



## Philosophical Magazine Series 5

ISSN: 1941-5982 (Print) 1941-5990 (Online) Journal homepage: <http://www.tandfonline.com/loi/tphm16>

# XX. On the law of molecular force

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To cite this article: William Sutherland M.A. B.Sc. (1887) XX. On the law of molecular force , Philosophical Magazine Series 5, 24:147, 168-187, DOI: [10.1080/14786448708628077](https://doi.org/10.1080/14786448708628077)

To link to this article: <http://dx.doi.org/10.1080/14786448708628077>



Published online: 29 Apr 2009.



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XX. *On the Law of Molecular Force.*  
*By WILLIAM SUTHERLAND, M.A., B.Sc.\**

[Concluded from p. 134.]

IT is not difficult to illustrate how profoundly the relations of pressure and density of saturated vapour may be affected by capillary action at temperatures near the critical. Sir William Thomson has shown (Proc. Roy. Soc. Edinb., Feb. 1870) that, if inside a closed vessel containing a liquid and its vapour a capillary tube dips into the liquid, the pressure of saturation  $p$  of the vapour in contact with the free curved surface of the liquid in the capillary tube is connected with  $\varpi$ , the pressure of saturation of the vapour in contact with the plane surface, by the equation

$$p = \varpi - \frac{E\sigma}{\rho - \sigma} \left( \frac{1}{r} + \frac{1}{r'} \right),$$

where  $E$  is the surface energy of the liquid per unit area,  $\sigma$  the average density of the vapour between the levels of the free surfaces of the liquid inside and outside the capillary tube,  $\rho$  the density of the liquid,  $r$  and  $r'$  are the principal radii of curvature of the curved surface of the liquid in the tube, reckoned as positive when the surface is concave to the vapour, that is when the liquid rises in the tube.

At temperatures near the critical, when  $\sigma$  becomes nearly equal to  $\rho$ , the factor  $\frac{\sigma}{\rho - \sigma}$  becomes very large. It has been

assumed by some writers that  $E\left(\frac{1}{r} + \frac{1}{r'}\right)$  vanishes at the critical temperature, and therefore becomes very small at temperatures near the critical, on the supposition that, as the critical temperature is the limiting temperature at which capillary elevation or depression can occur in a tube, the plane surface is naturally the limiting form which the free surface of the liquid in a capillary tube attains at the critical temperature. But that the plane surface is not a limiting case is shown by such an ordinary example as the convex meniscus of mercury in a glass tube. However, we have the definite experiments of Wolf (*Ann. de Chim. et de Phys.* 3 sér. xlix., 1857) to show that the plane surface is not the limiting form of a capillary meniscus at the critical temperature; for he found that sulphuric ether, sulphide of carbon, naphtha, and alcohol at temperatures near their

\* Communicated by the Author.

critical were depressed in capillary tubes of 2 millim. diameter, and presented markedly convex surfaces. Thus, for these substances,  $E\left(\frac{1}{r} + \frac{1}{r'}\right)$  acquires a measurable negative value, and the whole expression  $-\frac{E\sigma}{\rho - \sigma}\left(\frac{1}{r} + \frac{1}{r'}\right)$  may acquire a large positive value at temperatures near the critical. We thus see how the pressure of saturation of  $\text{CO}_2$  for temperatures below but near the critical temperature, as obtained by experiments in capillary tubes, might differ greatly from those obtained by experiments in large vessels. This, then, illustrates the origin of the apparent conflict between the experiments of Regnault and of Andrews.

Some experiments of Kayser's (Wiedemann's *Ann.* xv.) bring out in a clear manner the difference between the laws of compressibility and dilatation of a fluid as studied in capillary tubes and in large vessels. When  $\text{SO}_2$  is compressed at  $0^\circ\text{C}$ . in a vessel containing a quantity of powdered glass, it shows no pressure of saturation; its isothermal is a continuous curve representing quite a different relation between pressure and volume from that which holds when  $\text{SO}_2$  is compressed free from capillary restraint.

The full explanation of these facts will be forthcoming only when the capillary theory of Laplace and Gauss receives completion in regard to the matter which, as it left their hands, it has proved inadequate to explain, namely, the influence of temperature in capillary phenomena. The equation of Gauss for the potential energy of a mass of liquid enclosed in a solid vessel contains three terms, representing the potential energy of the liquid due to gravity, that which corresponds to the mutual attractions of its molecules, and that which corresponds to the attractions between the molecules of the liquid and those of the solid; four terms should be added to make the equation complete as regards the whole mass of a fluid partly liquid and partly vapour,—namely, a term to represent the potential energy of the vapour due to gravity, that which corresponds to the mutual attractions of the molecules of vapour, that which corresponds to the actions between liquid and vapour, and finally that which corresponds to the actions between solid and vapour.

Having discovered that the discarded equation is thus in excellent agreement with Regnault's work on  $\text{CO}_2$  in bulk, and that the differences between its results at  $35^\circ\cdot5$  in the neighbourhood of the critical point and those of Andrews and Amagat are traceable entirely to the experimental circumstances, I resumed my study of it and proceeded to test its

power to give the pressures of saturated vapour of  $\text{CO}_2$  as determined by Thilorier (*Ann. de Chim. et de Phys.* 2 sér. lx. 1835), Mitchell (*Journ. Franklin Inst.* xxvi. 1838), Faraday (*Phil. Trans.* 1845), Regnault (*Mém. de l'Acad. des Sciences*, xxvi.), and Andrews (*Proc. Roy. Soc.* xxiii. 1874-75).

To Maxwell (*Journ. Chem. Soc.* 1875) we owe the method of obtaining the pressure of saturation of a fluid at any temperature from its characteristic equation. Accepting James Thomson's suggestion that the isothermal for a fluid below its critical temperature, when traced by means of the characteristic equation for the fluid, ought to be a continuous curve lying partly above and partly below the isopiestic of saturation, he showed from thermodynamical considerations that the area enclosed by the part above the isopiestic should be equal to that enclosed by the part below. Expressed in symbols, this is

$$P(v_3 - v_1) = \int_{v_1}^{v_3} p dv,$$

where  $P$  is the pressure of saturation at temperature  $T$ ,  $v_3$  is the volume of the saturated vapour at  $T^\circ$ , and  $v_1$  the volume of the liquid at  $T^\circ$  and pressure  $P$ ; so that  $v_3$  and  $v_1$  are the greatest and least of the three real roots for  $v$  of the characteristic equation, when the temperature has the value  $T$  and the pressure the value  $P$ . Applying this condition to the equation for  $\text{CO}_2$ , we obtain the following equation for the pressure of saturation at  $T^\circ$  as a function of  $T$ :—

$$P(v_3 - v_1) = \int_{v_1}^{v_3} \left( \frac{aT}{v} e^{\frac{b}{v\sqrt{T}}} + \frac{cT - l}{v^2} \right) dv,$$

where  $v_3$  and  $v_1$  are the greatest and least real roots of the equation

$$Pv = aTe^{\frac{b}{v\sqrt{T}}} + \frac{cT - l}{v}.$$

The only part of the integral which is not integratable is that involving the exponential factor, which, however, can be expressed as the difference of two exponential integrals which are now regarded as primary, since the tabulation of values for them by Soldner, Bretschneider, and more elaborately by J. W. L. Glaisher (*Phil. Trans.* 1870). However, as the values of  $v_3$  and  $v_1$  are indeterminable functions of  $P$  and  $T$ , we are unable to use the tables in the present application of the integral, and must content ourselves with determining  $P$  graphically—that is, by tracing the isothermal for certain

definite numerical values of T, and then by trial drawing the isopiestic for P so that it cuts off equal areas.

In the subjoined table I give the pressures of saturation as found by the different experimenters and by Maxwell's principle with the characteristic equation. Two series of determinations by Regnault are given. Regnault is the only observer who has reduced his air-manometer pressure to true metres of mercury; but I have not thought it worth while to apply any correction to the results of the other observers, in view of the other larger sources of error that cannot be allowed for. I have simply multiplied their pressures in atmospheres by  $\cdot 76$ . The first row of numbers gives the temperatures of observation and the second the corresponding saturation pressures.

Saturation Pressures of CO<sub>2</sub>.

	Thilorier.	Mitchell.	Faraday.	Regnault, I.	Regnault, II.	Andrews (capill. tubes).	Maxwell's principle and equation.
Temp. C...	30·00	30·00	.....	30·90	29·30	28·3	30
Pressure...	55·48	54·72	.....	53·35	54·41	53·5	49
Temp. C...	0	0	0	0·25	0·18	0	0·21
Pressure...	27·36	27·36	29·26	27·17	26·82	26·63	26·2
Temp. C...	.....	.....	-26·10	-25·8	-25·5	.....	-25·50
Pressure...	.....	.....	13·53	12·9	12·9	.....	13·35

It will be seen that the equation gives results as good as are to be looked for in view of the differences in the different experimental determinations. The only number that is quite out of harmony with all the experimental determinations is 49, the pressure of saturation yielded by the equation for 30°; but when we see that at 30°·9 Regnault gets 53·35 in his first series, and that he finds a pressure greater by 1 metre, namely 54·41, in his second series for a temperature 1°·6 lower, which is equivalent to a difference of 2 metres out of 50 in measurements made at the same temperature, we cannot regard the difference of 49 from the experimental numbers as serious, especially when we find Faraday's estimate

at  $0^{\circ}$  greater by about 2 metres out of 30 than the mean of Regnault's determinations at nearly the same temperature.

If we desire to carry the application of our equation to much lower temperatures, we are met by the difficulty that solid  $\text{CO}_2$  melts according to Faraday at a temperature of  $-57^{\circ}$  under a pressure of 5.33 atmospheres; and according to Regnault, at a temperature of  $-78^{\circ}.2$  solid  $\text{CO}_2$  evaporates freely into the air under a pressure of 760 millim. Now at these temperatures and pressures a kilogramme of  $\text{CO}_2$  can exist entirely in the solid, entirely in the liquid, and entirely in the gaseous state; so that its true and complete characteristic equation has three real roots for  $v$  corresponding to these three states, and it must also have two real roots corresponding to physically impossible homogeneous passage from the gaseous to the liquid and from the liquid to the solid states. Thus at these temperatures and pressures our equation ought to give five real roots for  $v$ , which it does not do, nor does any equation yet proposed. But it is enough for the present if we bridge the discontinuity between the gaseous and liquid states; much experimental work remains to be done before we can do so for the solid and liquid states by means of a single continuous equation. However, to get an idea as to how far the equation, when applied by means of Maxwell's principle, assumed still to hold, would succeed in giving the pressure of saturation at these temperatures, I made the necessary calculations, and found for the pressure of saturation at  $-57^{\circ}$  5 metres of mercury, instead of 5.33 atmospheres as Faraday determined it, and at  $-78^{\circ}$  1.5 metres or 2 atmospheres, instead of 1 atmosphere as Regnault found it or 1.14 atmosphere as Faraday.

When we pass on to test the equation by its power to give the volume of liquid  $\text{CO}_2$  at different temperatures and pressures, we are met by remarkable discord amongst the experimental results. The subjoined table contains the volume in litres of a kilogramme of liquid  $\text{CO}_2$  under pressures of 100, 200, and 300 atmospheres, as determined in capillary tubes by Caillietet and Hautefeuille (*Comptes Rendus*, xcii.) at the temperatures  $0^{\circ}$  and  $-23^{\circ}$  C., as determined in capillary tubes by Amagat for  $18^{\circ}$  C. (*Ann. de Chim. et de Phys.* 5 sér. xxii.), and as furnished by the equation for the same temperatures.

Volumes of 1 kilogramme of Liquid  $\text{CO}_2$ , in litres.

	18°.		0°.		-23°.	
	Amagat.	Equation.	Cailletet and Hautefeuille.	Equation.	Cailletet and Hautefeuille.	Equation.
100 atmosph.	1.169	1.266	1.016	1.153	0.916	1.064
200    "	1.065	1.142	0.962	1.071	0.888	1.010
300    "	1.025	1.064	0.931	1.016	0.869	0.971

It will be observed that the volumes given by the equation are all larger than those given by experiment. But at the lower pressures the disagreement is such as we are not unprepared to meet if we admit that capillary action alters the critical temperature from  $42^{\circ}8$  to  $31^{\circ}$ , and also produces the discrepancies between Amagat's and Andrews's determinations for  $35^{\circ}5$ ; for from the numbers tabulated before for  $35^{\circ}5$  we see that the deformation of the isothermals due to capillary action is greatest for pressures about 100 atmospheres, and we cannot expect the deformations to disappear in a sudden manner as we pass from  $35^{\circ}5$  to  $18^{\circ}$ . At the higher pressures the numbers given by the equation for  $18^{\circ}$  approach towards equality with those of Amagat; but the differences between the equation numbers and Cailletet and Hautefeuille's for the same temperature still amount to about 10 per cent. even at the high pressures. But the determinations of these experimenters and those of Amagat are not reconcilable with one another, as can be seen by forming the products  $pv$  and converting to Amagat's units, and plotting the results on Amagat's diagrams representing all his own experimental results (*Ann. de Chim. et de Phys.* 5 sér. xxii.); and in a less striking manner we can see the discrepancies by noting that the expansion between  $0^{\circ}$  and  $18^{\circ}$  as reckoned from Amagat's and Cailletet and Hautefeuille's results is much greater than that reckoned from  $-23^{\circ}$  to  $0^{\circ}$ , although the latter interval is nearly 1.3 times the former. The following table shows this conflict in the experimental results:—

Changes of Volume of Liquid CO<sub>2</sub>.

	From 0° to 18°.	From -23° to 0°.
100 atmospheres ...	·153	·100
200    "    ...	·103	·074
300    "    ...	·094	·062

The following table contains a comparison of the volumes in litres of a kilogramme of liquid CO<sub>2</sub> in contact with its saturated vapour at different temperatures, as determined by Thilorier (*Ann. de Chim. et de Phys.* 2 sér. lx., 1835), Mitchell (*Journ. Franklin Inst.* xxvi., 1838), and Cailletet and Mathias (*Comptes Rendus*, cii. May 1886), and by the equation.

Volumes, in litres, of a kilogramme of Liquid CO<sub>2</sub> in contact with its Saturated Vapour.

Temp.	Thilorier.	Equa- tion.	Temp.	Mitchell.	Equa- tion.	Temp.	Cailletet and Mathias.	Equa- tion.
-20°	1·111	1·124				-23	0·965	1·124
0	1·205	1·242	0	1·08	1·242	0	1·087	1·242
30	1·670	1·600	23	1·36	1·450	13	1·220	1·346
						22	1·380	1·443

While the equation is found to give results in excellent accord with Thilorier's determinations, it is in serious discord with those of Mitchell and of Cailletet and Mathias. Unfortunately Thilorier does not describe how he determined his densities; so that we cannot imagine the cause of such a large difference as that which exists between his determinations 1·205 at 0° and 1·087, the value found by Cailletet and Mathias, or 1·08 by Mitchell at the same temperature. Mitchell obtained his results by weighing the liquid in minute bulbs. Cailletet and Mathias first determined the density of saturated vapour of CO<sub>2</sub> at different temperatures in capillary tubes; then they introduced liquid CO<sub>2</sub> in unequal quantities into two vertical tubes containing mercury and communicating with one another by a horizontal tube containing mercury; the two tubes were brought to the temperature desired, and the difference of level



of the mercury in them was observed, and also the height of each of the columns of liquid  $\text{CO}_2$ ; the density of the liquid was then obtainable in terms of these measurements, and the determined density of the saturated vapour. The vapour-densities were determined from  $-23^\circ \text{C.}$  to  $30^\circ$ , and the liquid-densities from  $-34^\circ$  to  $22^\circ$ ; and both sets of densities were then represented graphically in one diagram with temperatures for abscissæ and densities for ordinates. The two branches of the curve ought to pass into one another at the critical temperature; Cailletet and Mathias, completing the curve for the small portion that was not determined by experiment, according to the obvious tendencies of the determined portions, found the critical temperature to lie between  $31^\circ$  and  $32^\circ$ . Thus, again, we meet a determination of the critical temperature in discord with Regnault's work. Probably most of the discord can be traced to the determination of the vapour-densities in capillary tubes, in which it has been shown that the density of saturation near the critical temperature may be very different from the density of saturation of the vapour in contact with a plane surface of the liquid and at the same pressure. The form of Cailletet and Mathias's curve would have to be considerably altered if  $42^\circ.8$  is the true critical temperature of  $\text{CO}_2$ ; but how far a change in the density of the liquid would have to contribute to this alteration of form we cannot say.

Thus, then, with the experimental evidence at present available, we cannot construct any equation which will bridge over the discontinuity between the liquid and gaseous states satisfactorily; because, if it represents the results of some experiments, it will fail to represent others of equal weight. I can only draw attention to the fact that Thilorier, whose determinations of pressure agree excellently with Regnault's, found densities differing by as much as 15 per cent. from those of Cailletet and Mathias. There is certainly occasion for an experimental inquiry (and much promise of interesting results to those who have the facilities for making one) into the effect of extent of surface in contact with solid and curvature of surface on the compressibility and dilatibility of fluids. There ought to be a physical effect corresponding to each term in the equation of Gauss for the energy of a fluid enclosed in a solid.

Before passing on to consider the equation in its thermodynamic aspect, it may be well to give an idea of its correspondence with experiment at low pressures and high temperatures. Amagat has given (*Comptes Rendus*, xciii., 1881) the following values of the ratio  $\frac{pv}{p'v'}$  at different temperatures where  $p'$  is about 2.85 metres of mercury and  $v=2v'$ , and the

values of the same ratio, as calculated from the equation, are furnished for comparison :—

Values of  $\frac{pv}{p'v'}$ .

	50°.	100°.	200°.	300°.
Amagat .....	1·0145	1·0087	1·0040	1·0020
Equation .....	1·0144	1·0086	1·0028	1·0001

The agreement is satisfactory at the high temperatures, if it is remembered that the values of the ratio given by experiment cannot be considered to be free from an error of at least 1 in 1000. But it must also be borne in mind how limited the range of temperature is which I was restricted to using in determining the form of Dr. Walter's function  $\beta$ , on account of the unknown amount of distortion which the isothermal for 35°·5 experiences through capillary action both in Amagat's and Andrews's experiments, a distortion which is most serious at the most important part of the curve. I have shown that, as regards  $\text{CO}_2$ , the experimental evidence is in such a state that no form can with finality be proved to be the one fit and proper form. The equation which I have given possesses the merit of representing the compressibility of  $\text{CO}_2$  at 100° and at 70° up to a pressure of 400 atmospheres, of having revealed the important effect of capillary action on the circumstance of the critical state, and of giving the saturation pressures of  $\text{CO}_2$  almost exactly as they have been experimentally determined.

The discussion, to which I proceed, of our equation in the light of the thermal effects studied by Thomson and Joule when gases are allowed to escape from under pressure through porous plugs, and of Regnault's experiments on the expansion of gases, is now of the utmost importance, as in these experiments we have to do with changes in the molecular potential energy.

According to the law of the inverse fourth power, without further hypothesis, we saw that the potential energy of a number of molecules is  $\frac{2}{3}$  of the virial of their mutual attractions. Now, in the characteristic equation,  $\frac{2}{3} \cdot \frac{l}{v}$  is the virial of the molecular attraction, and  $\frac{2}{3} l \left( \frac{1}{v_1} - \frac{1}{v_2} \right)$  is the change of the virial on the expansion of the gas from volume  $v_1$  to volume  $v_2$ . Hence the change of molecular potential energy

due to the same expansion is  $l\left(\frac{1}{v_1} - \frac{1}{v_2}\right)$ . But, apart from molecular theory entirely, we have Thomson's thermodynamic equation for the cooling-effect  $\delta$  which a gas experiences in expanding through a porous plug from volume  $v_1$  to volume  $v_2$ ,—

$$K_p \delta = \int_{v_2}^{v_1} \left( \theta \frac{\partial p}{\partial \theta} - p \right) dv + p_2 v_2 - p_1 v_1;$$

where it is to be noted that  $\theta$  means temperature taken as the reciprocal of Carnot's function and measured on Thomson's absolute thermodynamic scale,  $K_p$  is the mean specific heat of the gas in dynamic units between its temperatures on the high- and low-pressure sides of the plug,  $p_2$  and  $p_1$  are the values of the pressure on the low- and high-pressure sides respectively, and  $v_2$  and  $v_1$  are the volumes occupied by a kilogramme of the gas at the pressures  $p_2$  and  $p_1$  and at the temperature which prevails on the high-pressure side of the plug.

From the characteristic equation we have

$$v \frac{\partial p}{\partial T} = a e^{\frac{b}{v\sqrt{T}}} \left( 1 - \frac{1}{2} \frac{b}{v\sqrt{T}} \right) + \frac{c}{v}.$$

Within the experimental range of temperature we may consider

$$\frac{\partial p}{\partial T} = \frac{\partial p}{\partial \theta},$$

and within the range of volumes we can replace  $e^{\frac{b}{v\sqrt{T}}}$  by  $1 + \frac{b}{v\sqrt{T}}$ ; whence

$$v \frac{\partial p}{\partial \theta} = a + \frac{1}{2} \frac{ab}{v\sqrt{T}} + \frac{c}{v} \text{ approximately;}$$

also

$$pv = aT + \frac{ab}{v\sqrt{T}} + \frac{cT-l}{v} \text{ approximately;}$$

$$\begin{aligned} \therefore \int_{v_1}^{v_2} \left( \theta \frac{\partial p}{\partial \theta} - p \right) dv &= \int_{v_1}^{v_2} \left\{ \frac{a}{v} (\theta - T) - \frac{1}{v^2} \left( \frac{ab(2T - \theta)}{2\sqrt{T}} - (\theta - T)c - l \right) \right\} dv \\ &= a\Delta \log \frac{v_2}{v_1} + \left( \frac{1}{v_1} - \frac{1}{v_2} \right) \left( l + \Delta c - \frac{ab(T - \Delta)}{2\sqrt{T}} \right), \end{aligned}$$

where, as before,  $\Delta = \theta - T$ .

Now, in the formation of the original equation for  $\delta$  it is supposed that heat is imparted to the gas on the low-pressure side of the plug, until at the constant pressure  $p_2$  prevailing

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there it acquires the temperature which it had on the high-pressure side. The escaping gas does work  $p_2 v_2$  on the atmosphere, but at the same time it has work  $p_1 v_1$  done on it by the gas behind, so that  $p_2 v_2 - p_1 v_1$  is the total external work done by the gas; but the gas also gains potential energy by expansion, so that the total loss of kinetic energy is equal to the sum of these two quantities. But  $K_p \delta$  is the quantity of energy which has to be given to the gas after its loss of kinetic energy to bring its temperature back to what it was on the high-pressure side. Now, if the temperature of a body were a function of only the kinetic energy of its molecules, we could say that  $K_p \delta$  is the change of the kinetic energy of a kilogramme of gas on account of the expansion; but the characteristic equation shows that temperature is not a function of only the kinetic energy, for it asserts that the kinetic energy of translation of the molecules in a kilogramme

is  $\frac{3}{2} \left( a e^{\frac{b}{v \sqrt{T}}} + \frac{c}{v} \right) T$ , whence we see that we cannot consider

$K_p \delta$  as giving accurately the total change of kinetic energy due to the performance of external work and the gain of potential energy. But if from  $K_p \delta$  we subtract  $p_2 v_2 - p_1 v_1$ , we shall get a remainder depending for the most part on the change of potential energy due to expansion. If, then, we bear in mind the values already given for the constants of the characteristic equation, and the value  $\cdot 7$  for  $\Delta$ , we see from the last equation above that the greater part of the said

remainder arises from the term  $l \left( \frac{1}{v_1} - \frac{1}{v_2} \right)$ , which, according to the molecular theory, expresses the change of molecular potential energy. The term  $a \Delta \log \frac{v_2}{v_1}$  is small in com-

parison with  $l \left( \frac{1}{v_1} - \frac{1}{v_2} \right)$ ; but its meaning is very important, as it is bound up with the difficult question of the dynamical explanation of the second law of thermodynamics. The term  $\Delta c \left( \frac{1}{v_1} - \frac{1}{v_2} \right)$  may be taken with  $a \Delta \log \frac{v_2}{v_1}$ , but it is really

negligible; while the last term,  $\frac{abT}{2 \sqrt{T}} \left( \frac{1}{v_1} - \frac{1}{v_2} \right)$ , neglecting  $\Delta$

in the numerator, arises from the fact that the relation between the kinetic energy of the molecules of a gas and its temperature involves the volume occupied, and therefore varies with expansion. In fact,  $-\frac{abT}{2 \sqrt{T}} \left( \frac{1}{v_1} - \frac{1}{v_2} \right)$  represents a heating-effect

due to this cause that almost exactly neutralizes the cooling-effect,  $a\Delta \log \frac{v_2}{v_1}$ , within the range of the actual experiments ; so that the part of the total cooling-effect not due to external work reduces, on numerical substitution, almost exactly to the value of the term  $l\left(\frac{1}{v_1} - \frac{1}{v_2}\right)$ . Thus, then, we see that the general discussion of the characteristic equation in the light of Thomson's equation for the cooling-effect shows that the potential energy of the molecules of a kilogramme of  $\text{CO}_2$  may be taken as represented by  $\frac{l}{v}$ , and is therefore  $\frac{2}{3}$  of the virial of their mutual attractions. Whence, in view of the general considerations adduced at the commencement of this paper, we may consider the law of the inverse fourth power to be established.

We will now proceed to calculate the total cooling-effects  $\delta$ , and compare them with those obtained experimentally for  $\text{CO}_2$  by Thomson and Joule ("Fluids in Motion," part ii., Phil. Trans. 1854 ; part iv., 1862 ; also 'Mathematical and Physical Papers of Sir William Thomson,' vol. i.; and Joule's Scientific Papers, vol. ii. pp. 247, 342) and by Regnault ("Sur la détente des Gaz," *Mém. de l'Acad. des Sciences*, xxxvii.).

Making the same approximations as previously, we get

$$p_2 v_2 - p_1 v_1 = \left(\frac{1}{v_1} - \frac{1}{v_2}\right) \left\{ l - \left( \frac{ab}{\sqrt{T}} + c \right) T \right\} ;$$

$$\therefore K_p \delta = \left(\frac{1}{v_1} - \frac{1}{v_2}\right) \left\{ 2l - \left( \frac{3ab}{2\sqrt{T}} + c \right) T \right\} + a\Delta \log \frac{v_2}{v_1}.$$

We see that, except for the small term  $a\Delta \log \frac{v_2}{v_1}$ ,  $\delta$  is proportional to  $\frac{1}{v_1} - \frac{1}{v_2}$ , or within the limits of pressure employed by Thomson and Joule to  $p_1 - p_2$ . This was the first result discovered by Thomson and Joule ; and, in accordance with it, they reduced their determinations to the one standard of the cooling-effect experienced by the gas in escaping through a porous plug into the atmosphere under a pressure in excess of the atmospheric by that of 100 English inches, or 2.54 metres of mercury.

In the following Table the numbers taken from Thomson and Joule's "Fluids in Motion," part ii., are marked II.; the others are from part iv. The values of  $K_p$  at different temperatures have been obtained by interpolating from

Regnault's data by the equation

$$K_p = 426(\cdot 187 + \cdot 00027t).$$

Cooling-effects experienced by  $\text{CO}_2$  when escaping at different temperatures through a porous plug into the atmosphere under an excess of pressure of 2·54 metres of mercury.

Temperature C. ....	7°·38.	7°·96.	19°·1.	35°·6.	54°.	91°·5.	93°·5.	97°·5.
Observed by Thomson } and Joule .....	4·367	4·215	3·876 II.	3·407	2·951	2·348 II.	2·164	2·135
Calculated from equation	3·940	3·920	3·670	3·330	3·010	2·470	2·453	2·395

When the great difficulty of these experiments with porous plugs is considered (they baffled Regnault himself, "*Sur la détente des Gaz*," p. 707), the agreement between the calculated and observed cooling-effects will be seen to be satisfactory. Regnault, while unable to get satisfactory results by the porous-plug method, obtained some valuable data by allowing gases to expand through a fine hole in a thin wall into a calorimeter, and also by allowing them to expand through silver capillary tubes of different lengths. As the excess of pressure which he employed was on the whole greater than the average excess in Thomson and Joule's experiments, and was such that we can no longer consider

$\frac{1}{v_1} - \frac{1}{v_2}$  as proportional to  $p_1 - p_2$ , I have applied Thomson's equation for the cooling-effect to the actual circumstances of each of Regnault's experiments.

Cooling-effects experienced by  $\text{CO}_2$  in escaping at different temperatures into the atmosphere under different pressure-excesses.

Temperature at the high pressure.	Excess of pressure, in millim. of mercury.	Observed by Regnault.	Calculated from equation.
-25° C.	7541	18·73	15·30
3	3354	5·43	5·50
3	7764	12·73	12·93
15	38591	81·96	73·80
100	4682	4·72	4·34
100	7921	9·88	7·30

If, for the moment, we set apart the results for  $15^{\circ}$  and  $-25^{\circ}$ , on account of the large sources of experimental error incident to the employment of the very high excess of pressure (38591 millim., or 50 atmospheres) in the one set and the low temperature in the other, we find the agreement to be excellent, except in the case of the high excess (7921) at  $100^{\circ}$ , where Regnault found a cooling of  $9^{\circ}88$ , and the equation gives  $7^{\circ}30$ ; but here the experiment is evidently at fault, because, while the pressure-excess is not much more than  $\frac{3}{2}$  of 4682, the cooling-effect is more than double  $4^{\circ}72$ —a result in complete disaccord with all Thomson and Joule's and Regnault's general results.

With regard to Regnault's number for  $15^{\circ}$ , obtained from capillary-tube experiments, we can see at once how the experiments are certain to yield too great a cooling-effect; for it is certain that the gas at the high-pressure end of the capillary tube, which is assumed to be all at the temperature  $15^{\circ}$  of the bath surrounding it, cannot be at that temperature quite close to the capillary tube, where the gas is doing work at the great rate due to the excess of pressure of 50 atmospheres; thus it is certain that the gas is cooled before it enters the capillary tube. Under these circumstances we may consider the agreement between the experimental cooling-effect  $81^{\circ}96$  and the theoretical one of  $73^{\circ}8$  to be all that could be expected. The same sort of remarks apply to the experimental determination at  $-25^{\circ}$  (the number given above is the mean of five determinations made by Regnault).

Thus, then, the experiments of Regnault, which the great experimenter lamented as having cost him all too dear in thought, effort, and time for the results achieved, no less than those which cost the great English experimenters so much time valuable to science, are of fundamental value to molecular physics, if it is allowed that the agreement between them and the results deduced from the characteristic equation for  $\text{CO}_2$  is such as to justify the statement that the potential energy of the molecules of a kilogramme of  $\text{CO}_2$  occupying a volume  $v$  is  $\frac{l}{v}$ , and is equal to  $\frac{2}{3}$  of the virial of the molecular attraction.

As Thomson and Joule and Regnault conducted expansion experiments on air, further light may be obtained by a brief discussion of them.

In constructing a characteristic equation for air I used Amagat's data for  $16^{\circ}$  (*Comptes Rendus*, xcix.), and his general result that, at  $100^{\circ}$  and up to 8-atmospheres' pressure, the departures of air from the Boyle-Mariotte law were too small to be measurable. These, with Regnault's value for the

coefficient of expansion of air under a pressure of one atmosphere, and for the density of air, led to the following equation :—

$$pv = \frac{avT}{v-c} - \frac{l}{v};$$

with the following values for the constants when the unit of pressure is that of a kilogramme weight per square metre and the unit of volume is a cubic metre,  $v$  being the volume occupied by a kilogramme of air :—

$$a=29\cdot3, \quad c=.001056, \quad l=12\cdot372.$$

This equation was intended for use only within the range of pressures of Thomson and Joule's experiments; but it happens to give the critical temperature and pressure of air with considerable accuracy. When these are determined as for  $\text{CO}_2$ , we get the critical temperature as  $-154^\circ \text{C.}$ , the critical pressure as 40 atmospheres, and the critical volume of a kilogramme of air as  $\cdot003167$  cubic metres. Wroblewski's determinations (Wiedemann's *Ann.* xxvi. 1885) make the critical temperature about  $-140^\circ \text{C.}$  and the critical pressure about 40 atmospheres. We have seen in the case of  $\text{CO}_2$  how a difference of  $\pm 10^\circ$  is possible between the true critical temperature of a gas and its critical temperature in a capillary tube; hence the above equation for air, though constructed on limited data, is probably as accurate an equation as is possible with our present data. The values of the ratio  $\frac{p_1 v_1}{p_0 v_0}$  given by it for  $4^\circ \text{C.}$  do not agree exactly with those given by Regnault's equation for  $4^\circ$ ,

$$\frac{p_1 v_1}{p_0 v_0} = 1 - \cdot0011054 \left( \frac{v_0}{v_1} - 1 \right) + \cdot00001938 \left( \frac{v_0}{v_1} - 1 \right)^2.$$

Thus, for example, when  $p_1 = 15$  atmospheres, Regnault's equation gives

$$\frac{p_1 v_1}{p_0 v_0} = 1\cdot0117;$$

while the equation above gives  $1\cdot0085$ . The difference is due to the fact that Regnault's determinations at  $4^\circ$  and Amagat's at  $16^\circ$  are not strictly reconcilable with one another. Amagat's were made in capillary tubes; but as he has pushed his determinations to higher pressures than Regnault, so as to pass the point for which  $pv$  is a minimum, and is thus likely to have obtained with more accuracy the general sense of the changes in  $pv$ , I adopted his results, seeing that the discrepancy is



more likely to be due to a slight misestimation on Regnault's part of the small differences of his ratios from 1 than to capillary action in Amagat's tube, which, at the temperature and pressure in question, must be slight; but the point is one not unworthy of being inquired into, whether the slight discord between Regnault's and Amagat's experiments is due to capillary action.

To determine from the equation the cooling-effects experienced by air in passing through porous plugs, we can write it in the form

$$\begin{aligned}pv &= aT\left(1 + \frac{c}{v}\right) - \frac{l}{v}; \\ \therefore v \frac{\partial p}{\partial T} &= a\left(1 + \frac{c}{v}\right); \\ \therefore \theta \frac{\partial p}{\partial \theta} - p &= a \frac{\Delta}{v} \left(1 + \frac{c}{v}\right) + \frac{l}{v^2}; \\ \therefore K_p \delta &= \int_{v_1}^{v_2} \left\{ a \frac{\Delta}{v} \left(1 + \frac{c}{v}\right) + \frac{l}{v^2} \right\} dv + p_2 v_2 - p_1 v_1 \\ &= a \Delta \log \frac{v_2}{v_1} + ac \Delta \left( \frac{1}{v_1} - \frac{1}{v_2} \right) + l \left( \frac{1}{v_1} - \frac{1}{v_2} \right) + p_2 v_2 - p_1 v_1.\end{aligned}$$

Here, as before,  $K_p \delta$  is the quantity of energy which has to be imparted to the gas on the low-pressure side to bring, not the kinetic energy, but the temperature of the gas to its original value on the high-pressure side. If we subtract  $p_2 v_2 - p_1 v_1$  from this, and neglect the term involving  $c$ , on account of its smallness, we have  $a \Delta \log \frac{v_2}{v_1} + l \left( \frac{1}{v_1} - \frac{1}{v_2} \right)$  as the amount of energy imparted to compensate not only for conversion of the amount of kinetic energy  $l \left( \frac{1}{v_1} - \frac{1}{v_2} \right)$  into potential energy, but also to compensate for the cooling  $a \Delta \log \frac{v_2}{v_1}$  which would occur even in a gas for which  $l=0$ , or in the ideal perfect gas.

Many writers have ignored this result of the difference  $\Delta$  which Thomson and Joule demonstrated to exist between the temperature of melting ice, as measured on the absolute thermodynamic and the air-thermometers, and they have asserted that, for a perfect gas whose equation is  $pv=aT$  the cooling-effect obtainable must be zero; whereas, while the equation for air at temperatures near  $100^\circ \text{C.}$  may be written  $pv=aT$ , Thomson and Joule were able to demonstrate a quite measurable cooling-effect at that temperature. Before the cooling-effect for a body can be zero, its equation must be

$pv=a\theta$ . The import of the term  $a\Delta \log \frac{v_2}{v_1}$  is therefore thermodynamical, and cannot at present be explained on purely molecular grounds. Its relative importance in the case of air is much greater than in that of  $\text{CO}_2$ ; for at  $0^\circ \text{C}$ . its value is  $\frac{3}{10}$  of that of  $l\left(\frac{1}{v_1}-\frac{1}{v_2}\right)$ , and at  $100^\circ$  it is  $\frac{2}{3}$  of it. Taking account of the fact, then, that  $a\Delta \log \frac{v_2}{v_1}$  has nothing to do directly with the forces acting between the molecules, we find, in the purely thermodynamic estimate of the energy imparted to the expanding gas to keep its temperature constant, the term  $l\left(\frac{1}{v_1}-\frac{1}{v_2}\right)$ . But this is the term which our theory of molecular force would lead us to expect as representing the change of kinetic energy due to increase of potential energy. Hence we may consider it as proved that the molecular potential energy of a kilogramme of air occupying a volume  $v$  is  $\frac{l}{v}$ .

For the total cooling effect we get, on substituting for  $p_2v_2-p_1v_1$  its value,

$$K_p\delta = a\Delta \log \frac{v_2}{v_1} + \left(\frac{1}{v_1} - \frac{1}{v_2}\right)\{2l - ac(T - \Delta)\}.$$

As  $v_1$  and  $v_2$  are directly proportional to  $T$ , if  $p_1$  and  $p_2$  have always the same values at different temperatures, the term  $acT\left(\frac{1}{v_1}-\frac{1}{v_2}\right)$  is constant, and when evaluated numerically is almost equal to  $a\Delta \log \frac{v_2}{v_1}$ , within the range of Thomson and Joule's experiments; so that  $K_p\delta$  reduces nearly, but not quite, to  $2l\left(\frac{1}{v_1}-\frac{1}{v_2}\right)$ ; whence we find the cooling-effect proportional to  $p_1-p_2$ , which is the experimental result.

Cooling-effects for Air escaping at different temperatures through porous plugs into the atmosphere under an excess of pressure of 100 English inches, or 2.54 metres of mercury.

Temperature C. ....	$7^\circ.1$ .	$17^\circ$ .	$39^\circ.5$ .	$92^\circ.8$ .
Observed by Thomson } and Joule .....	.88	.86 II.	.75	.51
Calculated from equation	.96	.93	.86	.72

The calculated numbers are all larger than the observed ; but we must take account of the smallness of the quantities and the magnitude of the possible experimental errors : thus, the experimental cooling for  $17^{\circ}$ , namely  $\cdot 86^{\circ}$ , is the mean of the results of seven series of experiments, the extremes being  $\cdot 806^{\circ}$  and  $\cdot 958^{\circ}$ . Moreover, Regnault's determinations seem to show that Thomson and Joule's results for air are perhaps somewhat too small. Thus, as the mean of six series of experiments at about  $16^{\circ}$  C., in which air expanded twelve times in succession through the fine hole between the successive chambers of a calorimeter before it passed from the high-pressure to the low-pressure states, Regnault found the cooling-effect due to a pressure-excess of 1 metre of mercury to be  $\cdot 3548^{\circ}$ , which corresponds to a cooling-effect of  $\cdot 9012^{\circ}$  for a pressure excess of 100 English inches. Again, Regnault, by expanding air through a silver capillary tube 2.5 metres long, found the cooling-effect at about  $16^{\circ}$  to be  $\cdot 377^{\circ}$  for a pressure-excess of 1 metre of mercury—that is,  $\cdot 9576^{\circ}$  for an excess of 100 English inches. These are the only two definite determinations made by Regnault for air ; and we find that their mean,  $\cdot 93^{\circ}$ , is identical with the number given by the equation for  $17^{\circ}$ .

Van de Waals (Wiedemann *Beiblätter*, i.), with an equation founded on Regnault's determinations, obtains a cooling-effect at  $17^{\circ}$  almost identical with Thomson and Joule's result ; but in his equation for the cooling-effect, the term  $a\Delta \log \frac{v_2}{v_1}$ , arising from the difference between the absolute thermodynamic and absolute air-thermometric scales, is omitted ; if included, it would increase his theoretical effect by about  $\cdot 3$  of its own amount.

As far, then, as the experiments on the cooling of air by expansion are available as evidence, they go to show that the potential energy of the molecules of a kilogramme of air is  $\frac{l}{v}$ , and is equal to  $\frac{2}{3}$  of the virial of the molecular attractions.

Thomson and Joule and Regnault also conducted experiments on the cooling of hydrogen by expansion ; but its amount was too small for satisfactory measurement. Regnault obtained a slight cooling-effect ; so also did Thomson and Joule in their researches (part ii.) ; but in their researches (part iv.) they found a slight heating-effect. The only conclusion possible is that the real effect for hydrogen is smaller than the possible experimental errors.

From Amagat's experiments on hydrogen I obtained the

following equation :—

$$pv = \left( ae^{\frac{b}{v}} - \frac{c}{v} \right) T - \frac{l}{v};$$

where

$$a = 422 \cdot 14, \quad b = \cdot 012831, \quad c = \cdot 83497, \quad l = 376 \cdot 5;$$

the unit of pressure being that of a kilogramme weight per square metre, and the unit of volume a cubic metre,  $v$  being the volume of a kilogramme of hydrogen. Amagat's unit of volume is  $\frac{1}{3402}$  of that occupied by the gas at  $0^\circ$  and 760 millim. The critical temperature given by this equation is  $T = 30^\circ \cdot 56$  or  $t = -242^\circ \cdot 4$ ; the critical pressure is 22 atmospheres, and the critical volume of a kilogramme of hydrogen is  $\cdot 02076$  cubic metre.

Olszewski (*Comptes Rendus*, 101. p. 238) states that he has submitted hydrogen to pressures varying from 20 to 180 atmospheres at  $-220^\circ$  C. without getting it liquefied. The temperature  $-220^\circ$  was measured by means of a hydrogen-thermometer, on the assumption, I presume, that hydrogen under pressures near that of 1 atmosphere obeys Charles's or Gay-Lussac's law right down to that low temperature. The above equation fully justifies Olszewski's assumption, and his reliance on the hydrogen-thermometer; for whether it is used as a constant-volume or constant-pressure thermometer, its indications for volume or pressure near the normal, as calculated by Charles's or Gay-Lussac's law, are not appreciably different from those calculated from the above equation. This is an important fact in Physics—that there should exist a substance capable of giving regular thermometric measurements almost down to absolute zero.

We may regard the above-determined critical temperature of hydrogen as remarkably near the truth, considering how far beyond Amagat's experimental range we are extrapolating. Wroblewski (*Comptes Rendus*, 100. p. 979), by suddenly expanding hydrogen cooled down to the melting-point of solid nitrogen, from a pressure of 180 atmospheres to that of 1 atmosphere, got signs of liquefaction such as Olszewski had also obtained in a similar manner, while his thermopile in the fluid indicated  $-208^\circ$  or  $-211^\circ$ ; but he cannot say how nearly the thermopile itself actually came to the true temperature of ebullition of hydrogen under a pressure of 1 atmosphere.

The cooling effect for hydrogen at  $0^\circ$  C., expanding through plugs under a pressure-excess of 100 inches of mercury, is found from the above equation to be  $\cdot 2^\circ$ . Regnault found a cooling of  $\cdot 04^\circ$ , and Thomson and Joule (part ii.) found a cooling of  $\cdot 07^\circ$ ; but in their latest determination the effect found for hydrogen was an irregular heating-effect. This

shows the amount of experimental error possible in these very difficult experiments, and also shows the degree of accuracy which is to be looked for in the experiments on air and  $\text{CO}_2$ .

The only other experiments that I know to be on record on cooling by expansion are those which Hirn made with steam (*Théorie Mécanique de la Chaleur*); but before they can be studied in the same manner as those on  $\text{CO}_2$  and air have been in this paper, an equation on the pure "Virial" model will have to be constructed for steam.

The fields of application for the molecular law of the inverse fourth power are wide and inviting. In the theory of capillary action it ought to lead to the accurate determination of the size of the molecular domain in different substances under specified conditions, or, in other words, of the number of molecules in unit mass of all bodies. In the theory of elasticity its possibilities are vast; for, applied in connexion with the great accumulation of facts bearing on crystalline structure, it ought ultimately to render possible a general theory of the structure of molecules. But the most inviting direction for immediate research is towards the law of variation of  $l$  with variation in molecular constitution. It remains to be seen whether the experimental data at present available are sufficient to give a clue to it; but there is no doubt that the progress of molecular physics and chemical dynamics requires experimental data for the structure of the characteristic equations of a large number of bodies, for example of the members of many homologous series of organic compounds; for, before we can hope to understand the atomic forces at play in chemical action, we must possess a complete knowledge of molecular actions.

With  $\frac{G}{r^2} + \frac{M}{r^4}$  to express the law of molic force through the whole range of distances from molecular up to astronomical, one is tempted to speculate whether the law of the terms representing atomic or chemic force may not be expressed by one or more higher powers of  $\frac{1}{r^2}$ , representing a force insensible at molecular distances as the molecular term of molic force is insensible at astronomical distances, but sensible at atomic distances, with the associated idea that atomic distances are exceedingly small compared to molecular. This conception would (speaking in a purely relative manner) reduce the molecules almost to mathematical points, and would almost remove the difficulty as to the collisions of molecules. In this manner we can endeavour to realize all the actions of matter on matter as pure attractions.