n the Determination of Molecular Fields.—I. From the Variation of the Viscosity of a Gas with Temperature.

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CONTENTS.

§1. *Introduction.*

Until our knowledge of the disposition and motion of the electrons in atoms and molecules is more complete, we cannot hope to make a direct calculation of the nature of the forces called into play during an encounter between molecules in a gas. It is true that a step in this direction has recently been made by Debye,* who has investigated the nature of the field in the neighbourhood of a hydrogen atom, assumed to consist of a negative charge in motion in a circular orbit about a positive nucleus, and has shown how the pulsating field gives rise on the whole to a force of repulsion, as well as one of attraction on a unit negative charge. But it is difficult to see how this work can be extended to more complex systems. At present we can only hope to derive information by more indirect methods.

One such method is to assume a definite law of force, and then by the methods of the kinetic theory to deduce the appropriate law of dependence of the viscosity of a gas on temperature. Comparison with the actual law, as observed experimentally, serves to support or discredit the assumed law of molecular interaction. Unfortunately, the calculations involved in the application of the kinetic theory are so complicated that progress has been made only in certain simple cases. Thus, the original investigation by Maxwell† applied only

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* Debye, 'Phys. Zeit.,' vol. 22, p. 302 (1921).

† Maxwell, 'Scientific Papers,' vol. II, p. 26.

to molecules repelling as the inverse fifth power law. His work has since be generalised by Chapman* and Enskog,† and formulæ have been obtained the coefficient of viscosity in the case of (i) molecules, which repel according an inverse nth power law, (ii) molecules which behave on collision like rig elastic spheres and (iii) molecules which behave as rigid elastic spheres with weak attractive field of force surrounding them. Of these models the la generally referred to as Sutherland's model, is found to give the best agreeme between theory and experiment. But the agreement is by no means perfe As Schmidt,‡ Bestelmeyer,§ Vogel,‖ and others have pointed out, there considerable divergence from observed values at low temperatures.

In this paper, the necessary analysis has been effected for a new molecul model, leading, of course, to a new formula for the coefficient of viscosity. T molecules are supposed to repel according to an inverse nth power law, and attract according to the inverse third power. No attempt is made to justi this particular attractive field. Its only justification is that it renders th integrals tractable. The result obtained is that viscosity varies to a fir approximation according to the law $T/(T^{(n-5)/2(n-1)} + ST^{-\frac{1}{2}})$, where S is quantity independent of the temperature T, and n is the index of th assumed repulsive field. By making n tend to infinity, the usual Sutherlan formula is obtained; by putting S equal to zero, the usual result for molecule repelling according to the inverse nth power law (without attraction) obtained. The new relation between viscosity and temperature may accord ingly be regarded as more general than any yet given. Furthermore, from th formula for this particular model, reasons are adduced for inferring a corres ponding relation for attractive fields of a more general character.

The value of S for the Sutherland model has been shown by Enskog¶ an James** to be proportional to $\Delta \phi (\sigma)$, where $\phi (\sigma)$ is the work required t separate two molecules from contact to infinity against the attractive field and Δ is a pure number depending only on the nature of the field. In thi paper an analogous interpretation is given for the corresponding attractiv constant S used here. The numerical factor which it contains is a function o

* Chapman, 'Phil. Trans.,' A, vol. 216, p. 279 (1915).

† Enskog, "Kinetische Theorie der Vorgänge in mässig verdünnten Gasen," 'Inaug Dissertation,' Uppsala (1917).

‡ Schmidt, 'Ann. d. Phys.,' vol. 30, p. 399 (1909).

§ Bestelmeyer, 'Munich Dissertation' (1903).

‖ Vogel, 'Berlin Dissertation' (1914).

¶ Enskog, loc. cit.

** C. G. F. James, 'Proc. Camb. Phil. Soc.,' vol. 20, Part 4, p. 447.

index n of the repulsive field, and its evaluation for particular values of n (a somewhat laborious proceeding) has led to the unexpected result that S is negative for values of n less than 17.

The new formula is shown to give a remarkably good representation of the observed variation of viscosity with temperature. Thus, the viscosity of argon can be represented through a range of $370°$, the whole range observed, with no greater divergence than $0\cdot6$ per cent., whereas the best fit previously obtained by means of the Sutherland formula resulted in a divergence of as much as 8 per cent. at the lowest temperature. As the formula contains two adjustable constants, viz., n and S, it does not prove possible to determine the value of either uniquely. Thus in the case of argon, equally good agreement can be obtained for $n = 21$ with $S = 62\cdot45$ as for $n = 14\frac{1}{3}$ with $S = 38\cdot62$. We infer that viscosity results alone are not sufficient to determine absolutely the nature of molecular fields. All that we can infer is that any one of a certain specified range of molecular models is a possible one. For certain models the value of the repulsive force constants have been determined from a formula which is given in the paper. The present investigation leaves the nature of the attractive field undetermined, but it is, at any rate, separated (in its effect on viscosity) from the repulsive field.

A further investigation has been undertaken in order to obtain information about intermolecular fields from experimental work on the equation of state of a gas, and this forms the subject of a second paper.

§2. Statement of the Problem.

The formula, which Chapman[*] has given for the coefficient of viscosity of a gas whose molecules may be regarded as spherically symmetrical, is

$$\mu = \frac{5}{\pi} \frac{kT}{\kappa_0} (1 + \varepsilon), \tag{2.1}$$

where T is the temperature, k the usual gas content, and ε a small number which depends on the molecular model; it can in most cases be neglected in comparison with unity, being of the order $0\cdot01$. The symbol κ_0 is given by[†]

$$\kappa_0 = \frac{16}{15\pi^{\frac{1}{2}}} \int_0^\infty e^{-b^2} \phi^{(2)} (\tau y) y^6 \, dy. \tag{2.2}$$

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[*] Chapman, *loc. cit.*, equation (239), putting $\sum_0^\infty \gamma_r = \epsilon_c$ as in his Table V.

[†] Chapman, *loc. cit.*, equation (173).

where*

$$\phi^{(2)}(\tau y) = 10\tau y \int_0^\infty \{1 - P_2(\cos\chi)\} p \, dp. \tag{2.3}$$

Here P_2 is a zonal harmonic of the second order, p is the perpendicular distance between one molecule and the direction of motion of a second relative to it before an encounter, and χ is the angle turned through by the relative velocity during the encounter. Further, τ is a function of the temperature and of the mass of the colliding molecules given by†

$$\tau^2 = \frac{2kT}{m_1 + m_2} = \frac{1}{j(m_1 + m_2)} \tag{2.4}$$

and‡

$$\tau y = C_R = \frac{V(m_1 m_2)^{\frac{1}{2}}}{m_1 + m_2}. \tag{2.5}$$

Here V is the relative velocity before collision, C_R is a variable used by Chapman, which we introduce here merely to facilitate reference.§ In a simple gas, of course, $m_1 = m_2$ and so $\tau y = V/2$.

For any molecular model χ has first to be found in terms of p and V. This requires an investigation of the dynamics of collision, to which we proceed in the next paragraph. It, also, involves an integration and then the integrals (2.3) and (2.2) are in turn to be effected.

Only in the particular cases mentioned in the preceding paragraph has it been possible to effect this triple integration. Even then, two of the integrals have to be evaluated by quadrature, but the peculiar feature of these models is that one integral can be calculated and so an explicit relation between viscosity and temperature can be established. The investigation of this paper shows that this can also be done in the case of another model owing to certain dynamical properties which it possesses in an encounter.

§3. *The Dynamics of an Encounter.*

It is easy to show|| that if the potential of the field between two molecules when separated by a distance r is $\phi(r)$, then the motion of one relative to the other during an encounter is the same as that of a particle of unit mass about a fixed centre of force, of potential $(m_1 + m_2/m_1 m_2)\phi(r)$. Using polar

* Chapman, *loc. cit.*, equation (146).

† I here adopt Fowler's suggestion, 'Phil. Mag.,' vol. 43, p. 791 (1922), and write $1/2kT = j$ instead of the usual h.

‡ Chapman, *loc. cit.*, p. 291, equation (40).

§ Chapman, *loc. cit.*, equation (116) using equation (32).

|| Jeans, 'Dynamical Theory of Gases,' pp. 213, 214 (1921).

c-ordinates r, θ to denote this latter motion, we have the following equations c momentum and energy

$$r^2 \dot{\theta} = pV, \qquad (3.01)$$

$$\tfrac{1}{2}(\dot{r}^2 + r^2\dot{\theta}^2) = \tfrac{1}{2}V^2 - \frac{m_1 + m_2}{m_1 m_2}\phi(r). \qquad (3.02)$$

For the present we suppose the masses of the molecules in the encounter be different, so that we may apply the analysis in a later paper to a con- deration of diffusion. From these equations, we obtain an equation to etermine θ in terms of r,

$$\tfrac{1}{2}\left(\frac{dr}{d\theta}\right)^2 + 1 = \frac{r^2}{p^2} - \frac{m_1 + m_2}{m_1 m_2}\frac{2r^2\phi(r)}{p^2 V^2}$$

$$= \frac{r^2}{p^2} - \frac{2r^2\phi(r)}{p^2 E} \qquad (3.03)$$

here we have put

$$\frac{m_1 m_2}{m_1 + m_2}V^2 = E. \qquad (3.04)$$

In terms of the notation used above

$$E = (m_1 + m_2)\tau^2 y^2 = 2kTy^2 = y^2/j, \qquad (3.041)$$

form we shall require later.

It is clear from equation (3.03) that if a solution can be found for θ for any iven field of force, then a solution can also be found when an additional field f force, varying as the inverse cube of the distance, is superimposed. For to $\phi(r)$ we add a term λ/r^2, the equation (3.03) can be re-written

$$\frac{1}{r^2}\left(\frac{dr}{d\theta}\right)^2 + \left(1 + \frac{2\lambda}{p^2 E}\right) = \frac{r^2}{p^2} - \frac{2r^2\phi(r)}{p^2 E} \qquad (3.05)$$

which takes the same form as (3.03) on changing the variable form θ to ψ, ind writing q for p where

$$q = p\left(1 + \frac{2\lambda}{p^2 E}\right)^{\frac{1}{2}} \qquad (3.051)$$

and

$$\psi = \frac{q}{p}\theta. \qquad (3.052)$$

This device was first shown by Newton[*] by a geometrical method in connection with his work on "revolving orbits."

* 'Principia,' lib. i, prop. xliii; Lamb, 'Dynamics,' p. 266.

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Let us suppose that the force between two molecules at a distance r is given by

$$f(r) = \frac{\lambda_n}{r^n} - \frac{\lambda_3}{r^3} \tag{3.06}$$

so that

$$\phi(r) = \frac{\lambda_n}{(n-1) r^{n-1}} - \frac{\lambda_3}{2r^2}. \tag{3.07}$$

Replacing λ in equation (3.05) by $-\lambda_3/2$ we find

$$\frac{1}{r^2}\left(\frac{dr}{d\psi}\right)^2 + 1 = \frac{r^2}{q^2} - \frac{2}{n-1}\frac{\lambda_n}{q^2 E r^{n-3}} \tag{3.08}$$

on making the substitutions (3.051) and (3.052).

Putting

$$\zeta = \frac{q}{r}, \qquad \beta = q\left(\frac{E}{\lambda_n}\right)^{1/n-1} \tag{3.09}$$

where

$$q^2 = p^2 - \frac{\lambda_3}{E},$$

we get

$$\left(\frac{d\zeta}{d\psi}\right)^2 = 1 - \zeta^2 - \frac{2}{n-1}\left(\frac{\zeta}{\beta}\right)^{n-1}$$

so that if ψ is measured from the asympote to the orbit before the encounter $(r = \infty, \zeta = 0)$, we have

$$\psi = \int_0^\zeta \frac{d\zeta}{\left\{1 - \zeta^2 - \frac{2}{n-1}\left(\frac{\zeta}{\beta}\right)^{n-1}\right\}^{\frac{1}{2}}}. \tag{3.10}$$

It follows from equation (3.052) that the angle between the asymptotes of the orbit considered above is given by*

$$2\theta_0' = 2\left\{1 - \frac{\lambda_3}{p^2 E}\right\}^{-\frac{1}{2}} \int_0^{\zeta_0} \frac{d\zeta}{\left\{1 - \zeta^2 - \frac{2}{n-1}\left(\frac{\zeta}{\beta}\right)^{n-1}\right\}^{\frac{1}{2}}}$$

$$= 2\left\{1 - \frac{\lambda_3}{p^2 E}\right\}^{-\frac{1}{2}} \theta_0 = \frac{2p}{q}\theta_0, \tag{3.11}$$

where

$$\theta_0 = \int_0^{\zeta_0} \frac{d\zeta}{\left\{1 - \zeta^2 - \frac{2}{n-1}\left(\frac{\zeta}{\beta}\right)^{n-1}\right\}^{\frac{1}{2}}}. \tag{3.111}$$

The upper limit ζ_0 is the one positive real root of

$$1 - \zeta^2 - \frac{2}{n-1}\left(\frac{\zeta}{\beta}\right)^{n-1} = 0, \tag{3.12}$$

* Jeans, 'Dynamical Theory of Gases,' p. 215 (1921).

ıd the integral is therefore a function of β only. The angle χ turned through uring an encounter is equal to $\pi - 2\theta_0'$, and may now be regarded as known. vidently $2\theta_0$ is the angle between the asymptotes in the absence of an ttractive force. The latter has the effect of widening the angle between the symptotes.

§4. *The Coefficient of Viscosity.*

The next step in the calculation is the evaluation of $\phi^{(2)}(\tau y)$ given by quation (2.3). We have

$$1 - P_2(\cos \chi) = \frac{3}{2} \sin^2 \chi$$

$$= \frac{3}{4}(1 - \cos 4\theta_0')$$

$$= \frac{3}{4}\left\{1 - \cos\left(1 - \frac{\lambda_3}{p^2 E}\right)^{-\frac{1}{2}} 4\theta_0\right\}. \tag{4.011}$$

This is to be integrated [equation (2.3)] with respect to p, but θ_0 being a unction of β, it is convenient to change the variable from p to β. It follows rom the definition of β equation (3.09) that

$$p\,dp = q\,dq = \left(\frac{\lambda_n}{E}\right)^{2/n-1} \beta\,d\beta, \tag{4.01}$$

ınd

$$\left(1 - \frac{\lambda_3}{p^2 E}\right) = \left\{1 + \frac{\lambda_3}{E}\left(\frac{E}{\lambda_n}\right)^{2/n-1}\frac{1}{\beta^2}\right\}^{-1} \tag{4.02}$$

[or, from equation (3.09),

$$p^2 = \beta^2\left(\frac{\lambda_n}{E}\right)^{2/n-1} + \frac{\lambda_3}{E}.$$

Before proceeding with the general calculation we now show how to calculate $\phi^{(2)}(\tau y)$ in the simple case when the attractive force is weak compared with the repulsive field. This assumption is usually made in theoretical calculations concerned with the Sutherland model.*

In this case, we have at once

$$\cos\left(1 - \frac{\lambda_3}{p^2 E}\right)^{-\frac{1}{2}} 4\theta_0 = \cos 4\theta_0 - \frac{\lambda_3}{E}\left(\frac{E}{\lambda_n}\right)^{2/n-1}\frac{2\theta_0}{\beta^2}\sin 4\theta_0, \tag{4.03}$$

and so

$$1 - P_2(\cos \chi) = \frac{3}{2}\left\{\sin^2 2\theta_0 + \frac{\lambda_3}{E}\left(\frac{E}{\lambda_n}\right)^{2/n-1}\frac{\theta_0}{\beta^2}\sin 4\theta_0\right\}. \tag{4.04}$$

* Chapman, 'Phil. Trans.,' A, vol. 211, p. 433 (1911); 'Phil. Trans.,' A, vol. 216, p. 279 (1915); 'Phil. Trans.,' A, vol. 217, p. 115 (1916); Enskog, *loc. cit.*, C. G. F. James, ' Proc. Camb. Phil. Soc.,' vol. 20, p. 447 (1921).

Hence

$$\phi^{(2)}(\tau y) = 15\tau y \left(\frac{\lambda_n}{E}\right)^{2, n-1} \int_0^\infty \sin^2 2\theta_0 \, \beta d\beta + 15\tau y \frac{\lambda_3}{E} \int_0^\infty \frac{\theta_0 \sin 4\theta_0}{\beta} d\beta. \quad (4.05)$$

The integrands in each case are functions of β only, and so the integrals will be pure numbers depending on the nature of the repulsive field only, that is, on the value of n. The first has, in fact, been calculated by Chapman* by numerical quadrature for several values of n. To conform with his notation we write

$$I_2(n) = 4\pi \int_0^\infty \sin^2 \theta_0 \cos^2 \theta_0 \, \beta d\beta. \quad (4.06)$$

For the second we write

$$J(n) = \int_0^\infty \frac{\theta_0 \sin 4\theta_0}{\beta} d\beta. \quad (4.07)$$

It, also, can be computed, as is shown in the next paragraph, where its numerical value is given for various values of n.

We now obtain $\phi^{(2)}(\tau y)$ as a function of y only, for E is a function of V and so of y, thus

$$\phi^{(2)}(\tau y) = \frac{15 I_2(n)}{\pi} \frac{\lambda_n^{2/n-1} (\tau y)^{1-(4/n-1)}}{(2m)^{2/n-1}} + \frac{15 J(n) \lambda_3}{2m \, \tau y}. \quad (4.08)$$

This result is now to be substituted in the formula for κ_0 in equation (2.2), and the formula for the coefficient of viscosity is then given by equation (2.1).

In the more general case when λ_3 is not small enough to allow of the approximation implied in equation (4.03), we proceed somewhat differently. Referring to equation (4.011), we see that we require a more general expansion of

$$\cos\left(1 - \frac{\lambda_3}{p^2 E}\right)^{-\frac{1}{2}} 4\theta_0,$$

or, using the relation (4.02), of

$$\cos\left(1 + \frac{\lambda_3}{E}\left(\frac{E}{\lambda_n}\right)^{2/n-1} \frac{1}{\beta^2}\right)^{\frac{1}{2}} 4\theta_0.$$

Now the function $y = \cos \alpha (1 + x)^{\frac{1}{2}}$ satisfies the differential equation

$$4(1 + x) D^2 y + 2Dy + \alpha^2 y = 0, \quad (4.09)$$

whence it is easy to show that the coefficients of the expansion

$$y = Q_0 + Q_1 x + Q_2 x^2 + \dots + Q_n x^n + \dots$$

satisfy the relation

$$Q_{n+2} + \frac{2n+1}{2(n+2)} Q_{n+1} + \frac{\alpha^2}{4(n+1)(n+2)} Q_n = 0. \quad (4.10)$$

* Chapman, 'Manchester Lit. and Phil. Memoirs,' vol. 66, p. 1 (1922).

The first two coefficients Q_0 and Q_1 are obviously obtained by putting $= 0$ in y and Dy respectively.

We thus get

$$\cos\left(1 + \frac{\lambda^3}{E}\left(\frac{E}{\lambda_n}\right)^{2/n-1}\frac{1}{\beta^2}\right)^{\frac{1}{3}} 4\theta_0 = \cos 4\theta_0 + \frac{\omega}{\beta^2}\frac{\phi_1(\theta_0)}{2!} + \frac{\omega^2\phi_2(\theta_0)}{\beta^4 \cdot 2^2 \cdot 2!}$$

$$+ \dots + \frac{\omega^r}{\beta^{2r}}\frac{\phi_r(\theta_0)}{f(r)} + \dots \qquad (4.11)$$

here, for short, we have put

$$\omega = \frac{\lambda_3}{E} \cdot \left(\frac{E}{\lambda_n}\right)^{2/n-1}, \qquad (4.12)$$

nd the functions $\phi_r(\theta_0)$ are functions of θ_0 obtained from equation (4.10). hus, we find

$$\phi_1(\theta_0) = - 4\theta_0 \sin 4\theta_0 \qquad (4.13)$$

$$\phi_2(\theta_0) = 4\theta_0 \sin 4\theta_0 - (4\theta_0)^2 \cos 4\theta_0. \qquad (4.14)$$

Ve note that the first two terms of equation (4.11) are the same as the expres- ion (4.04) obtained for the simple case.

For any given value of ω the expansion (4.11) is now a function of β, vhich we assume can legitimately be integrated term by term.* We now uppose therefore the expansion (4.11) used in equation (4.011) and a value f $\phi^{(2)}(\tau y)$ obtained from equation (2.3). In the integration the change of ariable indicated in equation (4.01) is used. When the integration has been ffected through the infinite range of variation of β, we are left with a power eries in ω, each coefficient of which, though difficult to compute, is a pure umber. The first two coefficients are calculated for various values of the ndex of the repulsive field in the next paragraph.

Thus we get

$$\phi^{(2)}(\tau y) = \frac{15\tau y}{2}\left(\frac{\lambda_n}{E}\right)^{2/n-1}\int_0^\infty \left\{1 - \cos 4\theta_0\left(1 + \frac{\omega}{\beta^2}\right)^{\frac{1}{3}}\right\}\beta d\beta$$

$$= \frac{15\tau y}{2}\left(\frac{\lambda_n}{E}\right)^{2/n-1}\left[\frac{2I_2(n)}{\pi} + J_1(n)\frac{\omega}{2!} + J_2(n)\frac{\omega^2}{2^2 2!} + \dots J_r(n)\frac{\omega^r}{f(r)} + \dots\right]$$

$$(4.16)$$

where $I_2(n)$ has been defined in equation (4.06) above and the coefficients $J_r(n)$ are new integrals given by

$$J_r(n) = -\int_0^\infty \frac{\phi_r(\theta_0)\, d\beta}{\beta^{2r-1}}. \qquad (4.17)$$

* The range of integration of β is from 0 to ∞, and it is not at once obvious that the coefficients of ω are finite at the lower limit. This is investigated at the end of the next paragraph.

The final step in the determination of the coefficient of viscosity is the calculation of κ_0 given in equation (2.2). We recall it here

$$\kappa_0 = \frac{16}{15\pi^{\frac{1}{2}}} \int_0^\infty e^{-y^2} \phi^{(2)}(\tau y) \, y^6 dy. \tag{4.18}$$

Now, by definition (4.12)

$$\omega = \frac{\lambda_3}{E} \cdot \left(\frac{E}{\lambda_n}\right)^{2/n-1}$$

and from equation (3.041)

$$E = 2kTy^2,$$

so that the contribution of the rth term of the series (4.16) to κ_0 is given by

$$\frac{8J_r(n)\lambda_n^{2/n-1}}{f(r)\pi^{\frac{1}{2}}(2m)^{\frac{1}{2}}} \left(\frac{\lambda_3}{\lambda_n^{2/n-1}}\right)^r (2kT)^{\frac{(n-5)-2r(n-3)}{2(n-1)}} \int_0^\infty e^{-y^2} y^{\frac{n-5-2r(n-3)}{n-1}+6} dy$$

$$= \frac{4J_r(n)\lambda_n^{2/n-1}}{f(r)\pi^{\frac{1}{2}}(2m)^{\frac{1}{2}}} \left(\frac{\lambda_3}{\lambda_n^{2/n-1}}\right)^r (2kT)^{\frac{(n-5)-2r(n-3)}{2(n-1)}} \Gamma\left(\frac{n-5-2r(n-3)}{2(n-1)}+\frac{7}{2}\right) \tag{4.19}$$

Hence

$$\kappa_0 = \frac{8I_2(n)\lambda_n^{2/n-1}}{\pi^{3/2}(2m)^{\frac{1}{2}}} \Gamma\left(4-\frac{2}{n-1}\right)(2kT)^{\frac{n-5}{2(n-1)}} \left\{1 + \sum_{r=1}^\infty S_r T^{-r\frac{n-3}{n-1}}\right\}, \tag{4.20}$$

where

$$S_r = \frac{\pi J_r(n)}{2f(r)I_2(n)} \left(\frac{\lambda_3}{\lambda_n^{2/n-1}}\right)^r \frac{\Gamma\left(\frac{n-5-2r\,.\,n-3}{2\,.\,n-1}+\frac{7}{2}\right)}{\Gamma\left(4-\frac{2}{n-1}\right)(2k)^{r\,\cdot\,\frac{n-3}{n-1}}}, \tag{4.21}$$

The coefficient of viscosity is given by

$$\mu = \frac{5kT}{\pi\kappa_0}, \tag{4.22}$$

and so

$$\mu = \frac{AT^{\frac{n+3}{2(n-1)}}}{1 + \sum_{r=1}^\infty S_r T^{-r\frac{n-3}{n-1}}}. \tag{4.23}$$

The quantity A, here introduced, is independent of the temperature and is given by

$$A = \frac{5\pi^{\frac{1}{2}}(mk)^{\frac{1}{2}}}{8I_2(n)\Gamma\left(4-\frac{2}{n-1}\right)} \left(\frac{2k}{\lambda_n}\right)^{\frac{2}{n-1}} \tag{4.24}$$

while the "attractive constants" S_r are given by equation (4.21) above, and so are functions only of the force constants λ_3 and λ_n and of the index of the repulsive power law n.

In the simple case at first considered in equation (4.03) the formula for the coefficient of viscosity reduces to

$$\mu = \frac{AT^{3/2}}{T^{\frac{n-3}{n-1}} + S}, \tag{4.25}$$

where A has the same value as before and S is given by

$$S = \frac{\pi J_1(n)}{2I_2(n) \Gamma\left(4 - \frac{2}{n-1}\right)(2k)^{\frac{n-3}{n-1}}} \frac{\lambda_3}{\lambda_n^{2/n-1}}. \tag{4.26}$$

When there is no attractive field, all the constants S_r vanish, of course, and the formula reduces to that already given by Chapman[*] and Enskog[†] for a gas in which the molecules repel according to the inverse nth power law.

Another special case which can be considered is the Sutherland model, consisting of a rigid sphere with an attractive field surrounding it. The formula appropriate to this case can be deduced from that given above by making n infinitely large. We then get

$$\mu = \frac{AT^{\frac{1}{2}}}{1 + S/T}, \tag{4.27}$$

which is the well known Sutherland formula. Further, in this case the form of this expression remains unchanged whatever the nature of the attractive field, although the constant S depends on the attractive field. Its value for attractive fields varying as inverse power laws has been worked out by Enskog[†] and James.[‡] In this case, it is found possible to give a simple physical interpretation of S, for it is shown to be a measure of the work required to separate two molecules from contact to infinity against the attractive field. Thus if $\phi(r)$ is the potential of two molecules separated by a distance r, and σ is the diameter of a molecule, then the value of S is given by[§]

$$S = \Delta_m \frac{\phi(\sigma)}{k},$$

[*] Chapman, 'Phil. Trans.,' A, vol. 216, p. 338, eqn. (251), using eqn. (183) (1915); *cf.* also 'Phil. Trans.,' A, vol. 211, p. 433 (1912); Jeans, 'Dynamical Theory of Gases,' 3rd edn., p. 287 (1921); and again Chapman, 'Memoirs Manchester Lit. and Phil. Soc.,' vol. 66, p. 7 (Appendix), 1922. In the first paper cited, it should be noted that $\lambda_n m^2$ is used as the force constant instead of λ_n (although the contrary is stated, p. 321), and in the other papers, the formulæ should all be multiplied by a factor $(2/n-1)^{2/n-1}$ (an error introduced by the unfortunate use of different variables by different writers in the formula (4.06) of this paper).

[†] Enskog, 'Inaugural Dissertation,' Uppsala, p. 94 (1917).

[‡] James, *loc. cit.*

[§] James, *loc. cit.*, p. 457.

where Δ_m is a number depending only on the index m of the attractive field (r^{-m}); its value varies from $0 \cdot 213$ to $0 \cdot 156$ as m varies from 4 to 9.

It is of interest to try to find some parallel physical interpretation of the constant S introduced above. Suppose two molecules repelling each other according to an inverse nth power law move towards each other in a direct encounter with a relative velocity equal to the average velocity of the molecules of a gas at 1° absolute. Then at the closest distance of approach

$$\frac{\lambda_n}{(n-1)\,\sigma^{n-1}} = \frac{3}{2}k, \tag{4.29}$$

and so

$$\sigma = \left(\frac{2\lambda_n}{3\,(n-1)\,k}\right)^{1/n-1}. \tag{4.30}$$

We shall define this distance σ as the " diameter " of such molecules. When molecules actually are rigid spheres, the force constant λ_n is infinite, and n is infinite, but $\lambda_n^{1/n-1}$ has a definite limiting value equal to the diameter.

Now the expression we have obtained for S is, writing δ for the numerical factors

$$S = \delta \cdot \frac{\lambda_3}{\lambda_n^{2/n-1}} \cdot \frac{1}{(2k)^{n-3/n-1}}. \tag{4.301}$$

Substituting for λ_n in terms of the quantity σ just given, we find

$$S = \frac{\delta}{3^{2/n-1}} \frac{\lambda_3}{2k\sigma^2} \left(\frac{4}{n-1}\right)^{2/n-1}$$

$$= \Delta \frac{\phi\,(\sigma)}{k}, \tag{4.31}$$

where $\phi\,(\sigma)$ is the work required to separate two molecules attracting according to the law r_3/r^3 from a distance σ to infinity, and Δ is a numerical factor. The formula for S is, on this convention, exactly parallel to that previously found for Sutherland's constant.

As S in Sutherland's case has the same form whatever the attractive field, so we may assume that in our case it would have the form (4.31), even when the attractive force is not limited to the inverse third power law. This would imply for S, when the attractive field is $\lambda_m\,r^{-m}$, a formula of the type

$$S = \frac{\lambda_m}{(m-1)\,k\sigma^{m-1}} \quad \Delta = \frac{\Delta'}{k^{n-m/m-1}} \cdot \frac{\lambda_m}{\lambda_n^{m-1/n-1}}, \tag{4.32}$$

where Δ' is a numerical factor. We may infer that the formula for the coefficient of viscosity for the general law of force $\lambda_n r^{-n} - \lambda_m r^{-m}$ is still given by equation (4.25), with the new meaning for S, here derived.

§5. *The Numerical Calculation of the Integrals* $I_2(n)$ *and* $J_1(n)$.

We have now to find the numerical value of the integrals $I_2(n)$ and $J_1(n)$, involved in the formula for viscosity. The integrals are defined as follows :—

$$I_2(n) = 4\pi \int_0^\infty \sin^2\theta_0 \cos^2\theta_0\ \beta d\beta, \qquad (5.01)$$

and

$$J_1(n) = \int_0^\infty \frac{\theta_0 \sin 4\theta_0}{\beta}\ d\beta, \qquad (5.02)$$

where θ_0 is a function of β and n given by the equation

$$\theta_0 = \int_0^{\zeta_0} \left\{ 1 - \zeta^2 - \frac{2}{n-1}\left(\frac{\zeta}{\beta}\right)^{n-1} \right\}^{-\frac{1}{2}} d\zeta. \qquad (5.03)$$

The upper limit is the one positive real root of the equation obtained by equating to zero the expression included in the brackets in the last equation.

Chapman* has evaluated the integral $I_2(n)$ for the odd values of n between 5 and 15 and for n equal to infinity. In the applications of the formulæ obtained in this paper, it will be necessary to know the value of $I_2(n)$ for values of n higher than 15, and so the work has been done for two more values of n, viz., $n = 21$ and $n = 25$. The method adopted is exactly the same as that given by Chapman in the paper cited. As part of this work is essential for the calculation of $J_1(n)$, it seems necessary to indicate the steps involved in the method.

By definition

$$1 - \zeta_0^2 - \frac{2}{n-1}\left(\frac{\zeta_0}{\beta}\right)^{n-1} = 0 \qquad (5.04)$$

and so

$$\beta^2 = \zeta_0^2 \left[\frac{2}{(n-1)(1-\zeta_0^2)}\right]^{2/n-1}. \qquad (5.05)$$

Hence it is easy to calculate β when ζ_0 is known, although the reverse process is difficult. We accordingly calculate the value of θ_0 from (5.03) for various values of ζ_0. The process is simplified by introducing new variables χ, χ_0 defined by

$$\zeta = \sin\chi, \qquad \zeta_0 = \chi_0 \qquad (5.05)$$

so that

$$\theta_0 = \int_0^{\chi_0} \{1 - (\sin\chi/\sin\chi_0)^{n-1}(\cos\chi_0/\cos\chi)^2\}^{-\frac{1}{2}} d\chi. \qquad (5.07)$$

The value of β appropriate to any chosen value of χ_0 is obtained from the relation

$$\beta^2 = \sin^2\chi_0 \left[\frac{2}{(n-1)\cos^2\chi_0}\right]^{-2/n-1}. \qquad (5.08)$$

* Chapman, ‘Memoirs and Proc. Manchester Lit. and Phil. Soc.,’ vol. 66, p. 1 (1922).

Finally the variable is changed from χ to z, where

$$z^2 = 1 - \lambda, \qquad \chi = \lambda \chi_0, \tag{5.09}$$

so that z ranges from 0 to 1 as λ varies from 1 to 0. The expression for θ then becomes

$$\theta_0 = 2\chi_0 \int_0^1 \left\{ \frac{1 - (\sin \lambda \chi_0 / \sin \chi_0)^{n-1} (\cos \chi_0 / \cos \lambda \chi_0)^2}{1 - \lambda} \right\}^{-\frac{1}{2}} dz$$

$$\equiv 2\chi_0 \int_0^1 \phi \, dz \equiv 2k\chi_0, \tag{5.10}$$

where ϕ represents the integrand and k denotes the integral of ϕ with respect to z from 0 to 1. Clearly k is a function of χ_0 and n, and is obtained by computing ϕ for various values of z from 0 to 1, while χ_0 and n remain fixed. Actually ϕ was calculated for the ten values $0, 0\cdot1, 0\cdot2 \, . \, . \, . \, 0\cdot9$ and $1\cdot0$ of z and the appropriate value of k obtained by applying Simpson's rule. This was done in turn for the values of $0°, 9°, 18°, \, . \, . \, . \, 81°$ and $90°$ of χ_0. The whole process is repeated for any desired value of n.

The limiting value of ϕ when $z \to 0$ is easily shown to be given by

$$\underset{z \to 0}{\text{Lt}} \, \phi = [\chi_0 \{ (n-1) \cot \chi_0 + 2 \tan \chi_0 \}]^{-\frac{1}{2}}$$

$$= \left[\frac{(n-3) \chi_0}{\sin 2\chi_0} \left\{ \frac{n+1}{n-3} + \cos 2\chi_0 \right\} \right]^{-\frac{1}{2}}, \tag{5.11}$$

and when $z = 1$, $\phi = 1$.

In calculating ϕ seven figure tables were used, so that k could be obtained correct to five significant figures. The result of the quadrature of ϕ gives for $2k$ the values :

χ_0	9	18	27	36	45	54	63	72	81
$n = 21$	1·06661	1·06916	1·07107	1·07385	1·07750	1·08192	1·08597	1·08552	1·06682
$n = 25$	1·05695	1·05799	1·05972	1·06232	1·06587	1·07041	1·07519	1·07713	1·06329

The value of $2k$ for $\chi_0 = 90°$ is unity for both values of n. The appropriate values of θ_0 are then obtained from equation (5.10) and used in the integrand for $I_2(n)$.

Having used χ_0 as the independent variable in the calculation of θ_0, we naturally use it too in the calculation of $I_2(n)$. With this change of variable, using the relation (5.05) we find

$$I_2(n) = f(n) \int_0^{\pi/2} \sin^2 2k\chi_0 \cos^2 2k\chi_0 \frac{\tan \chi_0}{(\cos \chi_0)^{4/n-1}} \left(\frac{n+1}{n-3} + \cos 2\chi_0 \right) d\chi_0 \tag{5.12}$$

where

$$f(n) = 2\pi \frac{n-3}{n-1} \left(\frac{2}{n-1} \right)^{2/n-1} \tag{5.13}$$

The integrand in $I_2(n)$ can be shown to vanish for $\chi_0 = 0°$ and $\chi_0 = 90°$ values of $n \geq 5$. Its value for values of χ_0 at intervals of $9°$ was computed, ing the appropriate values of k previously found. The following are the lues obtained:

χ_0	9	18	27	36	45	54	63	72	81
$n = 21$	....	0·00933	0·07170	0·16907	0·27616	0·32264	0·27818	0·17061	0·06489	0·00968
$n = 25$	....	0·00899	0·06205	0·16245	0·26521	0·30970	0·26684	0·16348	0·06181	0·00902

The value of $I_2(n)$ was then obtained by applying Simpson's rule to these mbers and multiplying the result by the appropriate value of $f(n)$. The ults obtained are quoted later.

n terms of the same variable χ_0, the integral $J_1(n)$ is given by

$$J_1(n) = \int_0^{\pi/2} \frac{n-3}{n-1} \cdot 2k\chi_0 \frac{\sin 8k\chi_0}{\sin 2\chi_0} \left(\frac{n+1}{n-3} + \cos 2\chi_0 \right) d\chi_0. \qquad (5.14)$$

in the case of $I_2(n)$ the value of the integrand was calculated for the values $9°, 18° . . . 81°$ and $90°$ of χ. The limiting value of the integrand en $\chi_0 \to 0$ is shown without difficulty to be zero, but the limiting value at upper limit $\chi \to 90°$ is not so easily obtained. The difficulty lies in the fact t k is itself a function of χ_0, and it is necessary to investigate the value of χ_0 for values of χ_0 in the neighbourhood of $90°$.

We see from equations (5.07) and (5.10)

$$= 2k\chi_0 = \int_0^{\chi_0} \left\{ 1 + \frac{1}{2} \left(\frac{\sin \chi}{\sin \chi_0} \right)^{n-1} \left(\frac{\cos \chi_0}{\cos \chi} \right)^2 + \dots \right.$$

$$\left. \dots + \frac{1 \cdot 3 \cdot 5 \dots 2r-1}{2 \cdot 4 \cdot 6 \dots 2r} \left(\frac{\sin \chi}{\sin \chi_0} \right)^{r(n-1)} \left(\frac{\cos \chi_0}{\cos \chi} \right)^{2r} + \dots \right\} d\chi_0.$$

hen χ_0 differs from $\pi/2$ by a small quantity ψ, it is easy to show that the incipal part of the integral of the $(r+1)$th term of this expansion is given

$$\frac{1 \cdot 3 \cdot 5 \dots 2r-1}{2 \cdot 4 \cdot 6 \dots 2r} \int_0^{(\pi/2)-\psi} \left(\frac{\cos \chi_0}{\cos \chi} \right)^{2r} d(\cos \chi) = - \frac{1 \cdot 3 \cdot 5 \dots 2r-1}{2 \cdot 4 \cdot 6 \dots \dots 2r} \frac{\psi}{2r-1}.$$

t follows that to the first order in ψ the complete integral is given by

$$\frac{\pi}{2} - \psi - \int_0^{(\pi/2)-\psi} \left\{ \frac{1}{2} \left(\frac{\cos \chi_0}{\cos \chi} \right)^2 + \frac{1 \cdot 3}{2 \cdot 4} \left(\frac{\cos \chi_0}{\cos \chi} \right)^4 + \dots \right\} d(\cos \chi)$$

$$= \frac{\pi}{2} - \psi + \int_\psi^1 \left[\left\{ 1 - \left(\frac{\cos \chi_0}{z} \right)^2 \right\}^{-\frac{1}{2}} - 1 \right] dz$$

$$= \frac{\pi}{2}.$$

In other words, when $\chi_0 = \pi/2 - \psi$,

$$\theta_0 = 2k\chi_0 = \frac{\pi}{2} + O(\psi^2). \tag{5.15}$$

From this result it follows at once that the integrand of $J_1(n)$ is zero at the upper limit of χ_0. Its value for the nine values of from 9° to 81° was then computed, as in the case of $I_2(n)$. For example, the values obtained in the case of $n = 21$ were :—

χ_0	0	9	18	27	36	45	54
Integrand of $J_1(21)$	0	0·65867	1·03440	0·91595	0·41881	−0·22441	−0·67537

63	72	81	90
−0·84103	−0·63497	−0·29520	0

The graph of the function with respect to χ_0 was a smooth curve, crossing the axis of χ_0 (in the case of $n = 21$) at 43°·3. The area of the curve was obtained by using Simpson's rule for the five abscissæ 0° to 36° (inclusive) and the five abscissæ 45° to 81°. Between 36° and 45° and between 81° and 90° the curve seemed so straight that it was thought best to take the mean of the ordinates and to multiply by the interval between them.

The results of the calculations for $I_2(n)$ and $J_1(n)$ are here collected together for purposes of reference

n	5	7	9	11	15	21	25	∞
$I_2(n)$	....	1·3700	1·1203	1·0435	1·0008	0·9723	0·9659	0·9626	1·0472
$J_1(n)$	....	−0·4829	−0·2758	−0·1649	−0·0953	−0·0177	0·05141	0·0804	0·2337

The value of $J_1(n)$ for $n = \infty$ was calculated by a straightforward integration. In this case, we have $k = \frac{1}{2}$ and $\theta = \chi_0$, so that

$$J(\infty) = \int_0^{\pi/2} 2\chi_0 \cos 2\chi_0 (1 + \cos 2\chi_0) \, d\chi_0 = \frac{\pi^2}{8} - 1.$$

This case corresponds to the molecular model of a rigid elastic sphere.

The interesting point to observe is the change of sign of $J_1(n)$ between $n = 21$ and $n = 15$, for the sign of $J_1(n)$ controls that of S.

It is convenient at this point to investigate the limiting value of the co-efficients of the powers of ω in the expansion (4.11). We found the coefficient of ω^r to be given by $\phi_r(\theta_0)/f(r)\beta^{2r}$, and we require the value of this as $\beta \to 0$. The variable θ_0 is a function of β and it is easy to show that Lt $\theta_0/\beta \to 1$ as $\beta \to 0$. Now when θ_0 is small, we can use a different expansion from that found in (4.11). We have

$$\cos \left\{ 1 + \frac{\omega}{\beta^2} \right\}^{\frac{1}{2}} 4\theta_0 = 1 - \frac{(4\theta_0)^2}{2!}\left(1 + \frac{\omega}{\beta^2}\right) + \frac{(4\theta_0)^4}{4!}\left(1 + \frac{\omega}{\beta^4}\right)^2 - \dots$$

rom which it is easy to see that the coefficient of ω^r is equal to

$$\frac{1}{\beta^{2r}}\left\{\frac{(4\theta_0)^{2r}}{2r!} + O\left(\theta_0^{2r+2}\right)\right\}.$$

This limit of this expression as $\beta \to 0$ is then clearly $4^{2r}/2r!$ Hence the coefficient of ω^r is finite for all values of β.

§6. *Comparison with Experimental Data.*

The possibility of obtaining information of intermolecular fields from a knowledge of the variation of viscosity of gases with temperature has long been recognised, and much experimental data has been accumulated, with that object in view.   Foremost among these are to be noted the researches carried out at Hallé between 1900–1909 by the pupils of Professor Dorn.   A review of this work has been given by K. Schmidt,* who has also compared the results with those calculated by means of the Sutherland formula.   In the cases where the viscosity was measured over only a small range of temperature, the agreement was fairly good, but in other cases, *e.g.*, argon, where the viscosity was measured at very low temperatures, the agreement is good only at high temperatures.   At the lowest temperature, there is a divergence of as much as 8 per cent.   Later researches by Kamerlingh Onnes and S. Weber† on the viscosity of hydrogen and helium at low temperatures showed conclusively that the Sutherland model was inadequate to represent the variation of viscosity.   At temperatures of the order of 20° absolute, the discrepancy in the case of hydrogen was as much as 100 per cent.

About the same time Vogel‡ carried out a series of experiments on viscosity at low temperatures.   He to a large extent confirmed the results of Kamerlingh Onnes and Weber, and showed conclusively the inadequacy of the Sutherland theoretical formula.

The formula which we now wish to compare with experiment can be written in the form

$$\mu = \mu_0 \left(\frac{T}{T_0}\right)^{3/2} \frac{T_0^{\frac{n-3}{n-1}} + S}{T^{\frac{n-3}{n-1}} + S}$$

where μ_0 is the coefficient of viscosity at a standard temperature T_0 (say 0° C.).   This is a special form of a more general one given in equation (4.23),

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* Schmidt, 'Ann. d. Phys.,' vol. 30, p. 399 (1909).

† Kamerlingh Onnes and S. Weber, 'Communications from the Phys. Lab. of Leiden,' Nos. 134A, B and C (1913).

‡ H. Vogel, 'Inaug. Dissertation,' Berlin (1914).

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in which an infinite series appears in the denominator, and it implies the existence of only a weak attractive field. We have now three quantities, n, S and μ_0, to determine from the observations. Instead of n, it is convenient to regard $(n - 3)/(n - 1)$ as the constant to be determined. For this we write x, and note that for Maxwellian molecules $x = \frac{1}{2}$ and for rigid elastic spheres $x = 1$, so that we consider values of x between these two limits. As x appears as an index, it is difficult to find a straightforward method of determining the three unknowns. Now Sutherland's formula corresponds to a fixed value of x, viz., $x = 1$, and in using it, values of S and μ_0 are calculated to give the best agreement with experiment. It appears, then, that the obvious method to be followed in our case, although somewhat laborious, is to assume different values for x and then to ascertain the best appropriate values of S and μ_0. From a comparison of the relative agreements obtained, one may hope to determine the best value of x.

In Table II are recorded the values of the viscosity of argon, given by K. Schmidt.* Taking the reading $\mu = 2,116 \times 10^{-7}$, corresponding to the temperature $- 0 \cdot 2°$ C., as a standard (or $\mu = 2,118 \times 10^{-7}$ at $273 \cdot 1°$ absolute), it is possible to calculate a series of values of S (for any fixed x) from the remaining values, given in the table, from the formula

$$S \left\{ 1 - \frac{\mu_r}{\mu_0} \left(\frac{T_0}{T_r} \right)^{1 \cdot 5} \right\} = \frac{\mu_r}{\mu_0} \left(\frac{T_0}{T_r} \right)^{1 \cdot 5} T_r{}^x - T_0{}^x.$$

In column 2 of Table I are recorded the values obtained corresponding to the Sutherland formula. We have omitted the values calculated from the temperatures $13 \cdot 17$, $- 20 \cdot 3$ and $- 40 \cdot 2$ as not being reliable enough, owing to the small range of temperature involved.

Table I.—Values of the Attractive Constant S of Argon.

T.	$x = 1$ $(n = \infty)$	$x = 0 \cdot 9$ $(n = 21)$	$x = 0 \cdot 85$ $(n = 14\frac{1}{3})$	$x = 0 \cdot 8$ $(n = 11)$	$x = 0 \cdot 7$ $(n = 7 \cdot 66)$
$183 \cdot 3$	$172 \cdot 8$	$67 \cdot 22$	$38 \cdot 76$	$21 \cdot 02$	$2 \cdot 72$
$99 \cdot 7$	$165 \cdot 5$	$66 \cdot 30$	$38 \cdot 27$	$21 \cdot 67$	$3 \cdot 66$
$-60 \cdot 2$	$153 \cdot 1$	$65 \cdot 25$	$41 \cdot 47$	$24 \cdot 64$	$6 \cdot 6$
$-78 \cdot 8$	$134 \cdot 8$	$56 \cdot 90$	$35 \cdot 56$	$20 \cdot 75$	$4 \cdot 9$
$-104 \cdot 4$	$136 \cdot 6$	$59 \cdot 07$	$37 \cdot 72$	$22 \cdot 63$	$6 \cdot 2$
$-183 \cdot 2$	$128 \cdot 2$	$59 \cdot 95$	$39 \cdot 95$	$25 \cdot 81$	$9 \cdot 4$
Value of S used	$174 \cdot 6$ (Schmidt)	$62 \cdot 45$	$38 \cdot 62$	$22 \cdot 75$	

* Schmidt, *loc. cit.* The viscosity for $-132 \cdot 3°$ C., given by Schmidt as $1106 . 10^{-7}$, is omitted as being inconsistent with the other values, as is clearly evident when μ is plotted against T.

We find, as Vogel did, a steady diminution of S with decreasing temperature. In order to test whether the same result holds for all values of x, the values of S have been worked out in the same way for $x = 0\cdot9, 0\cdot85, 0\cdot8$ and $0\cdot7$. In the last case, we find an increase of S with diminishing temperature, while in the intermediate cases the values are more nearly constant.

Table II.—Calculated and Observed Values of the Viscosity of Argon.*
$(\mu_{273\cdot1} = 2\cdot118 \times 10^{-4}.)$

T.	μobs. $\times 10^7$.	Model A.		Model B.		Model C.		Model D.	
		Calc.	Per cent. Error.	Calc.	Per cent. Error.	Calc.	Per cent. Error.	Calc.	Per cent. Error.
183·3	3,243	3,241	−0·03	3,221	−0·7	3,241	−0·06	3,255	+0·37
99·7	2,751	2,756	+0·18	2,744	−0·25	2,751	0	2,757	+0·22
13·17	2,207	2,203	−0·18	2,203	−0·2	2,204	−0·15	2,204	+0·14
−0·21	2,116	2,112	−0·18	2,116	0	2,116	0	2,116	0
−20·3	1,987	1,972	−0·7	1,980	−0·35	1,980	−0·35	1,980	−0·35
−40·2	1,854	1,829	−1·36	1,843	−0·6	1,844	−0·54	1,843	−0·6
−60·2	1,697	1,680	−0·9	1,700	+0·2	1,702	+0·29	1,701	+0·23
−78·8	1,575	1,539	−2·34	1,564	−0·7	1,567	−0·51	1,568	−0·45
104·4	1,379	1,338	−3·06	1,373	−0·4	1,376	−0·22	1,379	0
183·2	735·6	675·7	−8·25	728·8	−0·9	740·9	+0·71	752·8	+2·3

Model A corresponds to $n = \infty$, $S = 174\cdot6$; Model B to $n = 21$, $S = 62\cdot45$; Model C to $= 14\frac{1}{3}$, $S = 38\cdot62$; and Model D to $n = 11$, $S = 22\cdot75$.

Taking the mean values of S obtained in each of these cases, the values of μ were calculated from the formula given above, taking $\mu_0 = 2,118 \times 10^{-7}$, $T_0 = 273\cdot1$. The results obtained are to be found in Table II. There is clearly a marked improvement in the agreement between calculated and observed values over that obtained by Sutherland's formula. The agreement is best in the case of $x = 0\cdot85$, corresponding to $n = 14\frac{1}{3}$, where the divergence is nowhere greater than $0\cdot7$ per cent. The agreement in the case of $x = 0\cdot9$ can easily be improved by adjusting the value of μ_0. If this is taken to be $2,126 \times 10^{-7}$ instead of $2,118 \times 10^{-7}$, the results recorded in Table III are obtained, showing extreme variations of $-0\cdot5$ per cent. and $0\cdot6$ per cent.

* The values for Model A are taken from the paper by K. Schmidt, *loc. cit.*, p. 400, except that his value 1354 for $- 104\cdot4$ has been replaced by 1338 as a result of a recalculation. The value of μ_0 used by him was $2,114 \times 10^{-7}$.

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Table III.—The Viscosity of Argon calculated for $n = 21$, $S = 62 \cdot 45$ with $\mu_0 = 2{,}126 \times 10^{-7}$.

T	$\mu_{obs.} \times 10^7$.	$\mu_{calc.} \times 10^7$.	Per cent. diff.
183·3	3,243	3,235	−0·2
99·7	2,751	2,756	+0·2
13·17	2,207	2,213	+0·3
−0·21	2,116	2,124	+0·4
−20·3	1,987	1,989	+0·1
−40·2	1,854	1,851	−0·2
−60·2	1,697	1,708	+0·6
−78·8	1,575	1,571	−0·3
−104·4	1,379	1,379	0
−183·2	735·6	731·1	−0·5

Unfortunately there is no one model which gives obviously better agreement than any other. Equally good agreement is obtained for $x = 0 \cdot 9$ corresponding to $n = 21$ and $S = 62 \cdot 45$ as for $x = 0 \cdot 85$ corresponding to $n = 14\frac{1}{3}$ and $S = 38 \cdot 62$. We can only infer that viscosity results alone are not sufficient to determine uniquely the nature of the inter-molecular fields. The question is further discussed in the next paragraph with special reference to argon.

In some cases the Sutherland formula has given satisfactory agreement with experiment. Two such examples have been given by Breitenbach,* one of these being carbon dioxide. Equally good agreement can, however, be obtained by the use of the formula given in this paper. The results of the calculations for different molecular models are given in Table IV.

Table IV.—Calculated and Observed Values of Viscosity of CO_2.

T.	$\mu_{obs.} \times 10^7$.	Model A.		Model B.		Model C.		Model D.	
		Calc.	Per cent.	Calc.	Per cent.	Calc.	Per cent.	Calc.	Per cent.
302·0	2,682	2,685	+0·11	2,693	+0·4	2,689	+0·3	2,704	+0·8
182·4	2,221	2,218	−0·13	2,212	−0·4	2,200	−0·8	2,204	−0·8
99·1	1,861	1,861	0	1,856	−0·3	1,844	−0·85	1,844	−0·85
15·0	1,457	1,470	+0·9	1,472	+1·0	1,469	+0·8	1,466	+0·4
−20·7	1,294	1,292	−0·15	1,300	+0·3	1,300	+0·3	1,299	+0·3

Model A corresponds to $n = \infty$, $S = 239 \cdot 7$; Model B to $n = 14\frac{1}{3}$, $S = 58 \cdot 82$; Model C to $n = 9$, $S = 18 \cdot 25$; and Model D to $7 \cdot 66$, $S = 9 \cdot 3$.

A similar investigation for hydrogen and helium failed to improve the fit obtained by Kamerlingh Onnes,† taking μ proportional to $T^{0 \cdot 695}$ and $T^{0 \cdot 647}$

* Breitenbach, 'Ann. d. Phys.,' IV, vol. 5, p. 166 (1901); Jeans, 'Dynamical Theory of Gases,' 3rd edn., p. 285 (1921).

† Kamerlingh Onnes, *loc. cit.*

respectively. These were given as empirical formulæ, but they correspond theoretically to repulsive fields according to an inverse power, where the index is equal to 11·2 and 14·6 respectively. We may therefore take it that in these cases there is no appreciable attractive field.

§7. *The Molecular Field of Argon.*

From the values of n and S determined in the last paragraph, the corresponding values of the repulsive force constant λ_n can be found from the formula

$$\lambda_n^{2/n-1} = \frac{5m^{1/2}\pi^{1/2}(2k)^{\frac{n+3}{2(n-1)}}}{8\sqrt{2}\,I_2(n)\,\Gamma\left(4 - \frac{2}{n-1}\right)} \frac{T_0^{3/2}}{\mu_0\,(T_0^{\frac{n-3}{n-1}} + S)}. \tag{7.01}$$

Using the pairs of values $n = 14\frac{1}{3}$, S $= 38\cdot62$, and $n = 21$, S $= 62\cdot45$, and $n = 25$, S $= 72\cdot56$ obtained in the case of argon (columns 3 and 4 of Table II), we are led to the values of the force constants given in column 2 of Table V.*

Table V.—Repulsive Force Constants and " Diameters " of Argon.

n	$\lambda_n.$	$\sigma \cdot 10^8$ cms.
$14\frac{1}{3}$	$3\cdot573 \cdot 10^{-113}$	$4\cdot698$
21	$2\cdot818 \cdot 10^{-163}$	$3\cdot987$
25	$2\cdot610 \cdot 10^{-193}$	$3\cdot795$
∞	∞	$2\cdot84$

For purposes of comparison we use the notion of " diameters " introduced in §4, according to which

$$\sigma = \left(\frac{2\lambda_n}{3(n-1)k}\right)^{1/n-1}, \tag{7.02}$$

the results being given in column 3 of the same table. The value appropriate to the rigid sphere ($n = \infty$) is obtained by putting

$$\sigma = \operatorname*{Lt}_{n \to \infty} (\lambda_n)^{1/n-1} \tag{7.03}$$

in the equation (7·01), from which we have

$$\sigma^2 = \frac{5m^{1/2}\pi^{1/2}k^{1/2}}{48 I_2(\infty)} \frac{T_0^{3/2}}{\mu_0\,(T_0 + S)}. \tag{7.04}$$

* In the calculation for $n = 21$, we have taken $\mu_0 = 2\cdot126 \times 10^{-4}$ for $T_0 = 273\cdot1°$ absolute. The values of the attractive constant from which S was calculated in the case of $n = 25$ were $79\cdot21$, $77\cdot62$, $75\cdot61$, $66\cdot12$, $68\cdot42$ and $68\cdot41$, corresponding to the temperatures in Table I in descending order.

If the attractive field of argon were of the type considered in detail in this paper, the value of the attractive force constant could be obtained from S by means of equation (4.26), viz.,

$$\lambda_3 = \frac{2I_2(n)}{\pi J_1(n)} \Gamma\left(4 - \frac{2}{n-1}\right) (2k)^{\frac{n-3}{n-1}} \lambda_n^{\frac{2}{n-1}} S$$

$$= \frac{5m^{1/2}k^{3/2}}{2\pi^{1/2}J_1(n)} \frac{ST_0^{3/2}}{\mu_0(T_0^{\frac{n-3}{n-1}}+S)}. \tag{7.05}$$

There may be cases where it is of this type, so the formula is here put on record. The criterion is the dependence of S on n, as determined from the observations. If it changes from positive to negative as n decreases through the value $n = 17$, as does the theoretical function $J_1(n)$, then the attractive field may be regarded as of the inverse cube type. In the case of argon, the value of S remains positive down to the value $n = 7$, so that we must conclude that its attractive field is of a different kind from that considered here. Its nature must remain undetermined until a theoretical formula for S can be obtained for more general attractive fields.

§ 8. *Summary.*

(i) A new theoretical formula has been found for the coefficient of viscosity. This is obtained for a molecular model with a repulsive field $\lambda_n r^{-n}$ and an attractive field $\lambda_3 r^{-3}$.   The formula is $\mu \propto T^{3/2} \div (T^{\frac{n-3}{n-1}} + S)$. It may be regarded as a generalisation of the Sutherland formula.

(ii) Reasons are given for inferring a formula for the more general case of a repulsive field $\lambda_n r^{-n}$ and an attractive field $\lambda_m r^{-m}$.

(iii) It is shown that the " attractive constant " S may be positive or negative according to the nature of the repulsive field.   The numerical coefficients occurring in S are evaluated by quadrature for various values of n.

(iv) The formula is shown to represent the observed temperature variation of the viscosity of argon over the whole observed range ($-180°$ C. to $180°$ C.) with no greater deviation than $0 \cdot 6$ per cent.

(v) This agreement between theory and experiment can be obtained for more than one molecular model ; in fact, it is shown that the repulsive field (r^{-n}) of argon may have any index from 15 to 25.   The conclusion is reached that viscosity results alone are not sufficient to determine uniquely molecular fields.

(vi) The repulsive force constants (λ_m) of argon are calculated for three values of n, (14, 21 and 25).