I. The attraction of unlike molecules.—I. The Diffusion of gases

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I. The Attraction of Unlike Molecules.—I. The Diffusion of Gases. By William Sutherland.*

In my previous papers on the laws of molecular force the attractions of like molecules have been under consideration, and the results seemed to indicate that the laws of the attractions of unlike molecules would not be difficult to ascertain. With the hope of determining the general law of attraction of any two molecules, I adopted two methods as being at present available for giving values of the attractions of unlike molecules, namely, that of the Diffusion of Gases and that of the Surface-Tension of Mixed Liquids. Both methods have led to the same result, viz., that if the attraction between two molecules \( M_1 \) of mass \( m_1 \) at distance \( r \) apart be denoted by \( 3A_1m_1^2/r^4 \), and that between two molecules \( M_2 \) by \( 3A_2m_2^2/r^4 \), then the attraction between an \( M_1 \) and an \( M_2 \) is

\[
3 \sqrt{A_1A_2}m_1m_2/r^4,
\]

or the attraction of two unlike molecules is equal to the square root of the product of the attractions of the corresponding like molecules at the same distance apart. As the expression \( 3A_1m_1^2 \) for two like molecules can be split into two parts \( \sqrt{3A_1m_1^2} \), the general law of the attraction of any two molecules, like or unlike, can be stated thus:—Any two molecules attract one another with a force inversely proportional to the fourth power of the distance between them.

* Communicated by the Author.

Mr. William Sutherland on the

and directly proportional to the product of the parameters \(\sqrt{3\lambda m}\) characteristic of each. Although the parameter is written in the form \(\sqrt{3\lambda m}\) apparently involving the mass \(m\) it will be shown that \(\sqrt{3\lambda m}\) is independent of the mass \(m\) but is a function of the size of the molecule; it would therefore be better denoted by a single symbol \(\alpha\), so that the attraction between any two molecules \(M_1\) and \(M_2\) is \(a_1a_2/r^4\), or between two \(M_1\) is \(a_1^2/r^4\), the parameter \(\alpha\) being a function of the size of the molecule but not directly of its mass. Thus, with \(Gm_1m_2/r^3\) to denote the gravitational attraction of two molecules \(M_1\) and \(M_2\), the general expression for the force between them is

\[
Gm_1m_2/r^3 + a_1a_2/r^4.
\]

The dependence of the coefficient of diffusion of two gases on the attraction between their molecules was indicated in general terms in a recent paper on the Viscosity of Gases and Molecular Force (Phil. Mag., Dec. 1893). In that paper it was shown that in those parts of the kinetic theory of gases which depend on the number of encounters of a molecule per second (or, in other words, on its mean free path), the effect of molecular force cannot be neglected as of only secondary importance; it is fundamental. Thus the complete expression for the coefficient of diffusion of two gases will involve the attractions between their molecules in a manner now to be established; but as the kinetic theory of the diffusion of gases, even when simplified by treating the molecules as forceless, is in a little confusion (there being at least three forms of expression for the diffusion-coefficient in the field), it may be desirable to recapitulate briefly the theories of the diffusion of forceless molecules from the three points of view.

The first in time is that of Stefan, accepted by Maxwell; the second is O. E. Meyer's, given in his book on the 'Kinetic Theory of Gases;' and the third is that of Tait (Trans. Roy. Soc. Edin. xxxiii.), who has treated the diffusion of gases rather elaborately.

Stefan's theory is this:—If two gases are diffusing into one another, then at any point one has a general velocity \(\alpha_1\) in one direction, and the other a velocity \(\alpha_2\) in the other, the density of the first diminishes in the direction of \(\alpha_1\), of the second in that of \(\alpha_2\). Consider, then, an element of the first of section unity and length \(\delta x\) in the direction of \(\alpha_1\): the partial pressure due to its molecules at one end is \(p_1\), and at the other \(p_1 + \delta x dp_1/dx\), so that there is a driving pressure \(\delta x dp_1/dx\) which is resisted by a resistance like friction offered by the other gas in the length \(\delta x\), which may be denoted by
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$R \delta x$, and then any acceleration of the element of the first gas is due to the force $\delta x \left( \frac{dp_1}{dx} - R \right)$, but this acceleration can be neglected in comparison with either $\delta x \frac{d}{dx} \frac{dp_1}{dx}$ or $R \delta x$, and we have

$$R = \frac{dp_1}{dx}. \quad \ldots \quad \ldots \quad (1)$$

$R$ has now to be evaluated; it is the resistance offered by the molecules of the two sets in unit volume at $x$ to one another’s motion. Let $\nu$ be the number of encounters per second between $n_1$ molecules of the first set in unit volume and $n_2$ of the second, and let $\mu$ be the average value of the momentum communicated when a molecule of the first set with velocity $a_1$ collides with one of the second with velocity $a_2$ in the opposite direction, then

$$R = \nu \mu.$$

If $a_1$ and $a_2$ are the radii of the molecules of the two sets treated as spheres, and $3\kappa_1^2/2$ and $3\kappa_2^2/2$ are their mean square velocities, then (see for instance Tait, Trans. Roy. Soc. Edin. xxxii.)

$$\nu = 2n_1n_2(a_1 + a_2)^2\pi^\frac{3}{2}(\kappa_1^2 + \kappa_2^2)^\frac{3}{2},$$

$$\mu = \frac{2}{3} \frac{m_1m_2}{m_1 + m_2}(a_1 + a_2).$$

Now in diffusion the pressure remains constant, so that as many molecules of one sort pass in one direction as of the other in the other, or $n_1a_1 = n_2a_2$, and accordingly

$$R = \frac{4}{3} n_1n_2(a_1 + a_2)^2\pi^\frac{3}{2}(\kappa_1^2 + \kappa_2^2)^\frac{3}{2}a_1 \left(1 + \frac{n_1}{n_2}\right) \frac{m_1m_2}{m_1 + m_2}; \quad (2)$$

but $n_1m_1 = \rho_1$, the density of the first gas, and

$$\rho_1a_1 = \frac{\frac{dp_1}{dx} \kappa_1^2}{8 (\kappa_1^2 + \kappa_2^2)^\frac{3}{2}} \frac{m_1 + m_2}{m_2} \frac{1}{\pi^\frac{3}{2}(a_1 + a_2)^2(n_1 + n_2)}. \quad (3)$$

The coefficient of $\frac{dp_1}{dx}$ is by definition the coefficient of diffusion $D$; remembering that $\kappa_1^2/\kappa_2^2 = m_2/m_1$, we get

$$D = \frac{3}{8} \kappa_1 \left(\frac{m_1 + m_2}{m_2}\right)^\frac{3}{2} \frac{1}{\pi^\frac{3}{2}(a_1 + a_2)^2(n_1 + n_2)}. \quad (4)$$

Meyer’s method of proceeding is quite different. He says that as the density of one of the diffusing gases diminishes in one direction, then, if a plane is drawn anywhere at right angles to this direction, the density increases on one side and diminishes on the other, so that more molecules cross the
plane from the side of increasing density than from that of decreasing density, and diffusion results. Thus if \( n_1 \) is the number of molecules per unit volume at the plane, that at a small distance \( x \) from it will be \( n_1 + xdn_1/dx \). The number of molecules leaving an element \( dx \) after encounter in it to cross the plane before the next encounter must be proportional to \( n_1 + xdn_1/dx \), to \( dx \), to the mean number of collisions per second \( v_1/\lambda_1 \), where \( \lambda_1 \) is the mean free path of the molecules of the first set near \( x \), and finally to \( e^{-x/\lambda_1} \), the probability of a path greater than \( x \), so that the number of molecules of the first set which cross the plane from one side in unit time is proportional to

\[
\int_0^x v_1(n_1 + xdn_1/dx)e^{-x/\lambda_1} \, dx/\lambda_1
\]

(although \( x \) was stipulated to be small to justify the expression \( n_1 + xdn_1/dx \), no harm can come of integrating to \( \infty \), because the value of the integral becomes negligible for all values of \( x \) greater than a few times \( \lambda_1 \)). The number of molecules crossing from the other side is proportional to

\[
\int_0^x v_1(n_1 - xdn_1/dx)e^{-x/\lambda_1} \, dx/\lambda_1
\]

so that the excess accumulating in unit time on one side is proportional to

\[
2v_1 \int_0^x xe^{-x/\lambda_1} \, dx \, dn_1/dx \lambda_1,
\]

that is to \( 2v_1 \lambda_1 dn_1/dx \). The number of molecules of the other set crossing in the opposite direction is proportional to \( 2v_2 \lambda_2 dn_2/dx \). As these two expressions are not equal, there is a gain of molecules on one side of the plane and a loss on the other proportional to

\[
2(v_1 \lambda_1 dn_1/dx - v_2 \lambda_2 dn_2/dx);\]

and to preserve the uniformity of pressure Meyer supposes a bodily motion of the mixed gases to take place so as to carry this number of molecules in the opposite direction, of which the fraction \( n_1/(n_1 + n_2) \) belongs to the first set and \( n_2/(n_1 + n_2) \) to the second; thus the diffusion-stream of the first gas is proportional to

\[
2v_1 \lambda_1 \frac{dn_1}{dx} - \frac{2n_1}{n_1 + n_2} \left( \frac{v_1 \lambda_1}{dx} dn_1 + \frac{v_2 \lambda_2}{dx} dn_2 \right),
\]

that of the other being equal and opposite. On account of the uniformity of pressure, \( dn_1/dx = dn_2/dx \) and the diffusion-streams...
stream is proportional to
\[ \frac{2d n_1 n_2 \bar{v}_1 \lambda_1 + n_1 \bar{v}_2 \lambda_2}{n_1 + n_2}, \]
and the diffusion-coefficient to
\[ \frac{(n_2 \bar{v}_1 \lambda_1 + n_1 \bar{v}_2 \lambda_2)}{(n_1 + n_2)}. \]

The defect of Meyer's theory is that it takes no account of the actually existing diffusion velocities in the two sets. Supposing the process of diffusion to be arrested suddenly by some cause which then suddenly ceases to act, Meyer's method shows how the diffusion-streams would begin to flow again, but it cannot follow the process after that, because it takes no cognizance of the bodily motions existing in the two sets.

Tait's theory takes account of both Stefan's and Meyer's causes; he supposes the molecules of each medium besides their velocities of agitation to have velocities of translation en masse \( \alpha_1 \) and \( \alpha_2 \), and then calculates the quantities of each flowing in unit time across unit section, these quantities depending on \( \alpha_1 \) and \( \alpha_2 \) and on expressions similar to Meyer's. The velocities \( \alpha_1 \) and \( \alpha_2 \) are determined exactly as in Stefan's method, so that Tait's method labours under this difficulty, that he supposes each molecule of each set to have a certain velocity combined with the velocity of agitation, and yet this velocity is different from that of the set as a whole.

On theoretical grounds, therefore, Stefan's theory appears not to have been improved by the later attempts, and, further, it seems to me not to have been sufficiently recognized that Stefan has given satisfactory experimental proof of the soundness of his method of treating the diffusion problem; for exactly on the lines of his theory of the diffusion of two gases into one another he constructed a theory of the evaporation of a liquid into a gas, which led to a striking formula for the velocity of evaporation of a liquid, a formula verified by his own and Winkelmann's experiments. As Stefan's elegant theory of evaporation will only take a few lines to reproduce here, and as it gives a valuable method of determining diffusion-coefficients, it may as well be reproduced in the present connexion.

Suppose a tube half filled with a liquid whose properties are to be denoted by suffix 1 evaporating into an atmosphere with suffix 2, but with fresh liquid added from below so as always to keep the free surface of the liquid at a fixed mark on the tube; then, when a stationary state is established, there is a steady diffusion-stream of the vapour through the upper
half of the tube while the gas in the tube is at rest. Thus, in
Stefan's theory of diffusion already given, we have only
to put \( \alpha_2 = 0 \) and we can proceed at once to calculate the
velocity of evaporation in terms of the coefficient of diffusion.
In the expression (2) for \( R \), \( \alpha_1(1 + n_1/n_2) \) stands for \( \alpha_1 + \alpha_2 \), so
that if \( \alpha_2 = 0 \) the term \( n_1/n_2 \) in \( R \) drops out, and the equations
(3) and (4), which can be written \( \rho_1 \alpha_1 = D \frac{dp_1}{dx} \), will in the
case of evaporation have to be written
\[
\rho_1 \alpha_1 = D \frac{dp_1}{dx} \frac{n_1 + n_2}{n_2}.
\]

Let \( p_1 \) and \( p_2 \) be the partial pressures of vapour and gas, and
\( \rho \) the total pressure \( p_1 + p_2 \) at which the evaporation is going
on, then \( (n_1 + n_2)/n_2 = p/p_2 \); and if \( \rho \) is the density of the
vapour under some standard pressure \( P \), then \( p_1 \) can be taken
as equal to \( \rho p_1/P \) if the departure from Boyle's law is not
too great, and then the last equation becomes
\[
\frac{\rho_1 \alpha_1}{\rho p} = \frac{D \rho p}{P(p - p_1)} \frac{dp_1}{dx} \frac{d}{dx} \log \left( \frac{p}{p_1} \right);
\]
but \( \rho_1 \alpha_1 \) is the mass of vapour that crosses each unit section
of the tube in unit time, and in the steady state is constant:
therefore \( d \log \left( \frac{p}{p_1} \right)/dx \) is constant. Let \( h \) be the distance
of the liquid surface below the open end of the tube, where
\( p_1 \) is 0 while at the liquid surface it is \( p_s \) the saturation-
pressure of the liquid at the temperature of the experiment,
then
\[
d \log \left( \frac{p}{p_1} \right)/dx = \frac{\log p - \log (p - p_s)}{h},
\]
and the law of evaporation for a liquid whose surface is kept
at distance \( h \) below the open end of a tube is
\[
\rho_1 \alpha_1 = \frac{D \rho p}{P h} \log \frac{p}{p - p_s}.
\]

If the level of the liquid is not kept constant in the tube,
but is allowed to fall as the liquid evaporates, then, as \( \rho_1 \alpha_1 \) is the
mass which evaporates in unit time, if \( \sigma \) is the density of
the liquid and \( dh/dt \) the velocity with which the surface of
the liquid falls, \( \rho_1 \alpha_1 = \sigma dh/dt \), and then
\[
\begin{align*}
hdh &= D \frac{\rho p}{\sigma P} dt \log \frac{p}{p - p_s}, \\
\frac{1}{2}(h^2 - h_0^2) &= (t_1 - t_0) D \frac{\rho p}{\sigma P} \log \frac{p}{p - p_s}
\end{align*}
\]
This is Stefan's expression \( \text{(Sitz. Akad. Wien, lxviii. 1873)} \).
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In the case where the level of the liquid is allowed to fall the velocity of the gas is not exactly 0, and in a later paper (Sitz. Akad. Wien, xviii. 1890) Stefan has given a calculation wherein the small value of $\varepsilon$ is taken account of. By very simple experiments on the evaporation of ethyl oxide and carbon disulphide in test-tubes, Stefan verified his expression first as regards the relation of $h$ and $t$ at constant temperature, that is at constant $p_{n}$, and then as regards the very characteristic factor $\log \frac{p}{(p-p_{s})}$ in which the saturation-pressure enters, by studying the evaporation of ethyl oxide at temperatures ranging from 11°C. to 28°C., where the range in the saturation-pressure $p_{s}$ is from 302 millim. of mercury to 605.

Winkelmann has still more thoroughly verified Stefan's evaporation theory in applying it in an extended series of experiments to the determination of the diffusion-coefficients of a number of vapours into air, hydrogen, and carbon dioxide (Wied. Ann. xxii., xxiii., xxxiii., xxxvi.). As regards the formula (5) the most important part of Winkelmann's work is his further verification of the soundness of the factor $\log \frac{p}{(p-p_{s})}$ by varying $p$ in the case of water from 61 millim. to 749, while $p_{s}$ was about 1.5 millim.

The correctness of Stefan's formula (4) for the diffusion of gases composed of forceless molecules seems to me therefore to be well assured by the successful application of the principles involved in it to the details of the process of evaporation; and the foregoing brief sketch of his theory serves as the most natural introduction to a theory of gaseous diffusion wherein the attractions of molecules are taken account of.

Let us first see wherein the expression

$$D = \left( \frac{m_1 + m_2}{m_2} \right) \frac{3 \kappa_1}{8 \pi^2 (a_1 + a_2)^2 (n_1 + n_2)}$$

for the diffusion-coefficient of forceless molecules applies to natural gases and wherein it fails to apply. As $m_1 \kappa_1^2$ is proportional to absolute temperature $T$, and $n_1 + n_2$ is proportional to $p/T$, where $p$ is the pressure at which the diffusion goes on,

$$D \propto \frac{\frac{1}{m_1} + \frac{1}{m_2}}{p} \left( \frac{1}{a_1 + a_2} \right)^2 \cdot \cdot \cdot \cdot (6)$$

Thus the theoretical diffusion-coefficient varies inversely as the pressure, which has been proved experimentally by Loschmidt to be the case for the natural gases (Sitz. Akad.
Mr. William Sutherland on the Wien (lxii. 1871). The theoretical coefficient also varies as the \( \delta/2 \) power of the absolute temperature, but it has been shown by Loschmidt and Obermayer (Sitz. Akad. Wien, lxii., lxxvi., lxxxvii., xcvii.), in experiments on several pairs of gases, that their coefficients of diffusion vary more rapidly with temperature than according to the theoretical law. They found empirically that the coefficients vary as powers of the temperature, ranging from 1.75 to 2 instead of the 1.5 of the theory of forceless molecules. Here is where the effect of molecular force comes in, just as in the case of viscosity.

In connexion with viscosity it was shown that with like molecules the effect of molecular force on the number of collisions of spherical molecules of radius \( a \) is to make it the same as for forceless molecules in which \( (2a)^2 \) is increased to \( (2a)^2(1 + 2m/f(1/2a)/\sqrt{V}) \), where \( m^2f(1/2a) \) is the potential energy of two molecules in contact, and \( \sqrt{V} \) is the mean square of the relative velocity. So for unlike molecules of masses \( m_1 \) and \( m_2 \) and radii \( a_1 \) and \( a_2 \), with potential energy \( m_1m_2f(1/a_1 + a_2) \) at contact and mean relative squared velocity \( \sqrt{V} \), the effect of molecular force on the number of collisions is to make it the same as for a pair of forceless spheres with \( (a_1 + a_2)^2 \) enlarged in the ratio

\[
\left\{1 + (m_1 + m_2)f(1/a_1 + a_2)/\sqrt{V}\right\}.
\]

Now \( v_1^2 \) and \( v_2^2 \) denoting the mean squared velocities of \( m_1 \) and \( m_2 \),

\[
\sqrt{V} = v_1^2 + v_2^2 = \frac{3}{2}(\kappa_1^2 + \kappa_2^2),
\]

and

\[
\kappa_1^2 + \kappa_2^2 = \kappa_1^2(1 + \kappa_2^2/\kappa_1^2) = \kappa_1^2(1 + m_1/m_2),
\]

so that the ratio becomes

\[
1 + m_1m_2f(1/a_1 + a_2)/3m_1\kappa_1^2,
\]

or

\[
1 + m_1m_2f(1/a_1 + a_2)/m_1v_1^2,
\]

which may be written

\[
1 + C_2/T,
\]

and then the expression for the diffusion-coefficient of attracting molecules derived from (6) for forceless molecules is

\[
D \propto \frac{1}{p} \left( \frac{1}{m_1} + \frac{1}{m_2} \right)^{\frac{1}{2}} \left\{ \frac{1}{(a_1 + a_2)^2(1 + 1C_2/T)} \right\} \cdot \cdots \cdot (7)
\]

As the diffusion-coefficients are all referred to a pressure of one atmosphere, we have for the ratio of \( D_2 \) at \( T_2 \) to \( D_1 \) at \( T_1 \),

\[
\frac{D_2}{D_1} = \left( \frac{T_2}{T_1} \right)^{\frac{1}{2}} \frac{1 + 1C_2/T_1}{1 + 1C_2/T_2} \cdot \cdots \cdot \cdots \cdot (8)
\]
The experimental determinations for any one pair of gases are not numerous enough, or at widely enough separated temperatures, to test this theoretical relation between $D$ and $T$, but as the corresponding relation in viscosity has been verified experimentally over a temperature range of 1400 degrees, it is not necessary to have such verification here before proceeding. From a single determination of the ratio of $D_2$ to $D_1$ at any two temperatures $T_2$ and $T_1$ we can calculate from (8) a value of $\frac{1}{C_2}$ which is a measure of the potential energy of molecules 1 and 2 in contact. Loschmidt was the first to measure diffusion-coefficients at one, or at different temperatures, but as von Obermayer’s results are later and more elaborately determined it will suffice to use them. He has measured the diffusion-coefficients of six pairs of gases at ordinary temperatures, and at 61° C. (Sitz. Akad. Wien, lxxxi.), namely, those of carbon dioxide with air, hydrogen, and nitrogen monoxide $N_2O$, and those of oxygen with hydrogen, nitrogen, and carbonic oxide. In the following table are given for each pair of gases the two temperatures of v. Obermayer’s experiments, the values of the diffusion-coefficients at these temperatures, and the values of $\frac{1}{C_2}$ for each pair calculated therefrom. The diffusion-coefficients are given in terms of the centimetre and second as units, and are the volumes of the gases in cub. centim. measured at the temperature of the experiment and at a pressure of 1 atmosphere which pass in one second in a diffusion-stream where the fall of the partial pressure of each gas is 1 atmosphere in 1 centimetre:

<table>
<thead>
<tr>
<th>Pair of Gases</th>
<th>T</th>
<th>D</th>
<th>$\frac{1}{C_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2$ and Air</td>
<td>281</td>
<td>1.43</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>334.5</td>
<td>2.01</td>
<td></td>
</tr>
<tr>
<td>$CO_2$ and $H_2$</td>
<td>284</td>
<td>5.89</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td>334.5</td>
<td>7.73</td>
<td></td>
</tr>
<tr>
<td>$CO_2$ and $N_2O$</td>
<td>284</td>
<td>0.996</td>
<td>380</td>
</tr>
<tr>
<td></td>
<td>334.5</td>
<td>1.394</td>
<td></td>
</tr>
<tr>
<td>$O_2$ and $H_2$</td>
<td>286</td>
<td>7.36</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>334.5</td>
<td>9.97</td>
<td></td>
</tr>
<tr>
<td>$O_2$ and $N_2$</td>
<td>286</td>
<td>1.93</td>
<td>136</td>
</tr>
<tr>
<td></td>
<td>334.5</td>
<td>2.36</td>
<td></td>
</tr>
<tr>
<td>$O_2$ and CO</td>
<td>278</td>
<td>1.87</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>334.5</td>
<td>2.69</td>
<td></td>
</tr>
</tbody>
</table>

If the law of force is that of the inverse fourth power, or
the law of energy is that of the inverse cube, then

\[ m_1 m_2 f(1/a_1 + a_2) = m_1 m_2 \frac{A_2}{(a_1 + a_2)^3}, \]

and if we know relative values of \( a_1 \) and \( a_2 \), then \( C_5(a_1 + a_2)^3 \) will give relative values of \( A_2m_1m_2 \).

There are two sources of relative values of the molecular radii \( a_1 \) and \( a_2 \): first, the viscosity of the separate gases, and in my paper on the Viscosity of Gases and Molecular Force relative values of \((2a_1)^2\) are given as \((2a)^2\) (relative); the second source is values of \( \beta \) the limiting volume of a gramme of a substance as obtained from its characteristic equation as a liquid, and given for various substances in the papers on the "Laws of Molecular Force" (Phil. Mag., March 1893) and the "Viscosity of Gases and Molecular Force" (Phil. Mag., Dec. 1893); if \( M \) is the ordinary chemical molecular mass (weight) of the substance, then \( M\beta \) is proportional to \((2a)^3\) and \((M\beta)^{5/2}\) may be taken as giving a relative value of \( 2a \), and then \( a_1 + a_2 \) is given by \( (M\beta_1)^{5/2} + (M\beta_2)^{5/2} \).

The latter source of values of \( a \) is preferable at present, as it yields values for more substances than the former. For the gases of v. Obermayer's experiments we have the following values:

\[
\begin{array}{cccccc}
\text{gas} & H_2 & O_2 & N_2 & CO_2 & N_2O \\
\beta & 4.3 & 6.04 & 3.1 & 6.9 & 6.6 \\
M & 2 & 32 & 28 & 44 & 44 \\
(M\beta)^{5/2} & 1.025 & 1.34 & 1.415 & 1.56 & 1.535 \\
\end{array}
\]

There is no direct determination of \( \beta \) for CO, but from the molecular domains (volumes) of a number of carbon compounds I have deduced 1.35 as an approximate value of \((M\beta)^{5/2}\) for CO. With the above values we get for

\[ 10^{-1}C_5\{(M_1\beta_1)^{5/2} + (M_2\beta_2)^{5/2}\}^3 \]

the following values, which are relative values of \( A_2m_1m_2 \); air will be treated as pure \( N_2 \):

\[
\begin{array}{cccccc}
CO_2 & N_2 & CO_2 & H_2 & CO_2 & N_2O \\
O_2 & H_2 & O_2 & N_2 & O_2 & CO \\
656 & 182 & 1122 & 131 & 282 & 241 \\
\end{array}
\]

It should be noticed that these numbers show a large range of value, namely, from 131 to 1122. Now in the paper on the Viscosity of Gases and Molecular Force relative values are given for \( A_2m_1^2 \) or \( A_n^2 \), the corresponding factor in the expression for the attraction between like molecules; they are given as \( 10^{-1}M\beta C_5 \), which in the notation of this paper would be

\[ 10^{-1}C_5\{(M_1\beta_1)^{5/2} + (M_1\beta_1)^{5/2}\}^3, \]

and are now reproduced for the substances of v. Obermayer's experiments with the addition of an approximate value for CO:
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The value 68 for H\textsubscript{2} is the experimental one, which is very uncertain; the value 46 would bring H\textsubscript{2} into accord with all other bodies, as may be seen in the "Viscosity of Gases and Molecular Force."

The most natural relation to expect between \(\Delta m_1\) and \(\Delta m_2\), and \(\Delta m_3\) is

\[
(\Delta m_1)^2 (\Delta m_2)^2 = (\Delta m_3)^2,
\]

and accordingly we now give values of \(10^{-1}(M_1\beta_1C_1 M_2\beta_2C_2)\), obtained from the numbers just given, and the ratio of

\[
10^{-1}C_2\{ (M_1\beta_1)_{\frac{1}{2}} + (M_2\beta_2)_{\frac{1}{2}} \}^2 \]

given above to

\[
10^{-1}(M_1\beta_1C_1 M_2\beta_2C_2)\frac{1}{2}.
\]

The mean value of the ratio is 1.2, and the departures of some of the individual numbers from the mean, though large, are not larger than could be caused by only slight error in the experiments or the theory, for it must be remembered that the constants \(C_2\) occur in equation (8) in such a manner as to make their values when calculated from that equation very sensitive to small errors in the ratio of the diffusion-coefficients at two temperatures. Thus, notwithstanding the high degree of accuracy attained by v. Obermayer in his elaborate experiments, it must be allowed that the last series of numbers is as nearly constant as can be expected. To show this clearly it will be best to assume that the ratio is 1, and calculate \(C_2\) from the equation

\[
1C_2\{ (M_1\beta_1)_{\frac{1}{2}} + (M_2\beta_2)_{\frac{1}{2}} \}^2.
\]

and then by the equation (8) calculate values of the ratio of the diffusion-coefficients at v. Obermayer’s two temperatures for comparison with his experimental values:—

<table>
<thead>
<tr>
<th></th>
<th>CO\textsubscript{2} &amp; N\textsubscript{2}</th>
<th>CO\textsubscript{2} &amp; H\textsubscript{2}</th>
<th>CO\textsubscript{2} &amp; N\textsubscript{2}O</th>
<th>O\textsubscript{2} &amp; N\textsubscript{2}</th>
<th>O\textsubscript{2} &amp; CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exper. ....</td>
<td>1.41</td>
<td>1.33</td>
<td>1.49</td>
<td>1.31</td>
<td>1.32</td>
</tr>
<tr>
<td>Theory...</td>
<td>1.38</td>
<td>1.34</td>
<td>1.38</td>
<td>1.31</td>
<td>1.32</td>
</tr>
</tbody>
</table>

The largest discrepancy between theory and experiment amounts to 2 per cent., and it cannot be claimed that the ratio of the diffusion-coefficients at two temperatures, as measured experimentally, can be guaranteed correct to within 2 per cent., especially as the experimental measurements only
yield values of the diffusion-coefficients by the intervention of quite an elaborate theory of the experiment.

The outcome of the investigation so far, then, is that v. Obermayer's experiments (in continuation of Loschmidt's) on the temperature variation of diffusion establish at least the approximate truth of the law that the parameter \( \frac{1}{2} A_1 m_1 m_2 \) in the attraction of two unlike molecules of masses \( m_1 \) and \( m_2 \) is equal to the square root of the product of the parameters \( \frac{1}{2} A_1 m_1^2 \) and \( \frac{1}{2} A_2 m_2^2 \) for the like molecules. To test the truth of the law in an independent manner, some experiments have been carried out on the surface-tension of mixed liquids and will be described in another paper.

Meanwhile there is interesting matter to discuss in connexion with diffusion. It can be seen how desirable are experiments on the temperature variation of the diffusion-coefficients of many more pairs of gases. This variation could be prophesied for a large number of pairs of gases by calculating \( C_2 \) according to equation (9), using therein the values of \( \beta \) and \( C_1 \) given in the paper on the Viscosity of Gases and Molecular Force, but the calculations would possess more interest if carried out in connexion with the experiments than at present. However, as the diffusion-coefficients of many more pairs of gases have already been determined experimentally at one temperature, it seems at first sight to be possible to determine the corresponding values of \( C_2 \) from them in the following manner. Let us write our relation (7) in the form

\[
D = B T \left( \frac{1}{M_1 \beta_1} + \frac{1}{M_2 \beta_2} \right)^{\frac{1}{2}} \left\{ \left( M_1 \beta_1 \right)^{\frac{1}{2}} + \left( M_2 \beta_2 \right)^{\frac{1}{2}} \right\}^{\frac{1}{2}} \left( 1 + \frac{C_2}{T} \right), \tag{10}
\]

where \( B \) is a constant the same for all pairs, then for the six pairs of gases already studied, as we know all the variables, we can obtain values of \( B \) which ought to be all nearly the same. But when the calculation is made, using the lower value of \( T \) in each of v. Obermayer's experiments, which is about 284, it is found that \( B \), instead of being constant, is closely proportional to \( 1 + \frac{C_2}{T} \), as the following values show:

\[
\begin{array}{cccccc}
\text{CO}_2 & \text{N}_2 & \text{CO}_2 & \text{H}_2 & \text{CO}_2 & \text{N}_2 & \text{O}_2 & \text{H}_2 & \text{O}_2 & \text{N}_2 & \text{O}_2 & \text{CO} \\
10^6 B & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
2.09 & 1.53 & 2.19 & 1.58 & 1.73 & 1.69 & 1.11 & 1.12 & .94 & 1.17 & 1.17 & 1.16
\end{array}
\]

This curious result has some interesting bearings. In the first place, it means that the diffusion-coefficients of actual gases at temperatures about 284 absolute are related to one another almost as if the molecules were forceless spheres, and this explains why the investigators of
Attraction of Unlike Molecules.

diffusion have hitherto found fair agreement between the results of experiment at ordinary temperatures and the kinetic theory of forceless perfectly restitutional spherical molecules. The immediate effect of the result on our present inquiry is to render illusory the hope of obtaining values of $\alpha$ for the various pairs of gases for which Loschmidt and v. Obermayer have found values of the diffusion-coefficient at only one temperature near 284, for as regards these values we have just seen that the molecules behave almost as if forceless. It may be suggested that the failure of B to prove constant is due to inadequacy of Stefan's theory of diffusion, but the expressions for the diffusion-coefficient given by Meyer and Tait gave on trial about the same results as Stefan's; so that the failure of B to prove constant is not due to any peculiarity of Stefan's theory. We have to go deeper for the reason, and in doing so have to open up a very important department of molecular dynamics of which at present we know but little, namely, the nature of collisions between molecules. Hitherto in the kinetic theory it has been assumed that the forces called into play during the collision of two molecules are such as they would be if the molecules were perfectly restitutional spheres, and the assumption seems to have worked well as regards the general phenomena of gases; but in reality it was not required there, and could be replaced by the assumption that the translatory kinetic energy of a number of molecules is a constant fraction of their total kinetic energy. The usual assumption of perfect restitutionality causes no difficulty in connexion with the theory of the viscosity of a single gas, because the nature of the collisional forces between molecules is not directly involved in that theory; but in the theory of diffusion, as well as in that of the characteristic equation of the element gases, the forces involved in collision enter as an essential element of the calculation. Now in the paper on the Viscosity of Gases and Molecular Force, in connexion with the theory of the characteristic equation of the element gases, just such a discrepancy as we have encountered in diffusion cropped up between the behaviour of actual gases and the theory of a medium composed of attracting perfectly restitutional spheres; and it was pointed out that in some way, which at present must be called accidental, the departure from perfect restitutionality in the collisions compensated for a certain effect of molecular attraction in such a way as to make the molecules behave in one respect as if they were forceless. It seems desirable, therefore, to bring out clearly the parallelism of the two cases.

In the theoretical characteristic equation of a medium
made of attracting smooth perfectly restitutional spheres, one term is the virial of the collisional forces of all the spheres in unit mass which takes the form $\Sigma a\mu v/2$ (see Viscosity of Gases and Molecular Force), where $a$ is the radius of a sphere, $\mu$ the average momentum imparted to a sphere in a collision, and $v$ the average number of collisions per sphere per second, the summation to extend to all spheres in unit mass. This is closely similar to the expression which comes in in diffusion for the resistance experienced by one medium in passing through another, and which was written $\mu v$. In the virial expression $\mu$ is momentum due to velocity of agitation, while in the diffusion resistance $\mu$ is the momentum due to relative motion of the two media, which is very slow compared to the velocities of agitation. In the diffusion resistance $v$ denotes the number of collisions per second of a sphere of one set with the spheres of the other in unit volume. It was shown that $\Sigma a\mu v/2$ when evaluated takes the form

$$\frac{3}{2}RT\frac{b}{v-b}(1+\frac{C_1}{T})^\gamma;$$

so that the theoretical characteristic equation becomes

$$pv=RT\left\{1+\frac{b}{v-b}(1+\frac{C_1}{T})^\gamma\right\}-\frac{a}{v};$$

whereas Amagat's experiments on $H_2$, $O_2$, $N_2$, and $CH_4$ above the critical volume can be represented by the form

$$pv=RT\left\{1+\frac{b}{v-b}\right\}-\frac{a}{v};$$

so that the factor $(1+\frac{C_1}{T})^\gamma$ due to molecular force seems to fall out. Now in the diffusion expression it is a factor approximately equal to $1+\frac{C_2}{T}$ that appears to drop out; and the main difference between the two cases is that in diffusion the velocity of diffusion involved in the momentum is small compared to the average velocity of agitation involved in the $\mu$ of the collisional virial. Thus it appears that the momentum communicated from molecule to molecule in a collision is not transmitted in the same manner as with smooth perfectly restitutional attracting spheres, but that there is some mechanism by which the transmission is made to depend on the ratio of the potential energy at contact to the mean kinetic energy in such a manner as to make the final effect of the forces acting during the collision of molecules the same as if the molecules were both forceless and perfectly restitutional smooth spheres. The mechanism is probably that which preserves proportionality between the mean translatory kinetic energy and the mean vibratory energy of a molecule;
and the difference between the diffusion case and that of the collisional virial may perhaps lie in the fact that the mechanism does not operate in the same manner as regards the mass motion of diffusion and the molecular motion of heat. But the whole question of molecular collision is so large a one that it will require considerable research to itself; from the glimpse we have got into it, it appears that the momentum imparted to a molecule during a collision, instead of being $\mu$ as calculated on the assumption that the molecules are smooth perfectly restitutional spheres, is $h\mu$, where $h$ is a parameter characteristic of the pair of molecules colliding, and which we have found empirically in the case of diffusion to be approximately proportional to $1 + \frac{C}{T}$. It may be worth while noting a certain regularity in the departure from strict proportionality, or in the departure of $10^3\frac{B}{(1 + \frac{C}{T})}$ from constancy: for the two triatomic molecules CO$_2$ and N$_2$O its value is least, namely, 0.94; for the triatomic CO$_2$ with diatomic N$_2$ and H$_2$ it is 1.11 and 1.12; while for the three diatomic pairs O$_2$ with H$_2$, N$_2$, and CO, it is 1.17, 1.17, and 1.16.

With Loschmidt's and v. Obermayer's diffusion-coefficients for a number of pairs of gases at about 15°C, we can test more extensively our empirical relation that at about that temperature the diffusion-coefficient is proportional to

$$\frac{1}{M_1 + 1/M_2} \{ \frac{(M_1\beta_1)^{\frac{1}{2}}}{2} + \frac{(M_2\beta_2)^{\frac{1}{2}}}{2} \}^2.$$  

The data are available for sixteen pairs including the six already considered, and as the experimenters have reduced their results to values at 0°C by the approximate formula

$$D_{273}/D_T = (\frac{273}{T})^2,$$

which is near enough to the truth for small differences between $T$ and 273, we will take the values $D_{273}$ as suitable for our present purpose. The additional values required for $(M\beta^{\frac{1}{2}})/2$ are:

<table>
<thead>
<tr>
<th></th>
<th>CICH</th>
<th>C$_2$H$_4$</th>
<th>C$_2$H$_6$</th>
<th>SO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$</td>
<td>1.59</td>
<td>1.53</td>
<td>1.4 (near)</td>
<td>.55</td>
</tr>
<tr>
<td>$M$</td>
<td>16</td>
<td>28</td>
<td>30</td>
<td>64</td>
</tr>
<tr>
<td>$(M\beta)^{\frac{1}{2}}/2$</td>
<td>1.47</td>
<td>1.75</td>
<td>1.74</td>
<td>1.63</td>
</tr>
</tbody>
</table>

With these and the values already given, and the values of D reproduced from v. Obermayer and Loschmidt, the values of

$$\frac{1}{M_1 + 1/M_2} \{ \frac{(M_1\beta_1)^{\frac{1}{2}}}{2} + \frac{(M_2\beta_2)^{\frac{1}{2}}}{2} \}^2 D$$
Mr. William Sutherland on the

have been calculated as given along with the diffusion-coefficients in the following table:

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_{273}$</td>
<td>$D_{278}$</td>
<td>$D_{292}$</td>
<td>$D_{294}$</td>
<td>$D_{296}$</td>
<td>$D_{298}$</td>
</tr>
<tr>
<td>$H_2$ and $O_2$</td>
<td>667</td>
<td>135</td>
<td>205</td>
<td>291</td>
<td>248</td>
<td>199</td>
</tr>
</tbody>
</table>
| $N_2$ and $O_2$ | 645 | 191 | 201 | 135 | 193 | 190 *
| $CO$ and $O_2$ | 647 | 199 | 248 | 291 | 199 | 190 *
| $CH_4$ and $CO$ | 625 | 193 | 248 | 291 | 199 | 190 *
| $CO_2$ and $N_2$ | 532 | 203 | 203 | 178 | 178 | 122 |
| $C_2H_4$ and $CO$ | 486 | 207 | 207 | 194 | 194 | 208 |
| $C_2H_6$ and $C_2H_4$ | 484 | 209 | 209 | 209 | 209 | 209 |

The values of 

$$\frac{1}{M_1} + \frac{1}{M_2}$$

are nearly constant, though showing on the whole a tendency to increase with the number of atoms in the diffusing molecules, as we already noted in connexion with $10^3 B/(1 + 1 C_2/T)$ for the original six pairs of gases.

The last table can be greatly extended, thanks to the experiments carried out by Winkelmann for determining diffusion-coefficients according to Stefan's evaporation method founded on his equation marked (5) in the present paper. He has determined the rates of evaporation of a number of esters from $C_3H_6O_2$ to $C_9H_{18}O_2$, and ethyl oxide, carbon disulphide, and benzene in air, hydrogen, and carbon dioxide at different temperatures, and has calculated the corresponding coefficients of diffusion.

In order to obtain the values of $D_{273}$ it is necessary to obtain approximate values of $1 C_2$ for use in the equation

$$D_{273} = \frac{273}{T} \left( \frac{1 + 1 C_2}{2 + \frac{1}{2}} \right)^{\frac{1}{2}}$$

These can be calculated from equation (9) if we know $1 C_1$ and $M \beta$ for the esters. The values of $1 C_1$ can be obtained in the following manner:—In the paper on the Viscosity of Gases and Molecular Force it is shown that for compounds

$$M \beta \cdot 1 C_1 \cdot 10^{-2} = 21 M^3 \ell / 2,$$

where $\ell$ is the virial constant of molecular attraction in the characteristic equation of the substance; values of $M^3 \ell$ for a large number of bodies being given in the Laws of Molecular Force (Phil. Mag., March 1893) along with methods of calculating them for any body. As regards $M \beta$ for the esters, I have found by determining $\beta$ that for $C_n H_{2n} O_2$,

$$M \beta = 29 + 17.5 (n - 1)$$

approximately: thus all the data are to hand for calculating $1 C_2$ for each of Winkelmann's diffusing pairs.
Attraction of Unlike Molecules.

Values of \( \mathrm{C}_2 \).

<table>
<thead>
<tr>
<th>Substance diffusing into</th>
<th>( \mathrm{H}_2 )</th>
<th>( \text{Air} )</th>
<th>( \text{CO}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mathrm{C}_3\mathrm{H}_6\mathrm{O}_2 )</td>
<td>319.2</td>
<td>390</td>
<td>0.67</td>
</tr>
<tr>
<td>( \mathrm{C}_4\mathrm{H}_8\mathrm{O}_2 )</td>
<td>339.8</td>
<td>390</td>
<td>0.67</td>
</tr>
<tr>
<td>( \mathrm{C}<em>5\mathrm{H}</em>{10}\mathrm{O}_2 )</td>
<td>364.6</td>
<td>390</td>
<td>0.67</td>
</tr>
<tr>
<td>( \mathrm{C}<em>6\mathrm{H}</em>{12}\mathrm{O}_2 )</td>
<td>389.5</td>
<td>390</td>
<td>0.67</td>
</tr>
<tr>
<td>( \mathrm{C}<em>7\mathrm{H}</em>{14}\mathrm{O}_2 )</td>
<td>371.2</td>
<td>390</td>
<td>0.67</td>
</tr>
<tr>
<td>( \mathrm{C}<em>8\mathrm{H}</em>{16}\mathrm{O}_2 )</td>
<td>371.2</td>
<td>390</td>
<td>0.67</td>
</tr>
<tr>
<td>( \mathrm{C}<em>9\mathrm{H}</em>{18}\mathrm{O}_2 )</td>
<td>371.2</td>
<td>390</td>
<td>0.67</td>
</tr>
<tr>
<td>( \mathrm{C}<em>{10}\mathrm{H}</em>{20}\mathrm{O}_2 )</td>
<td>371.2</td>
<td>390</td>
<td>0.67</td>
</tr>
<tr>
<td>( \mathrm{C}<em>{11}\mathrm{H}</em>{22}\mathrm{O}_2 )</td>
<td>371.2</td>
<td>390</td>
<td>0.67</td>
</tr>
<tr>
<td>( \mathrm{C}<em>{12}\mathrm{H}</em>{24}\mathrm{O}_2 )</td>
<td>371.2</td>
<td>390</td>
<td>0.67</td>
</tr>
<tr>
<td>( \mathrm{C}<em>{13}\mathrm{H}</em>{26}\mathrm{O}_2 )</td>
<td>371.2</td>
<td>390</td>
<td>0.67</td>
</tr>
<tr>
<td>( \mathrm{C}<em>{14}\mathrm{H}</em>{28}\mathrm{O}_2 )</td>
<td>371.2</td>
<td>390</td>
<td>0.67</td>
</tr>
<tr>
<td>( \mathrm{C}<em>{15}\mathrm{H}</em>{30}\mathrm{O}_2 )</td>
<td>371.2</td>
<td>390</td>
<td>0.67</td>
</tr>
<tr>
<td>( \mathrm{C}<em>{16}\mathrm{H}</em>{32}\mathrm{O}_2 )</td>
<td>371.2</td>
<td>390</td>
<td>0.67</td>
</tr>
<tr>
<td>( \mathrm{C}<em>{17}\mathrm{H}</em>{34}\mathrm{O}_2 )</td>
<td>371.2</td>
<td>390</td>
<td>0.67</td>
</tr>
<tr>
<td>( \mathrm{C}<em>{18}\mathrm{H}</em>{36}\mathrm{O}_2 )</td>
<td>371.2</td>
<td>390</td>
<td>0.67</td>
</tr>
<tr>
<td>( \mathrm{C}<em>{19}\mathrm{H}</em>{38}\mathrm{O}_2 )</td>
<td>371.2</td>
<td>390</td>
<td>0.67</td>
</tr>
<tr>
<td>( \mathrm{C}<em>{20}\mathrm{H}</em>{40}\mathrm{O}_2 )</td>
<td>371.2</td>
<td>390</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Winkelmann's determinations include a number of isomers, as, for instance, propyl formate, ethyl acetate, and methyl propionate of the composition \( \mathrm{C}_4\mathrm{H}_8\mathrm{O}_2 \); and in the diffusion-coefficients about to be given I have taken the mean of the isomers in each case, so that, for instance, the mean diffusion-coefficient of the bodies just mentioned is given as the value for \( \mathrm{C}_4\mathrm{H}_8\mathrm{O}_2 \). When the broad principles have been established it will be time enough to take account of minor differences in the diffusion-coefficients of isomers. The following table contains the mean diffusion-coefficients obtained from Winkelmann's determinations at the temperatures of his experiments, and the values at \( 0^\circ \text{C} \) calculated by the last formula and the values of \( \mathrm{C}_2 \) just given.

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With these values of $D$ at 273 the values of

$$\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^{\frac{1}{2}}/\left\{\left(\frac{M_1\beta_1}{2}\right)^{\frac{1}{2}} + \left(\frac{M_2\beta_2}{2}\right)^{\frac{1}{2}}\right\}D_{273}$$

can now be calculated as for the gases, with the following results (treating air as $N_2$):

<table>
<thead>
<tr>
<th></th>
<th>$\text{C}_2\text{H}_4\text{O}_2^*$</th>
<th>$\text{C}_2\text{H}_5\text{O}_2^*$</th>
<th>$\text{C}<em>5\text{H}</em>{10}\text{O}_2^*$</th>
<th>$\text{C}<em>6\text{H}</em>{12}\text{O}_2^*$</th>
<th>$\text{C}<em>7\text{H}</em>{14}\text{O}_2^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2$</td>
<td>23</td>
<td>24</td>
<td>25</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>$\text{Air}$</td>
<td>22</td>
<td>23</td>
<td>24</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>27</td>
<td>27</td>
<td>28</td>
<td>28</td>
<td>20</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_3\text{O}_2^*$</td>
<td>$\text{C}<em>5\text{H}</em>{10}\text{O}_2^*$</td>
<td>$\text{C}<em>5\text{H}</em>{15}\text{O}_2^*$</td>
<td>$\text{C}<em>8\text{H}</em>{18}\text{O}_2^*$</td>
<td>$\text{CS}_2^*$</td>
<td>$\text{C}<em>9\text{H}</em>{18}^*$</td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>27</td>
<td>27</td>
<td>23</td>
<td>23</td>
<td>24</td>
</tr>
<tr>
<td>$\text{Air}$</td>
<td>26</td>
<td>27</td>
<td>22</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>30</td>
<td>31</td>
<td>25</td>
<td>26</td>
<td>27</td>
</tr>
</tbody>
</table>

It will be noticed that with hydrogen and air at the lower members of the ester series and $(\text{C}_2\text{H}_3)^2\text{O}$ and $\text{CS}_2$, the values are near to the 2 which was about the mean value for the gases, but that they increase steadily as the series is ascended; so that the result for vapours joins on continuously with that for gases, but shows a decided departure from our empirical result for gases that for temperatures near 0°C the diffusion-coefficients have nearly the same relative values as if the molecules were forceless. But it should be remembered that the results for vapours are all calculated on the assumption that they obey the gaseous laws, and therefore that care should be taken not to give much weight to them till it is ascertained, either theoretically or experimentally, what is the effect on the diffusion-coefficient of such departure from the gaseous laws as vapours show.

To carry the subject to the most suitable point at which to leave it at present, it seems best to take all the values of

$$\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^{\frac{1}{2}}/\left\{\left(\frac{M_1\beta_1}{2}\right)^{\frac{1}{2}} + \left(\frac{M_2\beta_2}{2}\right)^{\frac{1}{2}}\right\}D_{273}$$

which have been given in this paper and divide them by the corresponding values of $1 + 1\beta/273$, using only the theoretical values of $\beta$, calculated according to equation (9). In this way, according to equation (10), we ought for attracting smooth perfectly restitutional spherical molecules to get the constant $1/B_{273}^3$ the same for all pairs of substances; and the amount of departure from constancy will furnish a good measure of the present degree of incompleteness of the kinetic theory of diffusion, the chief cause of incompleteness being, in my opinion, the assumption of perfect restitutionality in each individual collision.
On Coloured Cloudy Condensation.

Values of

\[
\frac{1}{M_1 + 1/M_2} \frac{1}{2} \left( \frac{M_1 + 3}{2} \right)^{1/2} \left( \frac{M_2 + 3}{2} \right)^{1/2} D(1 + C_2/273) = \frac{1}{B273}.
\]

<table>
<thead>
<tr>
<th>(H_2) and</th>
<th>(H_2O)</th>
<th>(O_2)</th>
<th>(N_2)</th>
<th>(CO)</th>
<th>(CH_4)</th>
<th>(CO_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air and</td>
<td>1.44</td>
<td>1.44</td>
<td>1.53</td>
<td>1.33</td>
<td>1.35</td>
<td>1.123</td>
</tr>
<tr>
<td>(CO_2) and</td>
<td>1.35</td>
<td>1.22</td>
<td>1.23</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{H}_2 & \quad \text{N}_2\text{O} & \quad \text{C}_2\text{H}_4 & \quad \text{C}_2\text{H}_5\text{O}_2 & \quad \text{C}_3\text{H}_6\text{O}_2 & \quad \text{C}_3\text{H}_5\text{O}_2 & \quad \text{C}_3\text{H}_3\text{O}_2 \\
\text{Air and} & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots \\
\text{\(CO_2\) and} & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots \\
\text{H}_2 & \quad \text{C}_2\text{H}_4\text{O}_2 & \quad \text{C}_3\text{H}_6\text{O}_2 & \quad \text{C}_5\text{H}_10\text{O}_2 & \quad \text{(C}_3\text{H}_5)\text{O} & \quad \text{CS}_2 & \quad \text{C}_3\text{H}_3 \\
\text{Air and} & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots \\
\text{\(CO_2\) and} & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots \\
\text{H}_2 & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots \\
\text{Air and} & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots \\
\text{\(CO_2\) and} & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots & \quad \ldots \\
\end{align*}
\]

Winkelmann's values of the diffusion-coefficients for the vapours of water, the alcohols, and fatty acids have not been discussed in the present communication on account of the exceptional nature of these substances, but they will doubtless be of value when the time is ripe for a full discussion of the physical reasons of their exceptional behaviour.

Melbourne, January 1894.

II. Coloured Cloudy Condensation, as Depending on the Temperature and the Dust-contents of the Air. By Carl Barus.*

[Plate V.]

In the "koniscope" Mr. Aitken† has expressed the dust-contents of a given sample of air, in terms of the colour, or of the intensity of colour, or of the amount of exhaustion necessary to produce a given colour, when the cloudy condensation is produced by sudden expansion of the gas in a suitable tube, containing enough moisture to saturate the air. The importance of temperature is pointed out, but not evaluated. Mr. Aitken prefers to make the

* I have availed myself of the permission of the Editors of this Magazine to reproduce here a condensed account of certain parts of a forthcoming Bulletin of the U.S. Weather Bureau, believing the subject to possess some general physical interest.

† Aitken, Proc. Roy. Soc. London, ii. p. 425 et seq., 1892. For a review of the earlier history of the subject (for which there is no space here) the reader is referred to my papers in the American Meteorological Journal, ix. p. 488, 1893; x. p. 12, 1893. On reviewing my résumé I find that the tribute there paid to the breadth and thoroughness of Mr. Aitken's researches (many of which I have since repeated) is inadequate, I therefore feel bound to make this acknowledgment.