XI. *The Law of Attraction amongst the Molecules of a Gas.*

By **William Sutherland, M.A., B.Sc.*

* Communicated by the Author.

Many hypotheses have been advanced as to the law of force prevailing among the molecules of a gas, chiefly with a view to furnishing an explanation of part of the departures from Boyle's and Charles's laws; but, as they have not started from a clear experimental basis, they have led to no general result of any value. The clearest evidence which has yet been given of the actual existence of attractive forces amongst the molecules of gases was supplied by the difficult experiments conducted by Thomson and Joule between the years 1852 and 1862, and described in their papers in the "Philosophical Transactions" on the "Thermal Effects of Fluids in Motion." But of the two striking general conclusions which they were able to draw from their experimental results, no use has been made except that which they themselves made in employing them to obtain an accurate expression of the relations of volume, pressure, and temperature in the case of air. The object of the present paper is to show that Thomson and Joule's experiments prove that the molecules of a gas attract one another with a force inversely proportional to the fourth power of the distance between them, and directly proportional to the product of their masses. It is hoped, too, that the attention of physicists will be recalled to the power of Joule's method in attacking the great problem of molecular attractions in solids and liquids.
It will be remembered that Joule first attempted to get evidence of the molecular attractions or repulsions in a gas by allowing air to escape from under pressure in one vessel into vacuum in another, and by measuring the difference of temperature of the gas before and after. Stated as a general method, capable of application to all bodies to measure the alteration of their potential energy with the distance of their molecules, it is this:—Allow the body to pass instantaneously from one state to another without doing external work; the heat developed is the thermal equivalent of the change of potential energy. M. Edlund (Poggendorf, cxxvi.) made a study of some metal wires in this manner, but they were stretched, and of course the stretching had to be kept within the elastic limits. The application of these experiments was limited to the verification of one or two thermodynamic relations. To obtain anything closer than a first approximation to the law connecting the potential energy and dimensions of bodies, it would be necessary to subject liquids and solids to pressures increasing to the greatest possible extent, and measure their change of potential energy, when released, by the thermal effect. This law once obtained, the deduction of the law of force would be a pure question of mathematical analysis.

Joule's first method not proving delicate enough for the case of gases, he joined Thomson in the series of experiments referred to above. Their method may briefly be described thus:—

Compressed gas was allowed to expand through a porous plug into the atmosphere. It was always brought to a constant measured temperature on the high-pressure side of the plug, and its temperature was taken on the low-pressure side. It was found to be cooled. However, part of the cooling effect could be traced to the departure of the gas from Boyle's law in this manner:—A volume $v'$ of the compressed gas in expanding through the plug to volume $v$ would have work $p'v'$ done on it by the gas behind ($p'$ being the high pressure), while it would do work $pv$ on the atmosphere in front. But in all gases except H, at about normal pressure and temperature, $pv > p'v'$. Hence, on the whole, the expanding gas does external work, and must accordingly draw on its supply of heat and get cooled. The thermal equivalent of $pv - p'v'$ at about 15° was calculated by Thomson and Joule from known data for air and CO₂, and was found to represent in the one case about a fourth, in the other about a third, of the actual cooling. The rest of the cooling effect is due to a gain of potential energy by the molecules at the expense of their heat; in other words, the molecules of the expanding gas separate
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against their mutual attractions. The two important general results obtained were:

1. The total cooling effect is directly proportional to the difference of the pressures on the two sides of the plug.

2. The total cooling effect is inversely proportional to the square of the absolute temperature of the gas.

Although Thomson and Joule estimated the thermal equivalent of $pv - p'v'$ at $15^\circ$, they did not calculate its values at different temperatures and subtract them from the total cooling effect at the same temperatures, in order to get the parts of the cooling effect at these temperatures due to increase of the potential energy of the molecules. When this is done, the cooling effect due to increased potential energy, which we shall call $\theta$, is, like the total cooling effect in (1), directly proportional to the difference of the pressures on the two sides of the plug, because at a given temperature $pv - p'v'$ is very nearly proportional to $p - p'$. But (2) does not now hold for $\theta$. In its place we have this result, that the cooling effect due to increased potential energy is inversely proportional to the absolute temperature:

$$\theta \propto \frac{p - p'}{T}. $$

In obtaining the values of $pv - p'v'$ for air, Van der Waals's formula was employed,

$$\left(p + \frac{0.0037}{v^2}\right)(v - 0.0026) = 1.0011(1 + \alpha t),$$

the unit of pressure being that of a metre of mercury, and the unit of volume that occupied by a kilogramme of gas at $0^\circ$ C. and a pressure of one metre of mercury; $\alpha$ is the coefficient of expansion, and $t$ the temperature Centigrade.

Thomson and Joule give the cooling effects at different temperatures corresponding to difference of pressure of 100 inches, or 2.54 metres of mercury; so that to get values of $pv - p'v'$ corresponding to the same circumstances we must put $p = 76$ m., $p' = 3.3$ m. A kilogramme of gas is supposed to pass through the plug. Changing to ordinary units and dividing by the mechanical equivalent of heat $J$ and the specific heat of air $s$, we get finally the cooling effects $\frac{pv - p'v'}{Js}$, due to departure from Boyle's law, as tabulated below.

The following table contains in the first column absolute temperatures, in the second the actual total cooling effects at the corresponding temperatures for a difference of pressure of 100 inches or 2.5 metres of mercury (these are taken from
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Thomson and Joule's paper in the Phil. Trans. 1862; in the third the calculated cooling effect \( \frac{p v - p' v'}{J_s} \); in the fourth the value of \( \theta \) or actual cooling effect minus \( \frac{p v - p' v'}{J_s} \); and in the fifth the products \( T \theta \).

### Air.

<table>
<thead>
<tr>
<th>Absolute temperature, T.</th>
<th>Total actual cooling effect</th>
<th>Cooling effect, ( \frac{p v - p' v'}{J_s} )</th>
<th>Difference of the two cooling effects, ( \theta )</th>
<th>Product, ( T \theta )</th>
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<tbody>
<tr>
<td>273.0</td>
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<td>320</td>
<td>600</td>
<td>164</td>
</tr>
<tr>
<td>280.1</td>
<td>88</td>
<td>294</td>
<td>586</td>
<td>164</td>
</tr>
<tr>
<td>312.5</td>
<td>75</td>
<td>183</td>
<td>567</td>
<td>177</td>
</tr>
<tr>
<td>365.8</td>
<td>51</td>
<td>046</td>
<td>464</td>
<td>166</td>
</tr>
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</table>

Thus within a range of nearly 93° the product \( T \theta \) is practically constant, showing that the cooling effect due to increase of molecular potential energy is inversely proportional to the absolute temperature of the gas. The erratic number 177 is eliminated from the following table, in which, instead of the actual, experimental total cooling effects are used, those which Thomson and Joule calculated in the light of the fact that variation of the total cooling as the inverse square of the absolute temperature was the clear meaning of their experiments as a whole:—

<table>
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With the relation \( \theta \propto \frac{p - p'}{T} \) thus established, it is not difficult to see that it means that the attraction between any two molecules of the gas is proportional to the product of their masses, and inversely proportional to the fourth power of the distance between them.

For the mutual potential energy of the two molecules is inversely proportional to the cube of the distance between
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them; or we may say that the potential of a particle of mass \( m \) at a point distant \( r \) from it is given by the equation

\[
V = A \frac{m}{r^3}.
\]

Let us assume that the constant \( A \) is of such magnitude that \( V \) becomes negligible for values of \( r \) greater than a certain length \( R \), which corresponds to the radius of the sphere of action considered in most molecular theories, \( R \) being a large multiple of the distance between a molecule and its nearest neighbour and at the same time small compared to sensible distances. \( R \) is of the order of magnitude of, say, the thickness of a capillary film. Under these circumstances we can consider each molecule as uniformly distributed through the small region of space round it, which may be said to belong to it. Then any one molecule \( P \) may be supposed to be gathered into a particle at its centre, leaving the space which belongs to it in the form of a spherical vacuum, while all the other molecules have been spread out around it into a continuous matter of uniform density \( \rho \). To find the potential of a finite mass of gas at the centre of \( P \), let us describe a cone of small solid angle \( w \) with its vertex at \( P \), and terminating at the boundary of the gas \( AA' \); it cuts off the small area \( aa' \) on the surface of the vacuous sphere. Then for the potential at \( P \) of any element \( xx' \) distant \( r \) from \( P \) and of thickness \( dr \) we have

\[
A \frac{\rho w r^2 dr}{r^3};
\]

and therefore for the whole potential of the frustrum \( aa' A'A \),

\[
A \rho w \int_{r_1}^{R_1} \frac{dr}{r} = A \rho w \log \frac{R_1}{r_1},
\]

where \( Pa = r_1 \) and \( PA = R_1 \).

Let \( R_1 = nL \), where \( n \) is a large number so that \( L \) is a small but sensible length.
Then the above becomes \( A \rho w \log \frac{nL}{r_1} \),

\[ i.e. A \rho w \log n + A \rho w \log \frac{L}{r_1} \]

but \( r_1 \) is so excessively small in comparison with the sensible length \( L \) that \( n \) is negligible in comparison with \( \frac{L}{r_1} \). Hence we may write \( A \rho w \log \frac{L}{r_1} \) as equivalent to the above.

Hence for the potential of the finite mass of gas round \( P_1 \) at the centre of \( P \) we can take that of the sphere of matter of radius \( L \), which is,

\[ 4\pi \alpha \rho \log \frac{L}{r_1} \]

Hence for the mutual potential energy of the particle \( P \) and the whole mass of gas, we have

\[ 4\pi A \rho m \log \frac{L}{r_1} \]

and for the total potential energy of \( n \) molecules, leaving out of count those so near the boundary that a sphere of radius \( L \) cannot be described about them so as to lie wholly in the matter under consideration, we have,

\[ 2\pi A n \rho m \log \frac{L}{r_1} \]

changing from the numerical coefficient 4 to 2, because we must not count the mutual potential energy of any two particles twice over.

If now the mass of gas is allowed to expand (in Thomson and Joule's experiments it expanded by various amounts up to six times the original volume), the value of \( \log \frac{L}{r_1} \) remains practically constant, and the new value of the total potential energy is

\[ 2\pi A n \rho m' \log \frac{L}{r_1} \]

where \( \rho' \) is the density of the gas after expansion.

Therefore the change of potential energy is proportional to

\[ M (\rho - \rho') \]

\( M \) being the mass of gas.

Now the cooling effect corresponding to this will be obtained by dividing the above by \( JM s \), where \( s \) is the specific heat of
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the gas. Thus the cooling effect is proportional to

\[ \frac{p - p'}{J_s} \]

If \( T \) is the absolute temperature of the gas and \( p \) and \( p' \) the pressures corresponding to the densities \( \rho \) and \( \rho' \),

\[ \frac{p - p'}{J_s} \text{ is proportional to } \frac{p - p'}{T_s}. \]

In the case of air, \( s \) is practically constant, so that the theoretical cooling is directly proportional to the difference of pressures and inversely to the absolute temperature.

Thus the hypothesis of a force attracting according to the law of the inverse fourth power and the product of the masses yields the two results deduced from the experimental data.

It may be worth while mentioning that if the case is worked out for a very long cylinder of matter, attracting according to the Newtonian law, treated as a very prolate spheroid and expanded into another cylinder of the same section treated also as a spheroid, results in accordance with the above experimental results may be obtained, but with a third result, that the cooling effect would be proportional to the sectional area of the cylinder. Thus if the time ever comes when it will be practicable to look for the part of the cooling effect due to the mutual gravitation of the molecules, it will be found as a small fraction of the whole cooling effect, varying with the sectional area of the plug.

The only other gas on which Thomson and Joule conducted a sufficiently extended series of experiments to obtain definite results was CO₂. They were able to enunciate the same two general results as for air, only the total cooling effects were not so accurately proportional to the inverse square of the temperature. To evaluate the thermal equivalent of \( pv - p'v' \) at different temperatures for CO₂, Clausius' formula is used,

\[ p = 19.273 \frac{T}{v - 0.00426} - \frac{5533}{T(v + 0.00494)} \]

The unit of pressure is that of a kilogramme per square metre, and \( v \) is the volume in cubic metres of a kilogramme of CO₂.

But, in the first place, the formula shows how at a given temperature the value of \( pv - p'v' \) is very nearly proportional to \( p - p' \), so that, as in the case of air, we can assert that the cooling effect due to increase of molecular potential energy is proportional to the difference of pressure on the two sides of the plug.
In passing from the value of $pv - p'v'$ to the cooling effect $\frac{pv - p'v'}{J_s}$, which corresponds to it, account has been taken of the variation of $s$, the specific heat of CO$_2$, with temperature. E. Wiedemann's determinations (1952 at 0° C.; 2169 at 100°, 2837 at 200°) were adopted, the values at intermediate temperatures being obtained by interpolation. On reverting to the theoretical conclusion, it will be seen that the cooling is to be proportional to $\frac{p - p'}{T_s}$; and as $s$ varies with the temperature, it will be necessary to test the theory by seeing whether the product $T\theta s$ (for the constant value 100 inches of mercury for $p - p'$) is constant.

In the first of the following tables the total actual cooling effects are Thomson and Joule's experimental numbers (Phil. Trans. 1862); in the second the calculated total cooling effects were obtained by them on the supposition that the cooling effects were inversely proportional to the square of the absolute temperature.

### CO$_2$.

<table>
<thead>
<tr>
<th>Absolute temperature, $T_s$</th>
<th>Actual total cooling effect, $pv - p'v'$</th>
<th>Cooling effect, $\frac{pv - p'v'}{J_s}$</th>
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<td>308.6</td>
<td>3.41</td>
<td>1.04</td>
<td>2.37</td>
<td>148</td>
</tr>
<tr>
<td>327.0</td>
<td>2.95</td>
<td>0.89</td>
<td>2.0</td>
<td>141</td>
</tr>
<tr>
<td>370.5</td>
<td>2.14</td>
<td>-0.63</td>
<td>1.51</td>
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In the first of the above tables for CO$_2$, the products $T\theta s$ show decided enough departure from constancy; in fact $T\theta s$ would be nearly constant. The departure may be taken as showing the great value which similar experiments conducted on vapours compressed nearer and nearer to liquefaction and
then allowed to expand might possess. For in view of the facts that at 0° C. CO₂ liquefies under a pressure of about 40 atmospheres, while at 45° there is required 100 atmospheres to liquefy it, and that the pressure on the high-pressure side of the plug, in the experiments from which the above numbers were derived, reached 6 atmospheres, it becomes apparent that at the low temperatures the forces which are ultimately to produce cohesion in the liquid are hardly likely to be so closely represented by the monomial expression \( \frac{A}{r^4} \) as at the high temperatures. In fact, regarding the ultimate law of the action of one particle on another at any distance as a function of \( r \) of the form \( f\left(\frac{1}{r}\right) \) or \( f\left(\frac{1}{r^3}\right) \), and considering the law of gravitation as simply the first term of the expansion of the latter in ascending powers of \( \frac{1}{r^2} \), which expresses the action accurately enough within the limits of astronomical distances, we may look upon Thomson and Joule's experiments on air as showing how the second term, involving the inverse fourth power of \( r \), becomes appreciable at very small distances; in the case of CO₂ we may regard the above table as showing how the term \( \frac{1}{r^5} \) may begin to be appreciable, and how perhaps at still smaller distances still higher terms may appear and become predominant in producing cohesion and elasticity.

There remains one application of our theory which throws an interesting light on a fact to which Thomson and Joule drew attention more than once as being very remarkable. When a mixture of the two gases, CO₂ and air, is expanded through a plug, it might be expected that each would contribute its proportion of cooling effect according to its own amount and its thermal capacity. But such is far from being the case. Indeed, experiment showed that the cooling effect for pure O is greater than for pure N, and yet in air and other mixtures of the two gases the cooling effect is less than in either of the constituents under the same circumstances.

Let \( V_1 \) be the volume of a mixture of two gases before expansion, \( V_2 \) the volume after. Let \( V_{A1}, V_{B1} \), be the volumes of the two constituent gases A and B before expansion; \( V_{A2}, V_{B2} \), the volumes after. Suppose that there are \( a \) molecules of A and \( b \) molecules of B in the mass under consideration. We must first make a hypothesis as to the action of a molecule of A on a molecule of B. If the mutual potential of two
molecules of A at distance \( r \) apart is \( \frac{A m^2}{r^3} \), and of two molecules of B is \( \frac{B m^2}{r^3} \), we will assume that the mutual potential of a molecule of A and one of B at distance \( r \) is \( C \frac{\sqrt{AB} m m'}{r^3} \), where C is a constant.

Then for the mutual potential energy of all the molecules of A before expansion we have an expression

\[
2 \pi A \, a m \rho_A \log \frac{L}{r_1},
\]

where \( \rho_A \) means the density of the gas A when its \( a \) molecules are distributed through a volume \( V_1 \). Similarly for the mutual potential of the molecules of B before expansion we have

\[
2 \pi B \, b m' \rho_B \log \frac{L}{r_1},
\]

the value of \( r_1 \) being the same in each expression, because, according to Avogadro's law, the molecules of different gases under the same circumstances own equal volumes of space. Leaving the quantity \( L \) of the same value in both expressions, amounts to asserting that the molecular forces in the two gases are quantities of the same order of magnitude. For the mutual potential energy of a molecule of A and one of B before expansion we have

\[
4 \pi C \, \sqrt{AB} \, m \rho_A \log \frac{L}{r_1};
\]

and, therefore, for the mutual potential of the \( a \) molecules of A and the \( b \) molecules of B we have

\[
4 \pi C \, \sqrt{AB} \, b m' \rho_A \log \frac{L}{r_1}.
\]

But by proceeding in the other order, that is by writing down the mutual potential of the \( b \) particles of B and one of A and then summing for the \( a \) particles, we would obtain

\[
4 \pi C \, \sqrt{AB} \, a m \rho_B \log \frac{L}{r_1}.
\]

Thus for the total energy of the mixed gases before expansion we have the expression (omitting common constants)

\[
A a m \rho_A + B b \, m' \rho_B + 2 C \, \sqrt{AB} \, b m' \rho_A;
\]

and after expansion,

\[
A a m \rho_A + B b m' \rho_B + 2 C \, \sqrt{AB} \, b m' \rho_A.
\]
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\[ \rho_{A_i} \] denoting the density of the gas A when its \( a \) molecules are distributed through a volume \( V_2 \).

Then for the increase of potential due to expansion we have

\[ Aa'm(\rho_{A_i} - \rho_{A_i}) + Bbm'(\rho_{B_i} - \rho_{B_i}) + 2C \sqrt{AB} bm'(\rho_{A_i} - \rho_{A_i}). \]

Now the last term in this has the same value as

\[ 2C \sqrt{AB} am(\rho_{B_i} - \rho_{B_i}); \]

so that it may be replaced by the square root of the product of the two, namely

\[ 2C \sqrt{AB} am bm'(\rho_{A_i} - \rho_{B_i})(\rho_{A_i} - \rho_{A_i}). \]

Hence for the increase of potential energy we have the sum of the two expressions \( Aa'm(\rho_{A_i} - \rho_{A_i}) \); \( Bbm'(\rho_{B_i} - \rho_{B_i}) \); and \( C \) times twice the product of their square roots.

Now suppose that \( V_1 \) is the volume of the mixture at a pressure \( P_1 \); \( V_2 \) at a pressure \( P_2 \); the temperature \( T \) being the same in each case. Then \( \rho_{A_i} \) is to the density of the gas A at pressure \( P_1 \) in the ratio \( \frac{V_1}{V_2} \), and \( \rho_{A_i} \) is to the density of the gas A at pressure \( P_2 \) in the ratio \( \frac{V_2}{V_2} \), which is equal to the previous ratio. Thus the term \( Aa'm(\rho_{A_i} - \rho_{A_i}) \) may be written

\[ Aa'm \frac{V_1}{V_2}(\rho'_{A_i} - \rho_{A_i}), \]

where \( \rho_{A_i}', \rho_{A_i}' \) represent the densities of A at pressures \( P_1 \) and \( P_2 \).

But this is \( \frac{V_1}{V_2} \) times the gain of potential of a mass \( am \) of the gas A escaping from under pressure \( P_2 \) to pressure \( P_1 \); or, if we call \( \theta_{A} \) the cooling effect for A corresponding to \( P_2 - P_1 \), we may write it

\[ Js_{A} \rho_{A} V_{A_i} \theta_{A}, \]

where \( s_{A} \) is the specific heat of A.

For the other terms in the gain of potential by the mixed gases we can write corresponding expressions, and get for the result,

\[ Js_{A} \rho_{A} V_{A_i} \theta_{A} + Js_{B} \rho_{B} V_{B_i} \theta_{B} + 2CJ \sqrt{s_{A} \rho_{A} V_{A_i} \theta_{A} s_{B} \rho_{B} V_{B_i} \theta_{B}}. \]

To obtain the cooling effect corresponding to this we must first divide by \( J \), and then by the thermal capacity of the
mass operated on, which is

\[ s_A \rho_A V_{A_1} + s_B \rho_B V_{B_1}, \]

Therefore for the cooling effect \( \theta \) of the mixture we have

\[ \theta = \frac{s_A \rho_A \frac{V^2}{V_1} \theta_A + s_B \rho_B \frac{V^2}{V_1} \theta_B + 2C \sqrt{s_A \rho_A \frac{V^2}{V_1} \theta_A s_B \rho_B \frac{V^2}{V_1} \theta_B}}{s_A \rho_A \frac{V^2}{V_1} + s_B \rho_B \frac{V^2}{V_1}}. \]

To show with this formula how the cooling for a mixture of \( O \) and \( N \) may be less than for either of the gases alone under the same circumstances, let us suppose that \( \theta \) is less both than \( \theta_A \) and \( \theta_B \); we will see whether the supposition leads to a possible or impossible conclusion.

Let us denote

\[ \frac{V_{A_1}}{V_1} \text{ by } D, \text{ and } \frac{V_{B_1}}{V_1} \text{ by } D', \text{ remembering that } D + D' = 1; \]

also

\[ s_A \rho_A \text{ by } \alpha, \quad s_B \rho_B \text{ by } \beta. \]

Then the supposed inequalities become

\[ aD^2 \theta_A + \beta D^2 \theta_B + 2CDD' \sqrt{\alpha \beta \theta_A \theta_B} < (\alpha D + \beta D') \theta_A; \]

\[ \beta D^2 \theta_B + \alpha D^2 \theta_A + 2CDD' \sqrt{\alpha \beta \theta_A \theta_B} < (\alpha D + \beta D') \theta_B; \]

\[ \cdots aD \theta_A(D - 1) + \beta D^2 \theta_B - \beta D' \theta_A + 2CDD' \sqrt{\alpha \beta \theta_A \theta_B} < 0, \]

or

\[ -aDD' \theta_A + \beta D^2 \theta_B + \beta D' \theta_A + 2CD \sqrt{\alpha \beta \theta_A \theta_B} < 0; \]

\[ \cdots -aD \theta_A + \beta D' \theta_B - \beta \theta_A + 2D \sqrt{\alpha \beta \theta_A \theta_B} < 0. \]

Similarly

\[ -\beta D' \theta_B + aD \theta_A - a \theta_B + 2D \sqrt{\alpha \beta \theta_A \theta_B} < 0; \]

\[ \cdots \text{ adding } -\beta \theta_A - a \theta_B + 2C(D + D') \sqrt{\alpha \beta \theta_A \theta_B} < 0. \]

If \( C = 1 \), this becomes, since \( D + D' = 1 \),

\[ -(\sqrt{\beta \theta_A} - \sqrt{\alpha \theta_B})^2 < 0, \]

which is possible. If \( C \) is less than 1, the inequalities can also still exist together.

Thus that the cooling effect for a mixture of two gases should prove less than that for either of the constituents has been shown to be a possible consequence of the theory of molecular attractions.

By means of Thomson and Joule's experimental numbers for mixtures of air and \( CO_2 \) in different proportions, we propose finally to calculate the values of \( C \) obtainable from the cooling
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effects in different mixtures and see whether they agree; that is, whether our theory can be tested by its power to explain with any exactness a very peculiar experimental fact.

There are no systematized experimental results by means of which the value of $pv$ for different mixtures of air and $CO_2$ at different temperatures could be obtained directly; but the following argument will show that we can make use of our previous numbers for the values of $pv - p'v'$ at different temperatures in the case of air and $CO_2$, to deduce the numbers for any mixture of air and $CO_2$ at the same temperatures. Let $V_1$ be the volume of a mixture of the two gases at a certain temperature and a pressure $P_1$; as before, let $V_{A_1}, V_{B_1}$ be the volumes which the constituent gases in $V_1$ would occupy if separated at pressure $P_1$. Let $W_1$ be the potential energy of the mixed gases $W_{A_1}, W_{B_1}$ of the two separated gases; then actually to separate the two gases will require work,

$$W_1 - W_{A_1} - W_{B_1}.$$ 

Expand the separated gases to a condition represented by suffix 2, just as they were expanded in Thomson and Joule's experiments, that is without doing external work other than that corresponding to the values of $pv - p'v'$ for each gas; thus each of the separated gases would be cooled by the amount $pv - p'v'$ previously calculated, and each would be cooled by its respective amount $\theta_A$ or $\theta_B$, on account of the separation of molecules; so that altogether the gain of potential energy during the expansion will be the sum of $Js_A \theta_A$ and $Js_B \theta_B$ and the two corrections $pv - p'v'$. Thirdly, allow the gases to diffuse into one another. In this case the work required will be

$$-W_2 + W_{A_2} + W_{B_2}.$$ 

Hence the total gain of potential energy by the mixed gases on expanding from volume $V_1$ to $V_2$ is

$$W_1 - W_{A_1} - W_{B_1} - W_2 + W_{A_2} + W_{B_2} + Js_A \theta_A + Js_B \theta_B + (P_1 V_{A_1} - P_1 V_{A_2}) + (P_1 V_{B_1} - P_2 V_{B_2});$$

but

$$W_{A_1} - W_{A_2} = Js_A \theta_A; \quad W_{B_1} - W_{B_2} = Js_B \theta_B.$$ 

So that the total gain reduces to

$$W_1 - W_2 + (P_1 V_{A_1} - P_2 V_{A_2}) + (P_1 V_{B_1} - P_2 V_{B_2}),$$

and this corresponds to the total actual cooling effect observed by Thomson and Joule. The cooling effect denoted above by $\theta'$ is the equivalent of $W_1 - W_2$; to obtain $\theta$ then from the
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Experimental numbers we have to subtract from them the cooling effects corresponding to the terms \((P_1V_{A_1} - P_2V_{A_1})\).

Given that a volume \(V_{A_1}\) of air is cooled by \(\frac{P_1V_{A_1} - P_2V_{A_1}}{J_{s_A}}\), and that a volume \(V_{B_1}\) of \(CO_2\) is cooled by \(\frac{P_1V_{B_1} - P_2V_{B_1}}{J_{s_B}}\), we have for the cooling effect in the mixture:

\[
\frac{1}{J} \left( \frac{(P_1V_{A_1} - P_2V_{A_1})V_{A_1}\rho_A + (P_1V_{B_1} - P_2V_{B_1})V_{B_1}\rho_B}{V_{A_1}\rho_A + V_{B_1}\rho_B} \right).
\]

In this manner the \(pv - p'v'\) part of the cooling effect of the mixed gases has been calculated from the previously found values for pure air and \(CO_2\).

The table below contains in the first column the percentages of the two gases in the particular mixture; the second contains the temperature (absolute) \(T\) at which the gas escaped; the third contains the total actual cooling effect for a difference of pressure of 100 in. or 2.54 metres of mercury, observed by Thomson and Joule (Phil. Trans. 1862); the fourth contains the calculated values of the above expression for the cooling effect to be subtracted; the fifth contains the cooling effect \(\theta\) obtained by subtracting the numbers in the fourth column from those in the third; while the sixth contains the values of \(C\) obtained by substituting the corresponding values of \(\theta\) in the equation for \(\theta\).

### Mixtures of Air and \(CO_2\).

<table>
<thead>
<tr>
<th>Percentage composition of mixture.</th>
<th>Absolute temperature, (T)</th>
<th>Total actual cooling effect.</th>
<th>Cooling effect to be subtracted.</th>
<th>(\theta)</th>
<th>(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>68 air 32 (CO_2)</td>
<td>280</td>
<td>1.76</td>
<td>0.69</td>
<td>1.07</td>
<td>-72</td>
</tr>
<tr>
<td>89 air 11 (CO_2)</td>
<td>280</td>
<td>1.17</td>
<td>0.45</td>
<td>0.72</td>
<td>-76</td>
</tr>
<tr>
<td>62 air 38 (CO_2)</td>
<td>280</td>
<td>1.86</td>
<td>0.75</td>
<td>1.1</td>
<td>-57</td>
</tr>
<tr>
<td>68 air 32 (CO_2)</td>
<td>323</td>
<td>1.29</td>
<td>0.49</td>
<td>0.8</td>
<td>-8</td>
</tr>
<tr>
<td>88 air 12 (CO_2)</td>
<td>323</td>
<td>0.88</td>
<td>0.33</td>
<td>0.55</td>
<td>-6</td>
</tr>
<tr>
<td>57 air 43 (CO_2)</td>
<td>364</td>
<td>1.1</td>
<td>0.36</td>
<td>0.74</td>
<td>-73</td>
</tr>
</tbody>
</table>

The agreement between these values of \(C\) calculated from different mixtures at different temperatures is very fair, especially if the value 0.57 is left out of the count as being evidently affected by some error in the experiment from which it is deduced; because, if 1.07 is correct for the first value of \(\theta\),
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11 can hardly be right when the percentage of CO₂ has been increased from 32 to 38. Thus we can regard the experiments on mixed gases as furnishing confirmation of the truth of the law of the inverse fourth power for the attractions between molecules of gas.

The value of C which we have obtained for air and CO₂ (mean 17) throws an interesting light on a certain aspect of the phenomenon of diffusion. Suppose a volume $V_A$ of a gas containing $a$ molecules, and a volume $V_B$ of another gas B containing $b$ molecules, separated by an infinitely thin partition, then the potential energy of the two masses of gas is (leaving out common factors)

$$Aamp_A + Bbm'\rho_B.$$

When the gases are mixed together without change of pressure we can see from what has gone before that the potential becomes

$$Aamp_A \frac{V_A}{V_A + V_B} + Bbm'\rho_B \frac{V_B}{V_A + V_B} + 2C\sqrt{\frac{AB}{V_A + V_B}} \frac{V_A V_B}{(V_A + V_B)^2}.$$

Subtracting this from the previous expression, we get

$$Aamp_A \frac{V_B}{V_A + V_B} + Bbm'\rho_B \frac{V_A}{V_A + V_B} - 2C\sqrt{\frac{AB}{V_A + V_B}} \frac{V_A V_B}{(V_A + V_B)^2}.$$

If $C=1$ this is a complete square, and therefore necessarily positive; therefore when $C=7$ the expression is also positive, and for all values of $C$ less than 1 it must be positive; that is, the potential energy of the molecules diminishes by diffusion. Hence we may regard diffusion as partly due to the tendency of the molecules of the mixing gases to obey the dynamical principle that a position of stable equilibrium is a position of minimum potential energy. Diffusion is motion towards the position of stable equilibrium for the two gases.

However, the kinetic factor in the diffusion of gases is so predominant that this aspect is not of much importance. But in the case of liquids it is otherwise, and the form of our last expression suggests how the tendency of some liquids to mix and of others to refuse to mix may depend on the magnitude of a coefficient like C. Indeed, the study of the cooling effect of liquids and mixtures of liquids escaping from under pressure affords a splendid field for experimental inquiry. This paper will have possessed some value if it draws the attention of those who have facilities for such a research, to a field whose further exploration on the tracks of the pioneers must open valuable ground for Physical Science.

Melbourne, April 1886.