ART. LVI.—*On the Force of Effective Molecular Action*; by Professor W. A. NORTON.

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FOR the critical curve the molecular repulsion has very nearly the constant value, $0{\cdot}0052\frac{m}{r^2}$, from $x=3r$ to $x=7{\cdot}5r$; and according to Dr. Andrews, the pressure of condensation at the critical point for carbonic acid gas was seventy-five atmospheres. These data give for the molecular repulsion answering to one atmosphere, $\frac{0{\cdot}0052\frac{m}{r^2}}{75}=0{\cdot}0000693\frac{m}{r^2}$. This should then be the value of the minimum repulsive ordinate, that obtains when $x=3r$, in the curve for water at the point of ebullition (212° F.). This result gives for this curve $k=4{\cdot}931$. In this curve the same molecular repulsion occurs again at $x=115r$. Now taking 1581 for the ratio of expansion by volume of water converted into steam at 212° F., and for the distance between the effective molecules of the steam, $115r$, and putting $y=$ distance of the inner surface of the effective envelope from the center of the molecule, I have

$$\frac{115r+2r+2y}{3r+2r+2y}=\sqrt[3]{1581};$$

which gives $y=2{\cdot}76r$. This calculation proceeds on the supposition that the effective molecules have the same size in the vaporous as in the liquid state, but theoretically they should be larger; and we shall see in the sequel that the probable value of the diameter of the molecules of steam is $42{\cdot}25r$. If we adopt this estimate, the ratio of expansion by volume, 1581 to 1, gives for the diameter of the liquid molecule at 212° F., $10{\cdot}5r$.

Let us now see how far the well known laws of gases may be deduced from our molecular formula.

(1). *Avogadro's Law*, relative to the simple gases; that all simple gases contain in the same volume, at the same pressure and temperature, the same number of ultimate molecules. This law follows from the fact that for the large distances between contiguous molecules, that obtain in gases, the effective repulsion is very nearly the same at the same distance for all the values of k that can answer to the different gases; together with the large size of the effective gaseous molecules. The entire possible range of value for k, for gases and vapors, is from 0 to $4{\cdot}934$; since it is only between these limits that the effective molecular force is repulsive at all distances. We have already seen that when $k=4·931$, and $x=115r$, the effective repulsion is $0·0000693p$; and that this answers to one atmosphere of external pressure. When $k=0$ and $x=115r$, the effective repulsion is $0·00007561p$; and the distance x at which the repulsion becomes $0·0000693p$ is $120r$. But the distances between the centers of the molecules must be much greater than these values of x. It will soon appear that the law of Mariotte requires that the radius of the effective gaseous molecule, under a pressure of one atmosphere, be not less than $31r$. This gives for the distance between the centers of the molecules, under this pressure, $177r$ when $k=4·931$; and $182r$ when $k=0$. Now $\left(\frac{182}{177}\right)^3=1·086$. This is the highest ratio of volumes of two simple gases, under atmospheric pressure, that would be theoretically possible; unless the effective size of the molecules be supposed to diminish as k increases. But this is only an ideal extreme result. It will appear in the sequel that the values of k for the simple gases, oxygen, hydrogen and nitrogen, for which Avogadro's law, for a constant pressure and temperature, has been experimentally established, are included within narrow limits (probably 2 and 3). It thus becomes apparent that the extreme ratio of the number of molecules in the same volume cannot exceed 1·013, and may be much less.

(2.) *Avogadro's Law*, relative to compound gases; that the same volumes of these gases contain the same number of molecules, and the same number as equal volumes of the simple gases. The ordinary physical conception is that compound molecules are formed by the union of simple molecules, or of a certain number of their constituent atoms, and that these occupy the same volume that the simple molecules did. In some instances of chemical combination it necessitates the supposition that the formation of each new compound molecule is a result of the breaking up of several molecules of the combining substances. It also involves the improbable hypothesis that the space physically occupied by a molecule is wholly independent of the number of its constituent atoms. Upon the conception of variable ultimate molecules adopted in this and my previous paper, Avogadro's law simply implies that in the act of combination the effective molecules suffer a certain diminution of size, by the collapse of their envelopes. The same number of atoms may thus physically occupy the same volume as if they were closely to unite and form a compound molecule, upon the ordinary hypothesis. Thus in the formation of aqueous vapor by the combination of two volumes of hydrogen with one volume of oxygen, forming two volumes of the compound, a condensation of the individual molecules would take place, and as the result two ultimate molecules of hydrogen and one of oxygen would occupy the same volume that three molecules of either gas did before the combination. It is to be observed, in confirmation of this view of the process of combination, that the reduction in the size of the effective molecules, would be attended with an increase in the ratio k, and a consequent increase in the value of the attractive term in equation (1), for the same value of x (or graphically, a rise of the curve of effective molecular action; see fig. 3).

The compound should therefore be a more condensable gas, or vapor. We have already obtained for aqueous vapor, at 212° F., $k=4·931$; and it will appear hereafter that for oxygen, hydrogen, or nitrogen, the value of k must fall below 4, and is probably near 2. To obtain the theoretical size of the effective molecules of aqueous vapor, we have the equation $\frac{118r+62r}{115r+y'}=\sqrt[3]{\frac{3}{2}}$. This gives $y'=42·25r$, and radius of molecule$=21·12r$. The distance between the centers of contiguous molecules will be $157·25r$. In this equation $118r$ is the distance between contiguous molecules of oxygen or hydrogen before condensation, and answers to $k=2$, nearly; and $62r$ is the diameter of one of the molecules (see page 436): $115r$ is the distance between the same molecules after the condensation into aqueous vapor; when k has been increased to 4·931.

In all combinations of simple gases the degree of condensation that occurs is expressed by the ratio of the number of atoms in the "compound molecule," as shown by the ordinary molecular formula, to 2, the assumed number of the constituent atoms of "the molecule" of a simple gas. In this statement it is supposed that the constituent gases before combination are in the perfect gaseous condition, like oxygen, or hydrogen, and that the compound gas has the temperature at which it is in a similar condition; so far as these two suppositions are implied in Avogadro's law.

Mariotte's, or Boyle's Law, of the uniform compressibility, by volume, of gases under increasing pressure. Upon the present theory this law should obtain if the effective molecular repulsion be inversely proportional to the volume occupied by the same number of molecules, or to the cube of the distance between the centers of contiguous molecules. For each molecule would then be the center of a system of recurring impulses propagated in waves by the interstitial luminiferous ether, proportional in intensity to the number (n) of molecules in a unit of volume, and every line radiating from any point of the enclosure into the body of gas would sensibly intersect a molecule at a greater or less distance. To obtain the entire impulsive action (P) on the point considered, we have then only to conceive a hemisphere traced around this point, and that all the points of its surface are centers of radiating impulses proportional in intensity to n, and propagated according to the law of inverse squares. P should then be proportional to the intensity of the radiation at the points of the hemisphere, and therefore to n.

Now the expression for the effective molecular repulsion (equ. 1) consists of two terms of which the first, or attractive term, becomes relatively very small at the molecular distances that obtain, at moderate pressures, in gases (p. 346). The repulsive term, $\frac{m}{x^2}$, gives, then, very nearly the effective force, at such pressures; and more nearly in proportion as the ratio $\frac{n}{m}$ is smaller. Mariotte's law should then be satisfied, for considerable variations of pressure if the term $\frac{m}{x^2}$ should vary inversely as the cube of the distance (x') between the centers of contiguous molecules; that is, if $\frac{1}{x^2} \div \frac{1}{x'^3}$. If we denote by h the radius of the effective molecule, $x' = x + 2h$. As we are not in a position to determine à priori the law of variation of the size of the molecule under varying pressures, the only alternative is to adopt the hypothesis that $\frac{1}{x^2} \div \frac{1}{x'^3}$, deduce a series of values of the diameter $2h$, of the effective molecule that shall be in conformity with this hypothesis, and then test the results and hypothesis by deducing the theoretical deviations from the law of Mariotte in special cases, and comparing them with the deviations experimentally determined. Now I find that the hypothesis that $\frac{1}{x^2} \div \frac{1}{x'^3}$ is satisfied by the following values of $2h$, viz: 62·10, 62·00, 61·26, 60·32, 58·96, 57·12, 54·70, 51·58, 47·54, 42·24, 35·14, 30·53, 24·74, 16·89, 12·57,—answering respectively to the following values of u (equ. 2): 120, 115, 100, 90, 80, 70, 60, 50, 40, 30, 20, 15, 10, 5, and 3. Theoretically one gas differs from another in the value of k, and the larger this ratio the greater should be the deviations from the law of Mariotte, which strictly is fulfilled only when $k=0$, and so the attractive term in our formula equal to zero. These deviations should also increase as the pressure increases, since the attractive term will become relatively greater. The more permanent simple gases (oxygen, hydrogen, etc.), for which the law of Mariotte holds good over the greatest range of pressure, should then have the smallest values of the ratio k; and compound gases the larger values (see p. 435). We may now assume, as a basis for an approximate calculation, that the molecules of all the gases have equal diameters under equal pressures, and we may then compute for any supposed value of k the volume that should obtain under any supposed pressure, and compare it with the value that would result if the law of Mariotte were strictly fulfilled. Dr. Andrews, in his Bakerian Lecture on the continuity of the gaseous and liquid states of matter, states that under a pressure of forty-nine atmospheres, at the temperature 13°·09 C.; the volume of carbonic acid gas was "about $\frac{3}{5}$ of the volume that Mariotte's law would give." The critical temperature of the gas he found to be 30°·92 C., and we have seen (p. 357) that for the critical curve $k=4{\cdot}7$. This gives for the temperature 13°·09 C. $k=4{\cdot}75$ (very nearly). Now calculating the volume for this value of k, and under a pressure of 49 atmospheres, I obtain 0·648 of the volume (V) Mariotte's law would give. Experiment gave 0·60V. By what has already been stated (p. 434), the actual diameter of a molecule of carbon-dioxide, under the pressure of one atmosphere, should be less than $62r$, the diameter assumed for molecules of oxygen and hydrogen. Taking it $52r$, I have deduced from the hypothesis that $\frac{1}{x^2} \div \frac{1}{x'^3}$ another series of values of the diameter $2h$; and making a new calculation, I find the theoretical volume $=0{\cdot}613\text{V}$. The ratio of condensation from the perfect gas in the production of carbon dioxide (see p. 435) would lead us to conclude that the diameter of the molecule, at the temperature 13°·09 C. would be less than 50 (possibly as low as 40). Taking it at 40 I obtain by estimation the theoretical volume $=0{\cdot}58\text{V}$. I have made other similar test calculations, with the aid of Dr. Andrews' experimental determinations with similar results.

Gay Lussac's Law of the uniform variation of the volume of a gas under constant pressure, as well as of the elastic force under a constant volume, resulting from a change of temperature. This may be deduced from the principle which gives Mariotte's law, that the molecular repulsion varies inversely as the volume, and the principle that it is directly proportional to the coefficient of repulsion (m), which must be proportional to the absolute temperature. We have already seen that the elastic pressure of a gas should be proportional to the molecular repulsion (F). Now for the range of pressure for which the law of Mariotte holds good, we have

$$\text{F}=f=\frac{m}{x^2}=\frac{m'}{x'^3}=\frac{\text{C}m}{x'^3}.$$

The volume is represented by x'^3. If x' becomes $x'+dx'$, the volume becomes $(x'+dx')^3=x'^3+3x'^2dx'$ (very nearly). Thus the increase of volume is $3x'^2dx'$; and the ratio of increase $\frac{3x'^2dx'}{x'^3}$. But the increment dx' is due to an increase of temperature, and must answer to dm, while f remains constant. Thus $dx' = \frac{dm'}{3fx'^2}$, and therefore the ratio becomes

$$\frac{dm'}{fx'^3} = \frac{dm'}{m'} = \frac{dm}{m}.$$

For the case in which the volume is constant, while the temperature rises,

$$df = \frac{dm'}{x'^3}\text{; and } \frac{df}{f} = \frac{dm'}{fx'^3} = \frac{dm'}{m'} = \frac{dm}{m}.$$

Thus the ratio of the increase of volume is equal to the ratio of the increase of elastic pressure. We may assume that from a certain absolute temperature, T, m increases uniformly for each increment, 1° of temperature. Let t denote the actual temperature above T; then $m = c't$, and $\frac{dm}{m} = \frac{dt}{t}$. From which it appears that above T the increase of volume, or of the elastic pressure, takes place uniformly; that is, is equal in amount for equal increments of temperature. We may conclude from this investigation that Gay Lussac's law holds good only for that range of pressure and temperature within which the law of Mariotte is fulfilled; and that it is not strictly true for the more compressible gases and vapors, except at temperatures considerably above the point of condensation.

Specific Heat of Gases.—When the temperature of a gas is raised 1°, without change of volume, the heat is expended in exalting the vibratory state (i. e. the dynamic energy) of the molecular envelopes, and in augmenting their potential energy by expansion. It is obvious, then, that the specific heat of a gas, under a constant volume, should be some function of the ratio, k, since upon this must depend at a given temperature, the number of molecules in the unit of volume, and the mechanical condition of each molecule. The theoretical indications are that the specific heat of different gases, for the unit of volume, is directly proportional to the value of k; but as these cannot be adequately presented here we will assume this as an hypothesis and test it by the quantitative results to which it leads. To state the hypothesis with more precision, it is that the specific heat of a gas, when the volume is constant and the *initial* elastic pressure is one atmosphere, is, for a unit of volume, proportional to the value of k—it being understood that in the case of a compound gas the value of k considered is that which which obtains when the molecules are in the condition that immediately results from the formation of the gas from its constituents, and at the temperature at which the ratio of condensation is that proper to the gas.

When a gas is allowed to expand under a constant pressure, an additional amount of heat is expended in the work of this expansion in opposition to the external pressure. Now if n were equal to m the amount of heat thus expended should equal that which would be expended on the molecular envelopes. Let U denote the entire amount of heat expended when the pressure is constant, u that expended in the work of expansion, and u' that expended on the molecules directly; and we have $U=u+u'=u+su$. Each term is a function of the temperature, t; and, differentiating, we have $dU=du+sdu$. But we have seen that du equals the value which sdu would have if k, or $\frac{n}{m}$, were equal to unity. Denote it by e, and we obtain $dU=e+se$. But, since the specific heat under a constant volume is proportional to k, $\frac{se}{e}=\frac{k}{1}$; and thus $s=k$. This value of s gives $dU=(1+k)e$, and $sdu=ke$; from which $\frac{dU}{sdu}=\frac{1+k}{k}$. This is ratio of the specific heat under a constant pressure to the specific heat under a constant volume.

Let us now subject these theoretical results to the test of calculation. According to Pouillet the specific heat of aqueous vapor, under a constant volume, is 1·9600, and that of a mixture of one volume of oxygen and two volumes of hydrogen, 0·9277. The ratio of these is 2·113. For aqueous vapor we have seen that $k=4{\cdot}93$. Thus, $\frac{4{\cdot}93}{2{\cdot}113}$ $(=2\frac{1}{3})$ should be the value of k for the mixture of oxygen and hydrogen before condensation into aqueous vapor. This result, as will appear in the sequel, is in accordance with the results of Professor Pictet's experiments on the liquefaction of oxygen and hydrogen.

Taking the specific heat of carbon-dioxide, under a constant volume at 1·26, we have $\frac{1{\cdot}26}{0{\cdot}9277}=1{\cdot}36$, and $1{\cdot}36\times2\frac{1}{3}=3{\cdot}17$. This is the value of k for this gas under a pressure of one atmosphere, and in the condition in which it exists as the immediate product of the combustion of carbon. It is here tacitly supposed, in accordance with fact, that the specific heat of the gas, for equal volumes, and under the pressure of one atmosphere, is the same, when in the state of a vapor, at whatever temperature it is supposed to be formed from a liquid. Theoretically there should be a tendency to this state of things, since when the temperature is higher the number of molecules in the unit of volume, at the same elastic tension, is less, but at the same time the specific heat of each molecule should be greater, owing to the increased size of its envelope, and its consequent greater liability to expansion under the operation of the heat energy. For olefiant gas we have $\frac{1·553}{0·9277} = 1·674$; and $1·674 \times 2\frac{1}{3} = 4·2$, the theoretical value of k for this gas. These results enable us to test our expression for the ratio of the specific heats under a constant volume, and at a constant pressure, viz: $\frac{1+k}{k}$. For the mixture of oxygen and hydrogen $\frac{1+k}{k} = \frac{1+2\frac{1}{3}}{2\frac{1}{3}} = 1·430$. The experimental value is 1·410. For carbon-dioxide $\frac{1+k}{k} = \frac{3·17+1}{3·17} = 1·315$. According to experiment it is 1·338. For olefiant gas the ratio is $\frac{4·2+1}{4·2} = 1·24$, the same as obtained by experiment. For oxide of carbon I get $k = 2·60$ and ratio of specific heats $= 1·38$; experiment gives 1·428. For oxide of nitrogen $k = 3·396$ and ratio of specific heats $= 1·294$; experiment gives 1·343.

Professor J. Clerk Maxwell (Nature, March 10, 1875, p. 375) admits that the kinetic theory of gases has encountered a serious dilemma in the attempt to determine specific heats. He says, "We learn from the spectroscope that a molecule can execute vibrations of constant period. It cannot therefore be a mere material point, but a system capable of changing its form. Such a system cannot have less than six variables. . . . But the spectroscope tells us that some molecules can execute a great many different kinds of vibrations. They must therefore be systems of a very considerable degree of complexity, having far more than six variables;" and "every additional variable increases the specific heat, whether reckoned at constant pressure or at constant volume. But the calculated specific heat is already too great when we suppose the molecule to consist of two atoms only." The present theory encounters no such difficulty, since it regards the heat and light vibrations as pertaining to the atoms of the molecular envelopes, and the number of these is indefinitely great, and the determination of the specific heat requires no hypothesis of a definite number of atoms to be made. In the same connection Professor Maxwell has the following remark: "And here we are brought face to face with the greatest difficulty which the molecular theory has yet encountered, namely, the interpretation of $n+e=4·9$. He had previously remarked "that $n+e$, for air and several other gases, cannot be more than 4·9. For carbonic acid (?) and steam it is greater." Now $n+e$ answers to the ratio, k, on the present theory, and we have seen (p. 433) that this is 4·93 for steam, and less than 4·9 for the gases.

Diffusion of Gases.—The law of variation of the molecular repulsion, at the distances between gaseous molecules, given by equ. (1), leads to the result that if one layer of such molecules moves over another, so that those on one side of the plane of separation are opposite the vacant spaces between those on the other side, a force of effective repulsion directed toward this plane will supervene, which will operate to diffuse each set of molecules into the volume occupied by the other. Did space admit, we might show that when all the circumstances of the case, and the resistances in operation, are duly considered, the diffusion thus originating should conform to the known laws of diffusion; as that the velocity of diffusion of the individual molecules is inversely proportional to the square root of the molecular weights, &c. The force of diffusion of liquid molecules has a similar origin. Upon this view the force of diffusion is incidental to the inevitable internal agitations occurring in fluid masses; and may be brought into more lively action by artificial disturbances. The molecular repulsive or heat energy consumed in such effects is restored to the mass by the subsidence of the individual movements, perpetually recurring.

Comparison of the present with the kinetic theory of gases.—The theory of gases which has now been deduced from the general expression for the force of effective molecular action (equa. 1, or 2), is no less dynamical in its essential character than the kinetic theory. The dynamical system conceived to be in operation is, upon the one view, the translatory wave movements and atomic vibrations of the interstitial ether and ethereal atmospheres of the molecules, and upon the other, the movements of translation of the molecules themselves, and the vibrations of their constituent atoms. The doctrine of Energy, and the principles of the Mechanical Theory of Heat, are as applicable to the one as to the other theory. The essential correspondence of the two theories is abundantly evident from the fact that with equa. (1) an expression for the elastic pressure of a gas may be obtained that is a counterpart of that given by the equation of Clausius, viz: $p\mathrm{V}=\frac{2}{8}\mathrm{T}-\frac{2}{8}\Sigma\Sigma\frac{1}{2}\mathrm{R}r$. This may be inferred from the general consideration that the impulses upon any point, O, of the enclosure, of an ethereal wave in which the velocity of the radial pulsation increases from zero to a maximum, u, and then decreases to zero, is analogous to the impulse of a gaseous molecule whose velocity, u' is reduced to zero, and then restored in the recoil—the ethereal waves and the gaseous molecules alike impinging on the point from every variety of direction. To show it conclusively, let it be borne in mind that the central atoms of the molecules of the gas may, for each point O, of the enclosure, be conceived to be uniformly distributed over the surface of a hemisphere described around this point, so that each elementary part of the surface will be occupied by one such atom, and so will be a center of radiation of wave-impulses propagated to O (p. 436). Now let u be the maximum velocity of pulsation of the ethereal atoms in any wave, at the point O; m the mass of ether effective in the pulsation; s the minute space (equal to half the length of a wave) over which m moves while the velocity is increasing from zero to u, or decreasing from u to zero; and p_1 the mean impulsive force taking effect over the space s. Then for the wave impulses propagated along the normal at O, $p_1 \times 2s = mu^2$. Let n_1 denote the number of successive waves in the space, 1, and take for the unit of time the interval employed by the wave in traversing the distance, 1; and we have $n_1 = \frac{1}{2s}$ and $p_1 \times 2s \times \frac{1}{2s} = n_1 mu^2$, or $p_1 \times 1 = n_1 mu^2$. But $p_1 \times 1$ is the impulsive work of the waves in the unit of time, and may be taken as p', the force of pressure on an elementary area at O, due to the successive waves propagated along the normal at O. Now for a wave coming from a direction inclined under any angle φ' to the normal, the normal impulse will be $p' \cos \varphi'$, and the normal velocity of pulsation will be $u \cos \varphi'$. Thus $p' \cos \varphi' = n_{,} mu^2 \cos^2 \varphi'$; and for n' molecules having this angle of direction, $n'p' \cos \varphi' = n'n_{,} mu^2 \cos^2 \varphi'$. For the entire normal impulse at O, or the elastic pressure, p, on an elementary area at O, we have then, $p = \Sigma n'n_{,} mu^2 \cos^2 \varphi$. But the gaseous molecules lying in any angle of direction, φ, around the normal, form an elementary zone of the hemisphere, whose breadth is $d\varphi$, and altitude, in the normal direction, $d \cos \varphi$, or $\sin \varphi d\varphi$. If then n represent the number of molecules in the entire hemisphere, $n' : n :: \sin \varphi d\varphi : 1$; and $n' = n \sin \varphi d\varphi$.

$$\text{Thus } p = \int_0^{\frac{\pi}{2}} nn_{,} mu^2 \cos^2 \varphi \sin \varphi d\varphi = nn_{,} mu^2 \left(-\frac{\cos^3 \varphi}{3} \right)_0^{\frac{\pi}{2}} = \frac{nn_{,} mu^2}{3} = \tfrac{2}{3} \cdot \frac{nn_{,} mu^2}{2}. \quad \text{Now } \frac{nn_{,} mu^2}{2}$$

is the entire living force, or energy, of all the ethereal waves occupying at any interval of time the space unity on all the lines radiating from O; or included within a hemisphere traced around O with the radius 1. Calling this E, we have $p = \frac{2}{3}$E. But the hypothesis, which has been tested by quantitative determinations (p. 437), that the repulsive term in equ. (1) varies inversely as the cube of the distance, x', between the centers of the molecules, gives the same law of variation for the impulses received at O; and accordingly if T denotes the value of E, when $x' = 1$, $p = \frac{2}{3} \frac{\mathrm{T}}{x'^3} = \frac{2}{3} \frac{\mathrm{T}}{\mathrm{V}}$, in which V is the volume occupied by a given number of molecules, N, in terms of the volume, 1, occupied by the same number of molecules when the distance between their centers is 1.

If now we take account of the attractive impulses answering to the attractive term in equ. (1), it is plain that by a similar investigation we shall obtain for the diminution, d, of the elastic pressure at O, $d=\frac{2}{3}E'$. Accordingly for the actual pressure on an elementary area at O, we have

$$P=\tfrac{2}{3}E-\tfrac{2}{3}E'=\tfrac{2}{3}\frac{T}{V}-\tfrac{2}{3}E'=\tfrac{2}{3}\frac{T}{V}-\tfrac{2}{3}\frac{T'}{f(V)};$$

where T′ denotes the entire energy of the attractive waves that occupy at any instant a hemisphere described around O with the radius 1. It may be shown that unless the number of atmospheres of pressure be great, $f(V)=\text{const.}\,(V)^{\frac{3}{2}}$, approximately. This expression for P is, essentially, the counterpart to the value of p given in the equation of Clausius (p. 441). The first term is directly proportional to the coefficient of repulsion, m, and so to the temperature reckoned from the absolute zero; and inversely proportional to the volume, V, occupied by a given number of ultimate molecules, N. The other term varies from one gas to another proportionally to the coefficient of attraction, n, and varies for the same gas with the volume occupied by the same number of molecules, N; but does not change with the temperature, except as the volume may vary with the temperature, and the value of n also. In view of the result of this investigation it is hardly necessary to add that all the objections which have been urged against the doctrine that the elastic pressure of a gas is due to statical molecular repulsion are entirely inapplicable to the present theory.

For calculating the gaseous pressure in atmospheres I obtain the formula

$$P_{,}\overset{\text{atmos.}}{=1}\times q\left\{1-\frac{kq\left(3+\frac{236}{q^{\frac{1}{2}}}\right)}{13{,}924\left(1+\frac{q^{\frac{1}{2}}}{118}\right)^{2}\left(1+\frac{q^{\frac{1}{2}}}{59}\right)^{2}}\right\}\left(\frac{288^{\cdot\circ}5+t^{\circ}}{288^{\cdot\circ}5}\right)$$

in which $\frac{1}{q}$ = ratio of the volume, in the case of an ideal gas for which $k=0$ and $\frac{m}{x^2}\div\frac{m'}{x'^3}$, answering to the assumed value of u, to the volume at the pressure of one atmosphere, and the mean temperature, 15°·5 C., occupied by the same number of molecules; t° = temperature above the mean taken as a zero point, k = ratio of coefficients of attraction and repulsion, as before, for the gas and temperature considered. The value of k varies with the temperature. We have already seen (p. 439) that for a certain mixture of oxygen and hydrogen its estimated value is about $2\frac{1}{8}$; and that for carbon-dioxide it is 3·17, when the gas is in the condition and at the temperature referred to on page 438, and increases as the temperature falls, to 4·93 at about the temperature, $-80°$ C. At the critical temperature 30·°9 C., its value is 4·7.

The approximate value of k for any gas at any temperature may be readily obtained, for any other temperature for the same gas, by the empirical law that it is inversely proportional to the $\frac{1}{10}$ power of the absolute temperature. It is to be understood that the calculations are for the value of k at the maximum tension of the gas (vapor) at the temperature considered.

In the liquefaction of oxygen, hydrogen, and nitrogen, when the point of liquefaction, so styled, was reached, the distance, x, between the molecules, must have been reduced to $3{\cdot}5r$, or very nearly this. This distance answers to the point of ebullition of gases whose molecular curve lies just above the critical curve (for which $k=4{\cdot}7$). By specific heat ratios we obtain for oxygen, $k=4{\cdot}93\times\frac{0{\cdot}9765}{1{\cdot}96}=2{\cdot}456$. The reduction of temperature from 15·°5 C. to 145·°5 C. should materially augment this deduced value of k. If we assume that the empirical law holds for oxygen, as for carbonic acid, that k is inversely proportional to the $\frac{1}{10}$ power of the absolute temperature, we obtain $k=2{\cdot}64$. Now taking $u=3{\cdot}5$, I find $q=1156{\cdot}2$. Taking this value of q, and $k=2{\cdot}64$, the formula gives $P_{,}=272{\cdot}5$ atmospheres. The volume ratio for the actual gas, for which $k=2{\cdot}64$, I find to be $\frac{1}{650{\cdot}9}$. This gives for the density of the condensed gas, 0·881 the maximum density of water; on the hypothesis that the dimensions of the molecules are unaffected by the reduction of temperature. But theoretically this should be attended with a contraction of the effective molecules. If we assume the law of the consequent diminution in the volume of the gas to be the same as that of the increase of k from a fall of temperature, the density comes out 0·94. According to Professor Pictet's experimental determinations the elastic pressure of the condensed oxygen was 273 atmospheres; and the density 0·98.

If we suppose the original value of k (2·456) to remain unchanged and take $u=3{\cdot}5$, the formula gives $P_{,}=285$ atmospheres; and the density comes out 0·936, and after correction for temperature, 1·00. For $k=2{\cdot}6$, and $u=3{\cdot}5$, $P_{,}=277$ atmospheres; and the density is 0·91, or 0·975. For $k=2{\cdot}63$, and $u=3{\cdot}5$, $P_{,}=273{\cdot}6$ atmospheres; and the density is 0·888, or 0·952.

At the point of incipient condensation of carbon-dioxide, just below the "critical temperature" (31° C.), for which $x=7\cdot3r$ I find $q=271\cdot14$. With this value of q, and $k=4\cdot7$ I obtain $P_1=72\cdot2$ atmospheres. Dr. Andrews found the elastic pressure at the critical point to be 75 atmospheres. The small discrepancy results from the fact that the precise critical curve is slightly below that for $k=4\cdot7$, and the corresponding molecular repulsion is greater in the ratio of 51, or 52, to 40. Making the correction, we have for P_1 75 or 76 atmospheres.

These two examples must suffice for the present as illustrations of the applicability of the formula, and verifications of its accuracy.

From the point of view I have taken, chemical combinations consist, essentially, in changes effected in the condition of the molecules of the constituents, by which they are brought into approximate correspondence, and take up the relative positions suited to that uniform condition, just as a mass of similar molecules in that state would do. The change of state consists simply in the nearer approach of the envelopes to the central atoms of the molecules, or in a recess from them, from which results a change in the value of the ratio k, and in the corresponding curve of effective action. The determining cause of this change is the difference in the mechanical condition of the dissimilar molecules, more or less enhanced by the unequal operation of heat or electricity. The immediate result may be either an expansion of the one molecular envelope and collapse of the other, or a collapse of both incited by a flow of electric ether from the source of heat or electricity. The union of chlorine with hydrogen may be cited as a probable instance of the former, and the combustion of hydrogen as an instance of the latter. When metals are oxidized, or solids undergo combustion, we must suppose there is a flow of electric ether from the solid to the oxygen molecule, and the former molecule expands somewhat while the other contracts to the dimensions answering to the solid condition.

Heat, in its association with molecules, consists of the energy of recurring pulses and vibrations in the molecular envelopes, and has two modes of motion or two dynamical aspects, *radial* and *tangential.* The energy connected with the former, is the origin of its expansive force. The propagation of the latter, in ethereal waves of transverse vibration, constitutes the radiant heat emitted by bodies.

Heat energy may be expended not only in the expansion of bodies, but also in augmenting the potential energy of the individual molecules by enlarging their envelopes. In this way a certain amount of heat becomes latent in the process of liquefaction. A portion of the heat of vaporization is expended in a similar manner. The enlargement of the envelopes here alluded to consists in a recess of the effective envelopes from the central atoms. This should be attended with a certain diminution in the value of r, the distance between the centers of attraction and repulsion posited within the envelopes; and therefore with an increase in the value of $p\left(=\frac{m}{r^2}\right)$. In fact the quantitive determinations I have given, when compared with the results of experiment, indicate that p is materially larger at the same temperature, for liquids and aeriform bodies than for solids. An important tendency of the diminution of the value of r in liquefaction, is to antagonize the expansion directly due to the enlargement of the effective molecules and the attendant diminution in the coefficient n. According as the one or the other of these two tendencies preponderates, the mass will expand, or contract in the act of liquefaction. In the case of any special solid or liquid, the diminution of r with a rise of temperature tends to diminish the expansion, and by increasing p to make the decrement of tenacity less. Any differences in the value of r that may subsist with molecules of different substances, at the same temperature, can only have the effect to alter the positions of the substances on the molecular scale. Any changes or differences that may occur in the value of r, in the case of the gases, will have no effect on the molecular repulsion at those distances, x, for which F, in equ. 1, is sensibly equal to the second term, and therefore, as we have seen, the law of Mariotte holds good; since the repulsion will still be the same for the same actual distance between the molecules. At less distances the tendency should be to alter slightly the deviations from this law.

The value of the coefficient of attraction, n, depends on the excess of the attraction exerted by the central atom of a molecule on its envelope, over the repulsion exerted on it by the condensed luminiferous ether posited between the atom and envelope. The tendency of a recess of the envelope from the atom may be either to diminish, or augment the value of n. It thus may happen that by an increase of n, and a diminution of r, the value of F may be augmented by a certain rise of temperature; as when a bar of wrought iron is heated up to about 400° F. In the case of gases n may change somewhat with the temperature, and in the process of condensation.

The normal type of solidity is a fixed distribution of the ultimate molecules at the angles of successive cubes; and the fundamental principle of the stability of every such elementary cube is that each molecule is in equilibrium, by itself, with each of the others. As the distances are unequal, this implies that k is smaller in the diagonal direction than in the direction of the sides; and thus that the extension, or physical condition of the envelope is unequal in these directions. It is in this sense that "polarity of atoms" (ultimate molecules) exists. Instead of being an inherent property of the atoms, it is liable to change with varying relations to other molecules. When the mass varies in density from one point to another, there is a gradual variation in the size of the elementary cubes, or a gradual transition from cubes to parallelopipedons, or other geometrical figures, with attendant variations in the curves of effective molecular action. The molecular envelopes of different substances may be liable to different varieties of polar condition under the same circumstances, and so the substances may have different types of solidification, or crystallization. For the cubical system I obtain as the complete expression for the elastic resistance to a minute displacement of a single molecule, $f+2f'+1\frac{1}{3}f''$; in which f is the force of resistance developed between the displaced molecule and that lying in the direction of the side of the cube, by a displacement s, in this direction; f' the force of resistance of a molecule lying in the direction of a face diagonal, for the same displacement s, in this direction; and f'' the corresponding resistance of a molecule in the direction of the long diagonal. The value of the expression is the same in whatever direction the displacement occurs. The expression for the lateral force developed, as well as for the elastic resistance to shearing, in the direction of a side of the cube is $f'+1\frac{1}{3}f''$. For any reasonable suppositions that can be made with regard to the comparative values of f, f', and f'', the ratio of these two expressions lies between $\frac{1}{2}$ and $\frac{1}{4}$. The experimental ratios fall between these limits. The resistance to shearing is due to the diagonal forces.

When a body is heated to the point of liquefaction, the values of f' and f'', considered as resistances to tension, which are always less than f, vanish (that is, the curves fall below the axis of x). There is therefore no shearing resistance; which is one of the distinguishing features of a liquid. When the temperature of the liquid is raised above the point of liquefaction, effective repulsions must come into play in the diagonal directions. These repulsions are the operative cause of surface evaporation; and at the same time originate at the surface the "contractile force" which, by the variations it experiences from the contact of solids, is the determining cause of capillary phenomena.

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