have generally

$$pv = T \,.\, \text{const.};$$

and differentiating, under the supposition that p is constant, we obtain

$$pdv = dT \,.\, \text{const.};$$

whence the undetermined constant may be eliminated by means of the foregoing equation, and we have

$$dv = \frac{v}{T} dT.$$

Let us substitute this value of dv in the above equation, and at the same time note that, c' being the specific heat under constant pressure, the whole quantity of heat imparted to the gas in the case under consideration may be represented by $(qc'/A)dT$. In this manner we arrive at the equation

$$\frac{qc'}{A} dT = \frac{qc}{A} dT + \frac{pv}{T} dT,$$

whence we conclude that

$$\frac{q(c' - c)}{A} \cdot T = pv. \tag{10}$$

By means of this equation (9) becomes

$$H = \frac{c}{c' - c} \cdot pv. \tag{11}$$

20. Let us now return to the equation (6*a*) before established, and for brevity let us denote the *vis viva* of the translatory motion by K, then

$$K = \frac{3}{2}pv.$$

By combining this with the foregoing equation we obtain

$$\frac{K}{H} = \frac{3}{2}\left(\frac{c'}{c} - 1\right) . \tag{12}$$

The ratio of the *vis viva* of the translatory motion to the whole *vis viva* is thus reduced to the ratio between the two specific heats.

In order to compare with each other the values of the ratio K/H corresponding to different gases, it will be found convenient to introduce in the above formula, in place of the specific heats calculated with reference to the unit of weight, those calculated according to the unit of volume, which for distinction may be represented by γ and γ'. The equation then becomes

$$\frac{K}{H} = \frac{3}{2} \cdot \frac{\gamma' - \gamma}{\gamma} . \tag{13}$$

If we neglect deviations which arise from an imperfect gaseous condition, and conceive all gases to be in the ideal state, then, as I have shown in my memoir "On the Moving Force of Heat†," the difference $\gamma' - \gamma$ is the same for all gases. Hence the ratio *K/H is inversely proportional to the true specific heat of the gas calculated according to the unit of volume.*

† Poggendorff's *Annalen*, vol. lxxix, p. 394. *Phil. Mag.*, vol. ii, p. 1.

For those simple gases which manifest no irregularities with respect to their volume, and for those compound ones which suffered no diminution of volume during the act of combination, γ, and therefore K/H also, has the same value. For these gases we have approximately

$$\frac{\gamma'}{\gamma} = 1{\cdot}421,$$

hence

$$\frac{K}{H} = 0{\cdot}6315.$$

On the contrary, for those compound gases whose volumes during combination have been diminished, γ is greater, and consequently K/H less; and, in fact, it is less the smaller the volume of the combination compared with the sum of the volumes of its constituents, the latter being all considered gaseous.

Thus it is corroborated what was before stated, that the *vis viva* of the translatory motion does not alone represent the whole quantity of heat in the gas, and that the difference is greater the greater the number of atoms of which the several molecules of the combination consist. We must conclude, therefore, that besides the translatory motion of the molecules as such, the constituents of these molecules perform other motions, whose *vis viva* also forms a part of the contained quantity of heat.

Zurich, January 5, 1857.