

On the Determination of Molecular Fields. II. From the Equation of State of a Gas

J. E. Jones

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On the Determination of Molecular Fields.—II. From the Equation of State of a Gas.

By J. E. JONES, D.Sc., 1851 Exhibition Senior Research Student,
Trinity College, Cambridge.

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C O N T E N T S .

	Page
§ 1. Introduction	463
§ 2. The Second Virial Coefficient.....	465
§ 3. The Determination of the Force Constants.....	468
§ 4. The Molecular Field of Argon.....	469

1. *Introduction.*

The investigation of a preceding paper* has shown that the temperature variation of viscosity, as determined experimentally, can be satisfactorily explained in many gases on the assumption that the repulsive and attractive parts of the molecular field are each according to an inverse power of the distance. In some cases, in argon, for example, it was further shown that the experimental facts can be explained by more than one molecular model, from which we inferred that viscosity results alone are insufficient to determine precisely the nature of molecular fields. The object of the present paper is to ascertain whether a molecular model of the same type will also explain available experimental data concerning the equation of state of a gas, and if so, whether the results so obtained, when taken in conjunction with those obtained from viscosity, will definitely fix the molecular field.

Such an investigation is made possible by the elaborate analysis by Kamerlingh Onnes† of the observational material. He has expressed the results in the form of an empirical equation of state of the type

$$pv = A + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^4} + \frac{E}{v^6} + \frac{F}{v^8},$$

where the coefficients A ... F, called by him *virial coefficients*, are determined as functions of the temperature to fit the observations. Now it is possible by various methods to obtain a theoretical expression for B as a function

* 'Roy. Soc. Proc.' above.

† Kamerlingh Onnes, 'Communications Phys. Lab. of Leiden,' No. 71, or 'Proc. Sect. of Sciences, Amsterdam,' vol. 4, p. 125 (1902).

of the temperature* and a strict comparison can then be made between theory and experiment. Unfortunately the solution for B, although applicable to any molecular model of spherical symmetry, is purely formal and contains an integral which can be evaluated only in special cases. This has been done up to now for only two simple models, viz., a van der Waals molecule, and a molecule repelling according to an inverse power law (without attraction), but it is shown in this paper that it can also be evaluated in the case of the model, which was successful in explaining viscosity results. As the two other models just mentioned are particular cases of this, the appropriate formulæ for B are easily deduced from the general one given here.

By graphical means, it is then possible to test whether this model can also explain the experimental results of Kamerlingh Onnes. Fortunately, enough experimental results are available for the same gas, as that considered in the former paper, viz., argon, for it again to be considered in detail. For this gas, Keesom has already shown that a van der Waals model will explain the facts, but it is here found, as in the case of viscosity, that more than one kind of repulsive field is possible; in fact, a repulsion according to any power higher than 14 will suffice.

A method is here given of determining the force constants, both attractive and repulsive, from a comparison of the theoretical and experimental values for B. That of repulsion is found to be greater in all cases than the corresponding results obtained from viscosity, and so it does not prove possible to obtain a molecular model which will simultaneously explain the two sets of experimental facts.

The discrepancy between the two results may be due to the fact that the molecular fields determined by the two methods are not strictly comparable. One method gives the forces brought into play between molecules during an encounter, while the other gives a statistical average of the forces on any one molecule due to all those which surround it. In the one case, a mutual polarisation of the molecules may arise to affect the molecular field, while in the other, the symmetrical distribution of molecules, which is assumed, may imply a cancellation of all polarisation effects.†

* Jeans, 'Dynamical Theory of Gases,' 3rd ed., 1921, p. 132; Keesom, 'Comm. Phys. Lab. Leiden,' Supplement No. 24, 1912, or 'Proc. Sect. of Sciences, Amsterdam,' vol. 15 (1), p. 256; Core, 'Phil. Mag.,' August, 1923; J. E. Jones, 'Proc. Camb. Phil. Soc.,' vol. 22, pt. 2, p. 105 (1924).

† *Note added later*: A few days after this paper was communicated, further experimental work on the equation of state of argon was published, giving values of the second virial coefficient inconsistent with those of Kamerlingh Onnes, considered in the

On the Determination of Molecular Fields.

465

§ 2. *The Second Virial Coefficient.*

Theoretical calculations of the equation of state of a gas of moderately large dilution result in a formula of the type*

$$pv = kNT \left(1 + \frac{B}{v} \right),$$

where, as usual, p , v and T denote pressure, volume and temperature respectively, k the Boltzmann gas constant, N the total number of molecules in the gas, and B the second virial coefficient. The latter is a function of temperature only, its form depending only on the nature of the molecule. This equation of state is, like that of van der Waals, true only as a first approximation. It does not apply, for instance, at high pressures.

For molecules of spherical symmetry, which can be represented by a potential field $\pi(r)$, the formula for B is usually given as*

$$B = 2\pi N \int_0^\infty r^2 (1 - e^{2j\pi(r)}) dr, \quad (2.02)$$

where $2j = 1/kT$. An alternative form for B is†

$$B = \frac{2\pi N}{3kT} \int_0^\infty r^3 f(r) e^{2j\pi(r)} dr, \quad (2.03)$$

where $f(r)$ is the force between two molecules when separated by a distance r , and is obviously related to $\pi(r)$ by the equation

$$\pi(r) = - \int_r^\infty f(r) dr. \quad (2.04)$$

The identity of the two formulæ for B is easily established on integrating equation (2.03) by parts. The proof requires that

$$\lim_{r \rightarrow \infty} r^3 (e^{2j\pi(r)} - 1) = 0, \quad (2.041)$$

which is easily seen to be a condition that B shall remain finite. This places a restriction on the molecular models which are possible. For instance, if

$$f(r) = \frac{\lambda_n}{r^n} - \frac{\lambda_m}{r^m}, \quad (2.05)$$

the condition requires that neither n nor m shall have a value less than 4.

The difficulty of expressing B as an explicit function of the temperature is the body of this paper. The later values have been treated independently by the methods of this paper, leading to results more in line with those already obtained from viscosity measurements (*see* Appendix).

* Keesom, Core, J. E. Jones, *loc. cit.*

† Jeans, 'Dynamical Theory of Gases,' 3rd edn., p. 132, eqns. (331) and (335).

therefore the purely technical one of evaluating either of the integrals (2.02) or (2.03). This has been done in the case of only two simple models. Thus for molecules which repel according to an inverse power of the distance $\lambda_n r^{-n}$,*

$$B = \frac{2}{3}\pi N \left(\frac{2j\lambda_n}{n-1} \right)^{3/n-1} \Gamma \left(\frac{n-4}{n-1} \right), \quad (2.06)$$

while for molecules which behave as rigid spheres of diameter σ , surrounded by an attractive field of force of the type $\lambda_m r^{-m}$, Keesom† has shown that

$$B = \frac{2}{3}\pi N \sigma^3 \left\{ 1 - \sum_{\tau=1}^{\infty} \frac{3(2j\lambda_m)^{\tau}}{\tau! (\tau m - 1 - 3)} \right\}. \quad (2.07)$$

We now proceed to show that the integration can also be effected in the case of another model, whose field is represented by a repulsive force $\lambda_n r^{-n}$ and an attractive force $\lambda_m r^{-m}$. In this case, we have

$$\int_0^{\infty} r^3 f(r) e^{2j\pi(r)} dr = \int_0^{\infty} \left(\frac{\lambda_n}{r^{n-3}} - \frac{\lambda_m}{r^{m-3}} \right) e^{2j\pi_1(r)} e^{2j\pi_2(r)} dr, \quad (2.08)$$

$$\text{where} \quad \pi_1(r) = -\frac{\lambda_n}{(n-1)r^{n-1}}, \quad \pi_2(r) = \frac{\lambda_m}{(m-1)r^{m-1}}. \quad (2.09)$$

Expanding the second exponential, we find that the right-hand side consists of the difference of two integrals of the type

$$\int_0^{\infty} e^{-bx^{-q}} \left\{ x^{-s} + \frac{ax^{-p-s}}{1!} + \frac{a^2x^{-2p-s}}{2!} + \dots + \frac{a^px^{-\tau p-s}}{\tau!} + \dots \right\} dx.$$

Using the fact that

$$\int_0^{\infty} x^{-t} e^{-bx^{-q}} dx = \frac{1}{q} (b)^{\frac{1-t}{q}} \Gamma \left(\frac{t-1}{q} \right), \quad (2.10)$$

we then have

$$\begin{aligned} \int_0^{\infty} r^3 f(r) e^{2j\pi(r)} dr &= \frac{\lambda_n}{n-1} \sum_{\tau=0}^{\infty} \frac{1}{\tau!} \left(\frac{2j\lambda_m}{m-1} \right)^{\tau} \left(\frac{n-1}{2j\lambda_n} \right)^{\frac{\tau(m-1)+n-4}{n-1}} \Gamma \left(\frac{\tau m - 1 + n - 4}{n-1} \right) \\ &\quad - \frac{\lambda_m}{m-1} \sum_{\tau=0}^{\infty} \frac{1}{\tau!} \left(\frac{2j\lambda_m}{m-1} \right)^{\tau} \left(\frac{n-1}{2j\lambda_n} \right)^{\frac{\tau(m-1)+m-4}{n-1}} \Gamma \left(\frac{\tau m - 1 + m - 4}{n-1} \right). \end{aligned} \quad (2.11)$$

We shall find later in applying the theoretical formula that it is not necessary to deal with a clumsy expression of this kind. It is sufficient to express B as a function of a function of temperature. Thus, we shall find it convenient to write

$$\begin{aligned} \int_0^{\infty} r^3 f(r) e^{2j\pi(r)} dr &= \frac{\lambda_n}{n-1} \left(\frac{n-1}{2j\lambda_n} \right)^{(n-4)/(n-1)} \sum_{\tau=0}^{\infty} \frac{y^{\tau}}{\tau!} \Gamma \left(\frac{\tau m - 1 + n - 4}{n-1} \right) \\ &\quad - \frac{\lambda_m}{m-1} \left(\frac{n-1}{2j\lambda_n} \right)^{(m-4)/(n-1)} \sum_{\tau=0}^{\infty} \frac{y^{\tau}}{\tau!} \Gamma \left(\frac{\tau m - 1 + m - 4}{n-1} \right), \end{aligned} \quad (2.12)$$

* Jeans, 'Dynamical Theory of Gases,' 3rd edn., p. 134.

† Keesom, 'Comm. Phys. Lab. Leiden,' Supplement 24B, p. 32 (1912); 'Proc. Sect. of Sciences, Amsterdam,' vol. 15 (1), p. 256.

On the Determination of Molecular Fields.

467

where

$$y = \frac{2j\lambda_m}{m-1} \left(\frac{n-1}{2j\lambda_n} \right)^{(m-1)/(n-1)}. \quad (2.13)$$

After some reduction, the expression (2.12) further simplifies to

$$\frac{1}{2j} \left(\frac{2j\lambda_n}{n-1} \right)^{3/n-1} \sum_{\tau=0}^{\infty} \frac{y^{\tau}}{\tau!} \left\{ \Gamma \left(\frac{\tau \overline{m-1} + n-4}{n-1} \right) - \frac{m-1}{n-1} \Gamma \left(\frac{\tau \overline{m-1} + m-4}{n-1} \right) \cdot y \right\}. \quad (2.14)$$

We have next to express the power of $2j$ outside the series as a function of y . It is not difficult to show that

$$\left(\frac{2j\lambda_n}{n-1} \right)^{3/(n-1)} = \left(\frac{\lambda_n}{n-1} \cdot \frac{m-1}{\lambda_m} \cdot y \right)^{3/(n-m)}, \quad (2.15)$$

whence we get

$$\int_0^{\infty} r^{3f} (r) e^{2j\pi(r)} dr = \frac{1}{2j} \left(\frac{\lambda_n}{n-1} \cdot \frac{m-1}{\lambda_m} \right)^{3/(n-m)} F(y), \quad (2.16)$$

where

$$F(y) = y^{3/(n-m)} \sum_{\tau=0}^{\infty} \frac{y^{\tau}}{\tau!} \left\{ \Gamma \left(\frac{\tau \overline{m-1} + n-4}{n-1} \right) - \frac{m-1}{n-1} \Gamma \left(\frac{\tau \overline{m-1} + m-4}{n-1} \right) y \right\}. \quad (2.17)$$

This function can also be written in the form

$$F(y) = y^{3/(n-m)} \left\{ \Gamma \left(\frac{n-4}{n-1} \right) - \sum_{\tau=1}^{\infty} f(\tau) y^{\tau} \right\}, \quad (2.18)$$

where

$$\begin{aligned} f(\tau) &= \frac{m-1}{n-1} \cdot \frac{1}{(\tau-1)!} \Gamma \left(\frac{\tau \overline{m-1} - 3}{n-1} \right) - \frac{1}{\tau!} \Gamma \left(\frac{\tau \overline{m-1} + n-4}{n-1} \right) \\ &= \frac{3\Gamma \left(\frac{\tau \overline{m-1} + n-4}{n-1} \right)}{\tau! (\tau \overline{m-1} - 3)} = \frac{3\Gamma \left(\frac{\tau \overline{m-1} - 3}{n-1} \right)}{\tau! (n-1)}. \end{aligned} \quad (2.19)$$

Finally, we obtain for B the result

$$B = \frac{2}{3}\pi N \left(\frac{\lambda_n}{n-1} \cdot \frac{m-1}{\lambda_m} \right)^{3/(n-m)} F(y). \quad (2.20)$$

From this general formula the ones previously mentioned can be deduced as special cases. The first, equation (2.06), is obtained by putting $y=0$ and $\lambda_m=0$ in equation (2.12). To deduce the second, we observe that a rigid sphere molecule corresponds to a force $\lambda_n r^{-n}$ when $n \rightarrow \infty$, the diameter σ being given by

$$\sigma = \lim_{n \rightarrow \infty} \lambda_n^{1/n-1}. \quad (2.201)$$

Hence, from equation (2.13), we have for y in this case

$$y = \frac{2j\lambda_m}{m-1} \frac{1}{\sigma^{m-1}} = 2ju,$$

say, and making $n \rightarrow \infty$ in the expression for $F(y)$, we obtain

$$f(\tau) = \frac{3}{\tau! (\tau m - 1 - 3)},$$

leading at once to Keesom's result, already quoted.

§ 3. *The Determination of the Force Constants.*

The values of B which Kamerlingh Onnes* gives at various temperatures apply to a unit volume of the gas, and the appropriate value of B is denoted by B_N . We may say, then, that experiment gives

$$B_N = f(T),$$

while theory gives

$$B_N = \frac{2}{3}\pi v \left(\frac{\lambda_n}{n-1} \cdot \frac{m-1}{\lambda_m} \right)^{3/(n-m)} F(y), \quad (3.01)$$

v denoting the molecular concentration. The problem is now to investigate whether, for certain values of n and m , values of the force constants λ_n and λ_m can be found to make the above two functions identical.

The method we use is a modification of one already used by Keesom† for simple models. The experimental values are plotted on transparent paper with $\log T$ as abscissæ and $\log |B_N|$ as ordinates. On another piece of squared paper, $\log |F(y)|$ is plotted against $\log y$, the scale of $F(y)$ being the same as that of $\log B_N$, while the scale‡ of $\log y$ is taken to be $\frac{n-1}{n-m}$ that of $\log T$.

Further the scale of $\log y$ is made to increase in the opposite direction to $\log T$. If, by moving the experimental curve over the theoretical curve (keeping always the two sets of axes parallel) coincidence can be obtained, then the particular model considered is a suitable one.

* Kamerlingh Onnes, *loc. cit.*

† Keesom, *loc. cit.*

‡ This is done because y is proportional to the $\frac{m-n^{\text{th}}}{n-1}$ power of T , and the subsequent work requires that $\log y + \frac{n-m}{n-1} \log T$ shall be the same for any corresponding values of y and T .

On the Determination of Molecular Fields.

469

If coincidence is obtained by a parallel transformation (X, Y), then we have

$$\log y + \frac{n-m}{n-1} \log T = X, \quad (3.02)$$

$$\log B_N - \log F(y) = Y, \quad (3.03)$$

from which we have, on substituting the theoretical expressions for y and $F(y)$ from equations (2.13) and (3.01),

$$-\frac{m-1}{n-1} \log \frac{\lambda_n}{n-1} + \log \frac{\lambda_m}{m-1} = X + \frac{n-m}{n-1} \log k, \quad (3.04)$$

$$\frac{3}{n-m} \log \frac{\lambda_n}{n-1} - \frac{3}{n-m} \log \frac{\lambda_m}{m-1} = Y - \log \frac{2\pi\nu}{3}. \quad (3.05)$$

These are two equations to determine λ_n and λ_m . The explicit formulæ for them are then

$$\frac{3}{n-1} \log \frac{\lambda_n}{n-1} = \frac{3}{n-m} X + Y - \log \frac{2\pi\nu}{3} + \frac{3}{n-1} \log k, \quad (3.06)$$

$$\frac{3}{m-1} \log \frac{\lambda_m}{m-1} = \frac{3(n-1)}{(n-m)(m-1)} X + Y - \log \frac{2\pi\nu}{3} + \frac{3}{m-1} \log k. \quad (3.07)$$

The determination of molecular fields by this method requires, therefore, only the fitting together of theoretical and experimental curves to find the values of X and Y.

§ 4. The Molecular Field of Argon.

For reasons stated in the introductory paragraph, the gas to which we want to apply the analysis of this paper is argon. The experimental values of B_N for different temperatures for this gas can be deduced from certain data given in a paper by Kamerlingh Onnes and Crommelin.* In Table I, we give the values of $\log B_N$, calculated from the values of A_A , B_A given in their paper ($B_N = B_A/A_A$). These values, plotted against $\log T$, are shown in fig. 1.

In the preceding paper, we showed that, in the case of argon, the experimental variation of viscosity could be explained on the supposition that molecules repelled according to the law $\lambda_n r^{-n}$, and that n had any value between 14 and 25.

* Kamerlingh Onnes and Crommelin, 'Communications from the Phys. Lab. of Leiden,' No. 118B, p. 24 (1910). These values are chosen in preference to those of a later communication, No. 128, for the same reasons as those given by Keesom, 'Comm. Supplement No. 26,' p. 4 (1912), in his determination of the diameter of argon.

TABLE I.

T.	A _A .	B _A . 10 ³ .	log B _N .
293·49	1·07545	−0·60271	4·7486
273·1	1·00074	−0·73969	4·8687
215·38	0·78922	−1·30460	3·2182
186·05	0·68174	−1·63902	3·3811
170·59	0·62511	−1·81649	3·4631
163·22	0·5981	−1·92881	3·5083
159·30	0·5837	−1·97263	3·5290
157·24	0·5762	−2·03892	3·5488
153·90	0·5639	−2·04406	3·5592
152·86	0·5601	−2·05472	3·5646
151·89	0·5566	−2·05084	3·5664

In this paper, we choose for purposes of comparison the same values of n as there considered, viz., $14\frac{1}{3}$, 21 and 25.* As for m , we observe that Keesom found, in the case of the van der Waals model, comparatively little difference whether m had the value 4, 5 or 6, but concluded that 5 was the best. We, therefore, adopt this value for m for all values of n considered.

The values of the coefficients in $F(y)$, appropriate to these three models are given in Table III, the coefficient $f(\tau)$ having been defined above. The values appropriate to the rigid sphere model ($n = \infty$) are also inserted for comparison.

TABLE II.—*The Coefficients of F(y).*

	Model 1.	Model 2.	Model 3.	Model 4.
	$n = 14\frac{1}{3}, m = 5.$	$n = 21, m = 5.$	$n = 25, m = 5.$	$n = \infty, m = 5.$
$r\left(\frac{n-4}{n-1}\right)$	1·1932	1·1125	1·0896	1·0000
$f(1)$	2·8857	2·9205	2·9323	3·0000
$f(2)$	0·2667	0·2719	0·2748	0·3000
$f(3)$	0·0502	0·0492	0·0494	0·0555
$f(4)$	0·0095	0·0087	0·0085	0·0096
$f(5)$	0·0017	0·0014	0·0013	0·0015
$f(6)$	0·0003	0·0002	0·0002	0·0002

The peculiar behaviour of $f(\tau)$ for increasing values of n is due to the way in which $\Gamma(x)$ varies between $x = 1$ and $x = 2$.

The chief difficulty in the application of the method is the search for the right order of magnitude of y for which agreement is likely, as its range of

* The fraction in the first figure was introduced to simplify the arithmetic.

variation is from zero to infinity.* In the case of Model 2, the appropriate values of y were found to lie between 0.4 and 0.7. The corresponding values of $\log |F(y)|$ in this case were found to be

$y =$.4	0.425	0.45	0.475	0.50	0.55	0.60	0.65	0.70
$\log F(y) =$	2.9357	1.1896	1.3489	1.4728	1.5692	1.7183	1.8330	1.9266	0.0060

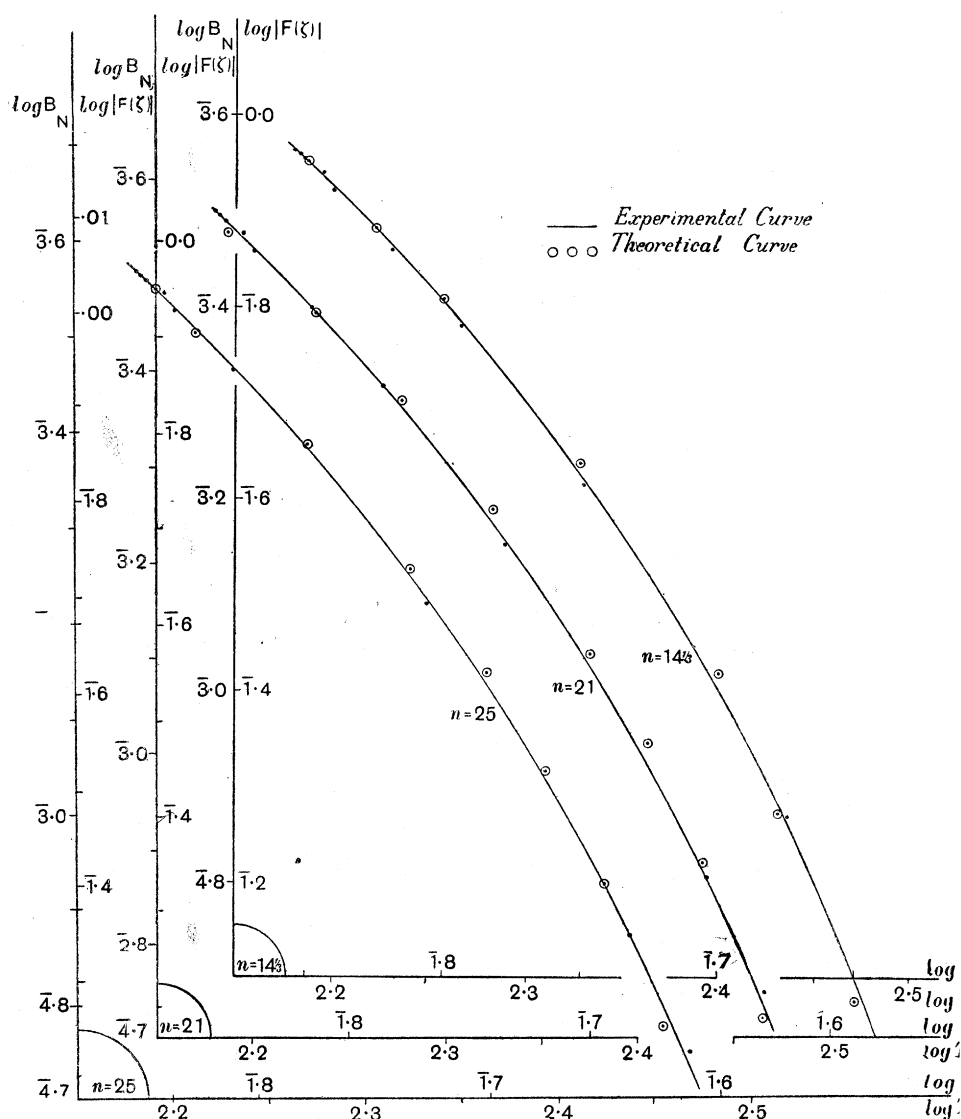


FIG. 1.—The second virial coefficient of argon, deduced from experiment, and the theoretical curves for various molecular models.

* It is easily seen that $F(y)$ is convergent for all values of y .

These are the points to be seen in the figure, the two curves having been superimposed to give the best fit. The results in the two other cases are included in the same figure, the appropriate axes with their respective scales being shown. The corresponding values of X and Y are shown in the accompanying Table III, where the values of the force constants deduced therefrom are also included.

Table III.—The Force Constants of Argon.*

n .	X .	Y .	Repulsive Force Constant.	Attractive Force Constant.
$14\frac{1}{3}$	1.3814	$\bar{3}.601$	$6.020 \cdot 10^{-112}$	$1.500 \cdot 10^{-43}$
21	1.6000	$\bar{3}.533$	$2.018 \cdot 10^{-161}$	$1.296 \cdot 10^{-43}$
25	1.6708	$\bar{3}.526$	$5.068 \cdot 10^{-191}$	$1.282 \cdot 10^{-43}$
∞	2.0500	$\bar{3}.414$	0 ($\sigma = 3.578 \cdot 10^{-8}$ cms.)	$1.009 \cdot 10^{-43}$

By the nature of the method, X and Y cannot be determined with absolute accuracy. In indicating the accuracy to be expected, it should be stated that in the case of the model $n = 25$, reasonable agreement could be obtained for values of X between 1.6683 and 1.674, with Y between $\bar{3}.533$ and $\bar{3}.520$. These figures indicate the extreme limits within which X and Y can lie. From $X = 1.6683$ and $Y = \bar{3}.533$, we find $\lambda_n = 5.727 \cdot 10^{-191}$ and $\lambda_5 = 1.301 \cdot 10^{-43}$, while, from the other pair of values, $\lambda_n = 4.578 \cdot 10^{-191}$ and $\lambda_5 = 1.270 \cdot 10^{-43}$.

In practice, these variations are almost negligible. Thus, the ratio of the distances at which the forces of repulsion (neglecting attraction) are equal is

$$r_1/r_2 = \left(\frac{5.727}{4.578} \right)^{1/25} = 1.008.$$

The values of the repulsive force constants are very much greater than those obtained from viscosity. In order to compare them, the "diameters" have been worked out from the formula of the former paper (neglecting the attractive field)

$$\sigma = \left(\frac{2\lambda_n}{3(n-1)k} \right)^{1/n-1}, \quad (4.01)$$

and the results are shown with those of viscosity in Table IV.

* In the case $n = \infty$, calculations based on Keesom's figures give $\sigma = 3.286 \cdot 10^{-8}$ with $\lambda_5 = 0.7795 \cdot 10^{-43}$. The work required to separate two such molecules from contact to infinity is $1.657 \cdot 10^{-14}$ ergs according to his work, $1.539 \cdot 10^{-14}$ ergs according to this. Here modern values of Loschmidt's number are used ($\nu = 2.705 \cdot 10^{19}$).

Table IV.—The “ Diameters ” of Argon (in Ångströms).
(Repulsive field only.)

n .	Equation of State.	Viscosity.
$14\frac{1}{2}$	5·806	4·698
21	4·935	3·987
25	4·726	3·795
∞	3·578	2·84

APPENDIX.

[*Note added 26th May, 1924.*—Since the above work was completed, further information has been published by Holborn and Otto,* who have obtained the isotherms of a number of gases, including argon, at temperatures ranging from 0° to 400° C. The results, thus obtained, have been analysed by them in the form

$$pv = A + Bp + Cp^2,$$

and values of A, B and C obtained at the different temperatures to fit the experimental facts. By an inversion of this series, it is easily seen that this expression corresponds to an expression of the type

$$pv = A \left(1 + \frac{B'}{v} + \frac{C'}{v^2} \right)$$

with $B' = B$. The values of B' thus obtained are then in the appropriate units directly comparable with the theoretical formula for the second virial coefficient given above. Unfortunately Holborn and Otto have used different units of pressure and volume from those usually taken. Their unit of pressure is 1 m. of Hg instead of 1 atmosphere, and their unit of volume is defined to be that of unit mass of gas at their unit pressure at 0° C. The change of units may be effected in the following way.

The equation of state having been expressed in the form

$$pv = A_T + B_T p + C_T p^2,$$

where A_T , B_T , C_T are known functions of temperature, suppose that the unit of pressure is changed so that at 0° C. the pressure p , measured in the new

* Holborn and Otto, ‘Zeit. für Phys.’ vol. 23, p. 77 (1924).

units, is given by P , where $p = \tau P$. Let the resulting change in the unit of volume (defined in each case to make the product of pressure and volume at 0°C. to be unity) be such that a volume v in the old units has a value V in the new units. If $v = mV$, we have

$$\tau m = A_0 + B_0 \tau + C_0 \tau^2,$$

where A_0 , B_0 and C_0 are the values of A , B and C at 0°C. It follows that

$$PV = \mathfrak{A} + \mathfrak{B}P + \mathfrak{C}P^2$$

where

$$\mathfrak{A} = \frac{A_T}{A_0 + B_0 \tau + C_0 \tau^2}, \quad \mathfrak{B} = \frac{\tau B_T}{A_0 + B_0 \tau + C_0 \tau^2}, \quad \mathfrak{C} = \frac{\tau^2 C_T}{A_0 + B_0 \tau + C_0 \tau^2}.$$

The product PV can then be expressed in powers of $1/V$ as described above.

From the values of A_0 , B_0 and C_0 given by Holborn and Otto (viz., 1.00130, 0.001298 and 0.000004 respectively) with $\tau = 0.76$, we obtain the values of $\log B_N$ (or $\log \mathfrak{B}$) given in the following table.

Values of the Second Virial Coefficient from the Experimental Work of Holborn and Otto.*

t .	$B_T \cdot 10^3$.	$\log B_N$.
0	-1.29786	4.9939 (n)
50	-0.64757	4.6920 (n)
100	-0.25229	4.2826 (n)
150	+0.06843	5.7159
200	+0.27443	4.3191
300	+0.65929	4.6997
400	+0.89886	4.8344

It thus appears that the value of B_N at 0°C. obtained from the results of Holborn and Otto differs considerably from that obtained from the results of Kamerlingh Onnes at the same temperature (the only one at which they have both worked); in fact, the whole of the values obtained from this later paper are inconsistent with those of Kamerlingh Onnes, as a glance at the accompanying figure shows. They are, however, consistent among themselves and can be considered independently by the methods of this paper. When so treated, they lead to definite values for the force constants, just as did the earlier experimental work.

The superposition of theoretical and experimental curves can in this case be

* Holborn and Otto, *loc. cit.* The (n) indicates that B_N is negative and that $\log |B_N|$ is given. It is used also in the figures for $\log |F(y)|$ as well.

obtained with some precision. For instance, a good fit can be obtained between observed values and the theoretical curve for the rigid-sphere model, with an attractive field $\lambda_5 r^{-5}$; the values thus obtained by two persons working independently were $X = 2.127$, $Y = 3.240$ in one case, and $X = 2.124$,

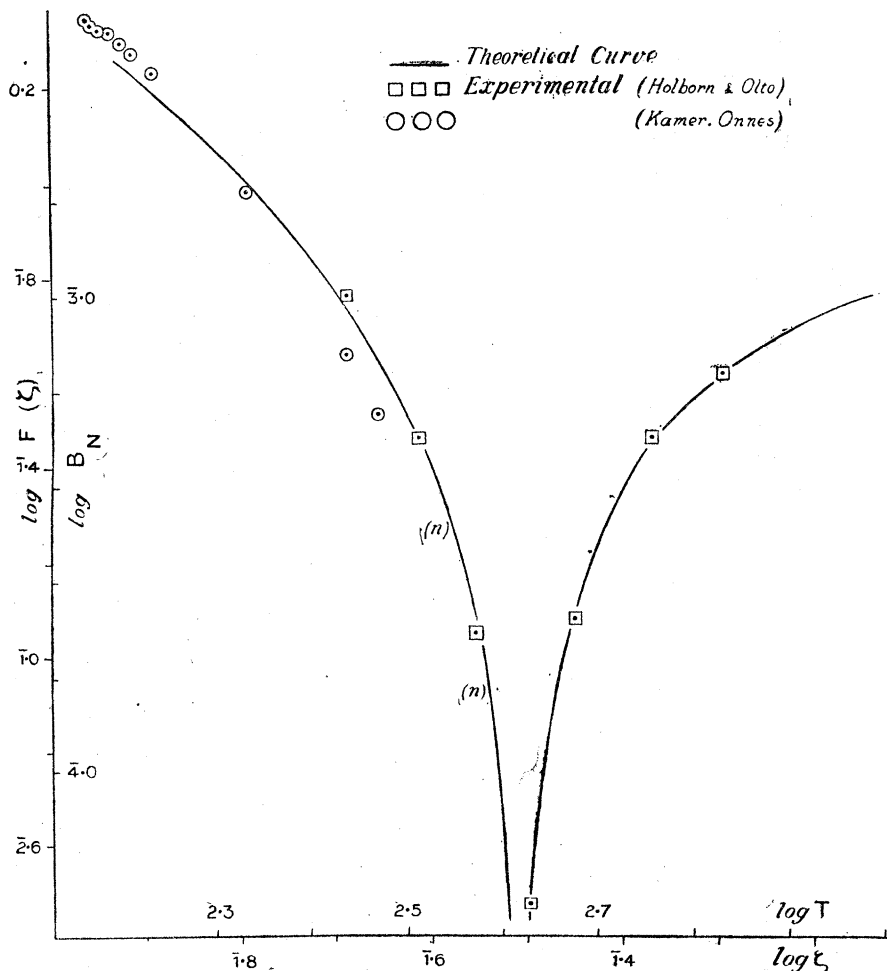


FIG. 2.—The theoretical curve for the second virial coefficient for an attracting rigid sphere model, with the experimental values for argon.

$Y = 3.240$ in the other.* These differences affect only the third decimal place of the calculated value of the diameter.

As in the earlier part of the paper, no one molecular model was found to give

* For precision a large scale is necessary. The one used was 1 inch for 0.1 change in $\log B_N$ and 2 inches for 0.1 change in $\log T$, so that $\log T$ and $\log B_N$ could thus both be plotted to the third decimal place.

obviously better agreement than the others. The best was probably that of a repulsive field according to the inverse $(14\frac{1}{3})^{\text{th}}$ power, with an attraction according to an inverse 5th power, but good agreement was found for all models in which the repulsive field was of a higher inverse power than the

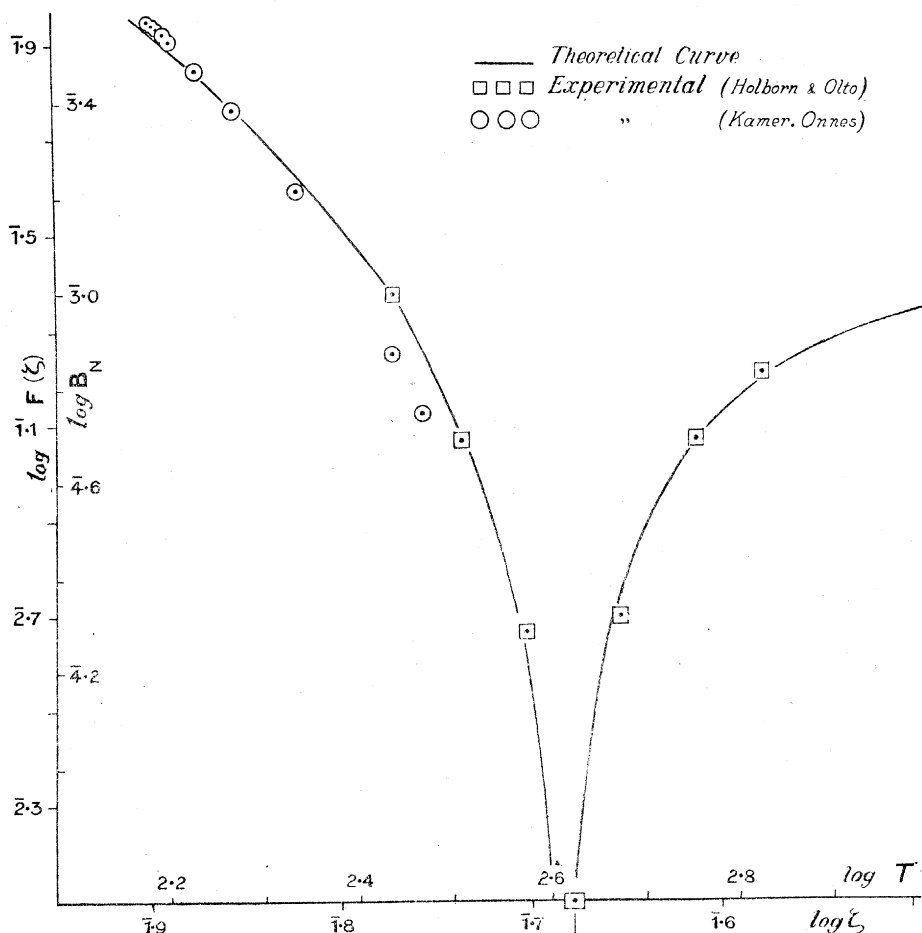


FIG. 3.—The theoretical curve for the second virial coefficient for the model $\lambda_2 r^{-9} - \lambda_3 r^{-5}$ with the experimental values for argon. (Scale of $\log y$ equals twice that of $\log T$.)

9th (with the same kind of attractive field). Figs. 2 and 3 show the relation between theory and experiment in the two extreme cases ($n = \infty$ and $n = 9$).*

* Theory indicates little change in the shape of the curve for the different models in the region required for argon, but for lower values of y (corresponding to higher temperatures) there are marked differences. For instance, the theoretical curve for small values of n quickly reaches a maximum on the right-hand portion and then diminishes asymptotically

On the Determination of Molecular Fields.

477

The appropriate values of X and Y for the various models, with the values of the repulsive and attractive force constants deduced therefrom, are given in the accompanying table. The values of λ_n and λ_5 are in all cases less than those deduced from Kamerlingh Onnes' results. For comparison, the values of the "diameter" σ are worked out by means of the formula (4.01) given above.* The diameter of the rigid sphere is now about 10 per cent. greater than that given by viscosity, whereas the former result is about 25 per cent. greater.

Force Constants of Argon deduced from the Experimental Results of Holborn and Otto.

n .	X .	Y .	Repulsive Force Constant (λ_n).	Attractive Force Constant (λ_5).	σ (in cms.).
∞	2.1260	3.240	0	$0.704 \cdot 10^{-43}$	$3.131 \cdot 10^{-8}$
25	1.7350	3.362	$2.955 \cdot 10^{-192}$	0.9256	4.128
21	1.6576	3.382	$2.338 \cdot 10^{-162}$	0.9612	4.342
$14\frac{1}{3}$	1.4290	3.458	$1.636 \cdot 10^{-112}$	1.1324	5.107
11	1.2098	3.542	$1.3065 \cdot 10^{-87}$	1.3832	6.030
9	0.990	3.622	$1.009 \cdot 10^{-72}$	1.6248	7.530

Recently argon† has been obtained in crystal form and its structure examined by X-ray analysis. The writer hopes in a later paper to use the information obtained above to make theoretical calculations of interatomic distances in crystalline argon. In this way the atomic field of argon may be determined more definitely than is possible by the present method.

The experimental work of Holborn and Otto is now being used to investigate the fields of helium and neon by the methods of this paper.

to zero, whereas for $n = \infty$ the curve rises asymptotically to a finite upper limit. It is interesting to observe that Holborn and Otto obtain experimentally maximum values for B_N in the cases of neon and helium.

* In the work of this Appendix I gratefully acknowledge the assistance given me in the numerical calculations by Mr. E. V. Whitfield, B.A., Trinity College, Cambridge.

† F. Simon u. Cl. v. Sinson, 'Die Naturwissenschaften,' vol. 11, p. 1015 (December, 1923).