

sociate the compound. Films sputtered in argon are easily removed mechanically, they show orientation readily and are easily poisoned. The rarity of mixed patterns, with the exception of III, is striking. Types D, E, and F are distinguished by their different modes of preparation. There is so far no evidence to suggest that they are fundamentally different.

We have refrained from suggesting any mechanism for the act of catalysis. Further experiments are needed to distinguish between various possible explanations, and are being made by one of us (G. I. F.). The work described in the present paper, which has taken two years and a half to complete, covers the main features of the catalytic process as directly observable, and shows the structure of the film at its various stages. We feel justified in expressing the view that the method of electron diffraction is likely to play as important a rôle in the study of the mechanism of heterogeneous catalytic reactions as is played by spectrographic methods in the study of gaseous reactions.

Free Paths and Transport Phenomena in Gases and the Quantum Theory of Collisions. I.—The Rigid Sphere Model.

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The necessity for the use of quantum mechanics in the theory of atomic phenomena is most clearly manifest in the study of collision processes. Diffraction effects have been observed in the scattering of electrons from crystals* and by atoms,† while the recent developments of molecular ray technique have made it possible to establish the existence of cross-grating spectra in the reflection of molecular beams from crystal surfaces.‡ In view of the importance of wave theory in these phenomena, it is clearly necessary to examine the conditions under which the classical theory of gases must be modified and

* G. P. Thomson, "Free Motion in Wave Mechanics."

† J. J. and G. P. Thomson, "Conduction of Electricity through Gases," vol. 2, Chapter III, Camb. Univ. Press (1933).

‡ Fraser, "Molecular Rays," Camb. Univ. Press (1931).

to determine the nature of the modifications. Such an investigation receives added importance owing to the possibility of experimental test by molecular ray methods. Also, considerable interest is attached to the possibility of direct experimental proof of the Bose-Einstein statistics for neutral atoms and molecules from collision experiments as has already been possible for α -particles.*

In order to develop the quantum theory of collisions in a form suitable for this purpose, we first discuss the simplest model which bears sufficient resemblance to the actual facts, and so we consider the rigid sphere model for gas atoms. This model has already proved valuable in the classical theory of transport phenomena and has the additional advantage of permitting an exact quantum mechanical solution. It will be seen that the results obtained by the use of this model are of great interest and suggest several new lines of investigation, both experimental and theoretical. Finally, a method for dealing with the general case of any law of force will be discussed.

§ 1. *The Physical Processes Involved and the Classical Formulæ.*

There is a large number of properties of gases which depend on the interaction energies of the atoms, and many of these properties have already been investigated for a variety of gases. We propose to discuss here only those properties which are directly related to collisions between the gas atoms, and of these the coefficients of viscosity and diffusion (including thermal diffusion) have long been known for various gases over a wide range of temperatures. To these we may now add the direct measurement of free paths, of the angular distributions of gas atoms scattered under various conditions, and of the mobilities of positive ions in pure gases. The latter measurements virtually consist in determining the diffusion coefficients of the ions in the gas.

The great value of these investigations is that, when correlated with a satisfactory theory, they lead to a knowledge of the fields of force between gas atoms, information of considerable value for chemistry, as well as providing a check on the theoretical formulæ obtained from quantum mechanical theory of atomic interactions. Laws of force have already been derived by Lennard-Jones for a number of gases with the use of classical theory in connection with observed coefficients of viscosity and diffusion and their variation with

* Mott, 'Proc. Roy. Soc.,' A, vol. 126, p. 259 (1930); Chadwick, 'Proc. Roy. Soc.,' A, vol. 128, p. 114 (1930); Blackett and Champion, 'Proc. Roy. Soc.,' A, vol. 130, p. 380, (1931).

temperature.* Direct test of these laws of force by means of free path measurements has no significance on classical theory, as the free path depends on the experimental definition of a collision and tends to zero as smaller and smaller deviations are included in the measurements. On the quantum theory this is no longer true, and it is possible to obtain very interesting and valuable information from direct observation of free paths.

Before discussing the quantum theory of collisions, we will give the classical formulæ for the various quantities involved, and convert them to a form convenient for quantum mechanical discussion.

The most complete classical theories of transport phenomena are due to Chapman† and Enskog,‡ who obtained the same final results; we shall use Chapman's formulæ throughout. For the coefficient of viscosity η of a simple gas at absolute temperature T , he finds

$$\eta = \frac{5}{4j^3 M^2} \left(\frac{2\pi}{jM} \right)^{3/2} \frac{1 + \varepsilon}{\pi R_{11}}, \quad (1)$$

where

$$j = 1/2\kappa T, \quad (2)$$

M is the mass of a gas atom, and κ is Boltzmann's constant. R_{11} is given by

$$R_{11} = \frac{1}{2} \int_{-\infty}^{\infty} V^2 Q_{\eta} e^{-\frac{1}{2}jMV^2} dV, \quad (3)$$

where

$$Q_{\eta} = \pi \int_0^{\infty} \sin^2 \theta dp^2, \quad (4)$$

p is the perpendicular distance between the asymptotes of the paths of two atoms while entering on collision and θ is the angle the relative velocity of the atoms is turned through by the collision. V is the relative velocity of the atoms before impact. Q_{η} has the dimensions of area and may be defined as the collision area effective in viscosity.

The quantity ε depends in a complicated way on collision phenomena in the gas (and hence on the law of interaction), but on the classical theory its value is never greater than 0.017. As quantum modifications are unlikely to alter the magnitude of ε sufficiently to make its calculation important, we shall neglect it in what follows; in a later paper its calculation will be considered using quantum mechanical collision theory.

* For a summary of this work see chap. X by Lennard-Jones in R. H. Fowler's "Statistical Mechanics," Camb. Univ. Press (1929), and 'Proc. Lond. Phys. Soc.,' vol. 43, p. 461 (1931).

† 'Phil. Trans.,' A, vol. 216, p. 279 (1916); vol. 217, p. 115 (1917).

‡ 'Inaug. Diss.' (Uppsala, 1917).

For the coefficient of diffusion between two gases (distinguished by suffixes 1 and 2) Chapman gives the formulæ

$$D = \frac{3}{16} \pi^{1/2} \left(\frac{M_1 + M_2}{j M_1 M_2} \right)^{7/2} \frac{1}{(\nu_1 + \nu_2) P_{12}} \frac{1}{1 - \epsilon_0}, \quad (5)$$

where M_1, M_2 are the masses of the gas atoms, and ν_1, ν_2 the number of atoms of each per cubic centimetre. P_{12} is given by

$$P_{12} = 2 \int_{-\infty}^{\infty} V^5 Q_D(1, 2) \exp. \left\{ \frac{j M_1 M_2}{M_1 + M_2} V^2 \right\} dV, \quad (6)$$

where

$$Q_D(1, 2) = \pi \int_0^{\infty} \sin^2 \frac{1}{2} \theta dp^2. \quad (7)$$

and is the collision area effective in diffusion.

ϵ_0 , like ϵ in expression (1), depends in a complicated way on the atomic collisions and also on the relative concentrations of the two gases. It is never very great—on classical theory its maximum value is 0.136—and so the quantum theoretical calculation of ϵ_0 will be deferred to a later paper.

The coefficient of thermal diffusion of a gaseous mixture cannot be written down in such a simple form, but it involves, in general, the interactions between molecules of the same kind as well as molecules of different kinds. As a consequence of this, the formula includes integrals of the form

$$P_{11} = 2 \int_{-\infty}^{\infty} V^5 Q_D(1, 1) \exp. \left\{ -\frac{1}{2} j M V^2 \right\} dV. \quad (8)$$

The mobilities of positive ions in pure gases are given in terms of the coefficient of diffusion D by means of Langevin's formula*

$$k = eD/\kappa T, \quad (9)$$

where e is the charge on the ion.

Examination of the classical theory shows that the only modifications which are introduced in the general formulæ above arise from the use of the Bose-Einstein, instead of classical, statistics, and this modification can be neglected except at extremely low temperatures and high densities. However, when we apply the formulæ to the consideration of any particular model, the use of the quantum theory of collisions between the gas atoms will affect the values of the cross-sections Q_n, Q_D in the formulæ (4), (7) above. The quantities $\epsilon,$

* *Ann. Chim. Phys.*, vol. 5, p. 245 (1905).

ϵ_0 will also be affected, but we neglect this at present for the reasons already stated.

In order to obtain Q_n , Q_D in forms convenient for quantum mechanical treatment, we must change the variable from the impact parameter p to the angle of scattering θ in relative co-ordinates.*

Since we are using relative co-ordinates we may discuss the collisions as if one atom is held at rest. Suppose, then, that we have a stream of N atoms per unit area per second incident with velocity v on this atom. Then the probable number of particles per second crossing a plane perpendicular to the direction of flight with angular momentum between J and $J + dJ$ is

$$2\pi N J dJ / M^2 v^2.$$

To obtain the number of particles deflected between angles θ and $\theta + d\theta$, which we write in the form

$$2\pi N I(\theta) \sin \theta d\theta,$$

where $I(\theta)$ has the dimensions of area, we make use of the fact that J may be expressed as a function of θ . Therefore

$$2\pi N I(\theta) \sin \theta d\theta = \frac{2\pi N J}{M^2 v^2} \frac{dJ}{d\theta} d\theta.$$

Now $J = Mvp$, so

$$p dp = I(\theta) \sin \theta d\theta. \quad (10)$$

Hence

$$Q_n = 2\pi \int_0^\pi I(\theta) \sin^3 \theta d\theta, \quad (11)$$

$$Q_D = 2\pi \int_0^\pi I(\theta) \sin^2 \frac{1}{2}\theta \sin \theta d\theta, \quad (12)$$

while the collision cross-section Q is given by

$$Q = 2\pi \int_0^\pi I(\theta) \sin \theta d\theta. \quad (13)$$

§ 2. The Quantum Theory of Collisions.

The function $I(\theta)$ for the scattering of a particle of mass m and velocity v by a field of force of potential $V(r)$ is given by

$$I(\theta) = \frac{1}{4k^2} \left| \sum_n (2n+1) (e^{2i\delta_n} - 1) P_n(\cos \theta) \right|^2, \quad (14)$$

* θ is the angle through which the direction of the relative velocity is turned.

where $k = 2\pi mv/h$ and the phases δ_n are obtained from the asymptotic form of the solution of the equation

$$\frac{d^2u}{dr^2} + \left\{ k^2 - \frac{8\pi^2m}{h^2} V(r) - \frac{n(n+1)}{r^2} \right\} u = 0, \quad (15)$$

which is finite at the origin. The phases are such that this asymptotic form is*

$$u \sim \sin(kr - \frac{1}{2}n\pi + \delta_n). \quad (16)$$

The collision cross-section will then be given by

$$Q = \frac{4\pi}{k^2} \sum_n (2n+1) \sin^2 \delta_n. \quad (17)$$

Before proceeding to discuss those properties of the phases which are important for our purpose, it is necessary to remark the modifications of treatment necessary when the colliding systems are of comparable mass. In this case we obtain the same expression as (14) in the co-ordinate system in which the position of one atom is defined relative to the other atom, but we must take for the mass m the reduced mass

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

where M_1, M_2 are the masses of the colliding atoms. $V(r)$ is now, of course, the interaction energy of the two atoms and v their relative velocity. In experimental observations of angular distributions, one measures the number of atoms scattered in a given direction relative to the direction of incidence. To convert the angular distribution in relative co-ordinates to the angular distribution relative to the direction of incidence, one merely uses the classical momentum and energy relations. In particular, if the atoms are of equal mass, the distribution per unit angle will be given by

$$I(2\Theta) \sin 2\Theta, \quad (18)$$

where Θ is the angle of scattering referred to the direction of incidence.

The most important property of the phases is that δ_n is small when

$$\frac{8\pi^2m}{h^2} V(r) \ll \frac{n(n+1)}{r^2}, \quad (19)$$

for such r that $kr \sim n + \frac{1}{2}$.

* Faxen and Holtsmark, 'Z. Physik,' vol. 45, p. 307 (1927).

Under these conditions it is possible to use an approximate expression for δ_n in the form*

$$\delta_n = \frac{4\pi^3 m}{h^2} \int_0^\infty V(r) \{J_{n+\frac{1}{2}}(kr)\}^2 r dr. \quad (20)$$

In the special case where all the phases are small, the series (14) may be summed to give, approximately,

$$I(\theta) = \frac{64\pi^4 m^2}{h^4} \left\{ \int_0^\infty V(r) \frac{\sin(2kr \sin \frac{1}{2}\theta)}{2kr \sin \frac{1}{2}\theta} r dr \right\}^2, \quad (21)$$

which is the well-known approximation due to Born.† Substituting this formula in (13) we see that the total collision cross-section Q will be finite if $V(r)$ vanishes at infinity faster than r^{-3} . This same result must hold for the exact formula (14), for, when n is sufficiently large, the exact and approximate series converge together by virtue of (19) and (20). As it is extremely unlikely that the interaction between atoms falls off as slowly as r^{-3} for large r , we see that the mean free path has a perfectly definite value depending on the law of force and so provides a further means of determining this law.

In the particular case of the low velocity limit of the cross-section, it is not yet possible to state the conditions under which the limit is finite, but it appears that, for a potential which vanishes more rapidly than r^{-3} at infinity, the limit is infinite only when very special relations are satisfied by the field of interaction. This is illustrated in the appendix for the case of an exponential field of force.

In the case of the collisions of gas atoms, it is easy to see that Born's approximation is only applicable to phases of very high order except for collisions at extremely low temperatures. As the ratio of wave-length to atomic diameter is considerably less than unity, an approximation based on classical theory will give satisfactory results for the phases of low order. Such an approximation is that given by Jeffreys.‡ This method gives for the solutions of the equation

$$\frac{d^2 u}{dr^2} + \left\{ k^2 - \frac{8\pi^2 m}{h^2} V(r) - \frac{n(n+1)}{r^2} \right\} u = 0,$$

the asymptotic forms $u \sim \sin \left[\frac{\pi}{4} + \int_{r_0}^\infty \{f(r)\}^{\frac{1}{2}} dr \right],$

$$\sin \left[\frac{\pi}{12} + \int_{r_0}^\infty \{f(r)\}^{\frac{1}{2}} dr \right]. \quad (22)$$

* Mott, 'Proc. Camb. Phil. Soc.,' vol. 25, p. 304 (1929).

† 'Z. Physik,' vol. 38, p. 803 (1926).

‡ 'Proc. Lond. Math. Soc.,' vol. 23, p. 428 (1924).

Here

$$f(r) = k^2 - \frac{8\pi^2 m}{h^2} V - \frac{n(n+1)}{r^2} \quad (23)$$

and r_0 is the largest zero of $f(r)$.

The first of these two solutions is zero at the origin and is the solution we require. Comparing (22) with (16) we obtain

$$\delta_n = \frac{1}{2}n\pi + \frac{1}{4}\pi + \int_{r_0}^{\infty} [\{f(r)\}^{\frac{1}{2}} - k] dr. \quad (24)$$

This approximation is satisfactory when

$$\frac{8\pi^2 m}{h^2} V(r)$$

is large compared with the centrifugal force term $n(n+1)/r^2$, and is strictly accurate in the classical limit of $h \rightarrow 0$. If, then, we wish to calculate the scattering of one gas atom by another, we may calculate the phases for small n by Jeffreys' method and for large n by Born's method. The former method will be accurate when δ_n is greater than unity, the latter when δ_n is less than unity. The intermediate phases may then be obtained by interpolation.

By using this method it is thus possible to consider various types of interactions between atoms.* However, before proceeding to such a detailed investigation, we will consider the collision of rigid spheres, for which we may readily find exact expressions for all the phases.

§ 3. *The Effect of Symmetry.*

Before expressing the formulæ (4), (7) in terms of the phases δ_n we must introduce a modification of the above formulæ which is necessary when the colliding atoms are similar. In this case it is impossible to distinguish experimentally between the incident and struck atoms, and the wave function describing the motion must satisfy certain symmetry properties with respect to the co-ordinates of the two atoms. In particular, if the atoms obey the Bose-Einstein statistics, the wave function describing their motion must be symmetric in the co-ordinates of the two atoms.

Since interchange of the atoms changes θ into $\pi - \theta$ we must take the scattered amplitude in this case in the form

$$2^{-\frac{1}{2}}\{f(\theta) + f(\pi - \theta)\},$$

* A preliminary account of this work was given in 'Nature,' vol. 130, p. 276 (1932). The cross-sections given there should be doubled.

where

$$f(\theta) = \frac{1}{2ik} \sum_n (e^{2i\delta_n} - 1) (2n + 1) P_n(\cos \theta).$$

This gives, for the function $I(\theta)$, the form

$$I(\theta) = \frac{1}{2k^2} \left| \sum_n (4n + 1) (e^{2i\delta_{2n}} - 1) P_{2n}(\cos \theta) \right|^2,$$

all odd harmonics being excluded. This modification has the effect of reducing the number of effective terms in the series and making the deviations from classical theory more marked at a particular energy of the particles than they otherwise would be.

We are now in a position to express the formulæ (4), (7) in terms of the phases δ_n . Firstly for the case of the viscosity, by using the formula

$$x^2 P_n(x) = \frac{(n+2)(n+1)}{(2n+3)(2n+1)} P_{n+2}(x) + \frac{4n^3 + 6n^2 - 1}{(2n+1)(2n-1)(2n+3)} P_n(x) \\ + \frac{n(n-1)}{(2n+1)(2n-1)} P_{n-2}(x),$$

we obtain

$$Q_\eta = \frac{4\pi}{k^2} \sum_n \left\{ \frac{4n^3 + 6n^2 - 2n - 2}{(2n-1)(2n+3)} \sin^2 \delta_n \right. \\ \left. - \frac{2(n+2)(n+1)}{2n+3} \cos(\delta_n - \delta_{n+2}) \sin \delta_n \sin \delta_{n+2} \right\}. \quad (25)$$

Then for the diffusion, using the formula

$$xP_n(x) = \frac{n+1}{2n+1} P_{n+1}(x) + \frac{n}{2n+1} P_{n-1}(x),$$

we have

$$Q_D(1, 2) = \frac{2\pi}{k^2} \sum \{ (2n+1) \sin^2 \delta_n - 2(n+1) \cos(\delta_n - \delta_{n+1}) \sin \delta_n \sin \delta_{n+1} \}. \quad (26)$$

In the special case of self-diffusion, which is important in the theory of thermal diffusion, the odd phases vanish and

$$Q_D(1, 1) = \frac{4\pi}{k^2} \sum_n (4n+1) \sin^2 \delta_{2n}, \\ = \frac{1}{2} Q. \quad (27)$$

These formulæ are to be compared with the formula (17) for the total cross-section Q .

§ 4. *The Elastic Sphere Model.*

If we consider the atoms as elastic spheres, we take the interaction energy $V(r)$ as given by

$$\begin{aligned} V(r) &= 0, & r > r_0 \\ &= \infty, & r < r_0. \end{aligned} \quad (28)$$

Under these conditions the wave function representing the relative motion must vanish at the boundary $r = r_0$. The wave equation from which to determine the phases δ_n is

$$\frac{d^2u}{dr^2} + \left\{ k^2 - \frac{n(n+1)}{r^2} \right\} u = 0, \quad (29)$$

for $r > r_0$. The solutions of this equation are, in terms of Bessel functions,

$$u = r^{\frac{1}{2}} J_{n+\frac{1}{2}}(kr), \quad r^{\frac{1}{2}} J_{-n-\frac{1}{2}}(kr),$$

so that the general solution is

$$r^{-\frac{1}{2}}u = A J_{n+\frac{1}{2}}(kr) + B J_{-n-\frac{1}{2}}(kr). \quad (30)$$

In order that this solution be zero at $r = r_0$ we must have

$$\frac{B}{A} = - \frac{J_{n+\frac{1}{2}}(kr_0)}{J_{-n-\frac{1}{2}}(kr_0)}. \quad (31)$$

Since

$$\begin{aligned} J_{n+\frac{1}{2}}(kr) &\sim r^{-\frac{1}{2}} \sin(kr - \frac{1}{2}n\pi), \\ J_{-n-\frac{1}{2}}(kr) &\sim r^{-\frac{1}{2}} \cos(kr - \frac{1}{2}n\pi), \end{aligned}$$

we thus see that

$$\delta_n = \arctan(-1)^{n+1} \frac{B}{A}, \quad (32)$$

and in particular

$$\delta_0 = -kr_0. \quad (33)$$

In Table I the phases δ_n are tabulated for various values of kr_0 . The number of multiples of π to add to the smallest solution of (32) for δ_n is determined from the number of zeros of the function $J_{n+\frac{1}{2}}(kr)$ eliminated by the field. As the existing tables of half order Bessel functions* were inadequate for our purpose, a number had to be calculated using the recurrence formulæ for the Bessel functions; it would be sufficient in many cases to use the asymptotic expressions for Bessel functions of large argument† in the relation (31).

* Watson, "The Theory of Bessel Functions," Camb. Univ. Press (1922). In using these tables it must be remembered that the definition of $J_{-n-\frac{1}{2}}(kr)$ given by Watson is $(-1)^n$ that given above.

† Watson, chaps. VII and VIII.

Table I.—Values of the phases $-\delta_n$ which occur in the quantum theory of the interaction of hard spheres for different values of kr_0 where r_0 is the sum of the radii of the spheres and $k\hbar/2\pi M$ their velocity, M being the “reduced mass.”

n	$kr_0 =$					
	30	20	10	5	3	2
0	30.00	20.00	10.00	5.00	3.00	2.00
1	28.46	18.48	8.53	3.63	1.75	0.89
2	26.96	17.01	7.16	2.47	0.84	0.26
3	25.49	15.59	5.89	1.50	0.28	0.04
4	24.05	14.22	4.73	0.79	0.06	0.003
5	22.65	12.90	3.68	0.32	0.007	
6	21.28	11.63	2.74	0.09		
7	19.94	10.42	1.93	0.02		
8	18.64	9.26	1.25	0.002		
9	17.37	8.15	0.72			
10	16.14	7.11	0.36			
11	14.95	6.11	0.14			
12	13.79	5.19	0.04			
13	12.66	4.32	0.01			
14	11.57	3.52				
15	10.53	2.79				
16	9.52	2.14				
17	8.55	1.56				
18	7.63	1.08				
19	6.74	0.68				
20	5.90	0.39				
21	5.10	0.21				
22	4.34	0.09				
23	3.65	0.03				
24	2.99	0.01				
25	2.37					
26	1.86					
27	1.39					
28	0.98					
29	0.66					
30	0.40					
31	0.24					
32	0.12					
33	0.05					
34	0.02					

The quantum theory formulæ for the hard sphere are then obtained by substituting the expression (32) for the phases in (17), (25), (26). The corresponding classical formulæ are

$$Q = \pi r_0^2, \quad (34)$$

$$Q_\eta = \frac{2\pi}{3} r_0^2, \quad (35)$$

$$Q_D = \frac{1}{2}\pi r_0^2. \quad (36)$$

In fig. 1 and Table II the classical and quantum theoretical values for Q_v , Q_D and the collision radius for the case of a hard sphere are compared. In all cases we notice that when the colliding particles are similar, there are deviations of 7% from classical theory for the first of these expressions

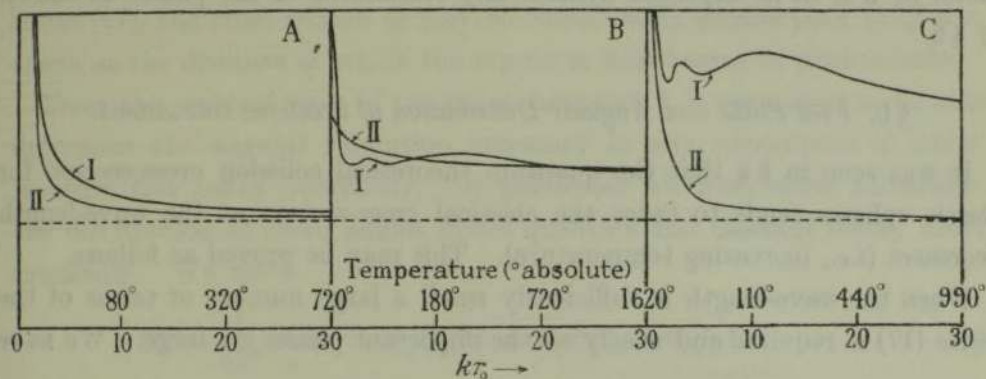


FIG. 1.—Illustrating the ratio of the quantum theoretical to the classical effective collision areas for the viscosity, collision radius, and diffusion, at different temperatures using the hard sphere model. The temperatures refer to helium atoms of diameter 2.1 Å. I, Identical atoms; II, dissimilar atoms; - - - - classical value. A, collision area effective in viscosity; B, collision radius effective in scattering; C, collision area effective in diffusion.

Table II.—Values of the ratio of the quantum theoretical to the classical areas effective in the viscosity, the collision radius, and the diffusion for the rigid sphere model, for different values of $kr_0 = 2\pi r_0/\lambda$ (λ the wave-length). I for identical atoms; II for different atoms.

kr_0	0	2	3	5	10	20	30	∞
Viscosity—								
I	16.00	2.28	1.76	1.47	1.23	1.11	1.07	1.00
II	8.00	2.17	1.78	1.41	1.14	1.06	1.04	1.00
Collision radius—								
I	2.83	1.52	1.58	1.55	1.61	1.53	1.48	1.41
II	2.00	1.73	1.66	1.62	1.55	1.50	1.46	1.41
Diffusion—								
I	8.00	2.30	2.50	2.40	2.59	2.34	2.19	2.00
II	4.00	1.65	1.42	1.17	1.11	1.04	1.02	1.00

when the wave-length is greater than one-fifth of the diameter of the atoms, but when the colliding atoms are unlike, the classical theory holds to this degree of accuracy up to wave-lengths as great as one-third of the sum of the atomic radii. Referring to the corresponding temperatures indicated in the figure for the collision of helium atoms, we see that, for light atoms, the

deviations from the classical theory are quite important from ordinary temperatures (300° K.) downwards.

For cross-sections we see that the calculated cross-section never tends to the classical, but to a value roughly twice this. It may be proved that this factor of 2 is to be expected without any calculation of the phases as shown in § 5.

§ 5. *Free Paths and Angular Distribution of Scattered Gas Atoms.*

It was seen in § 4 that the quantum theoretical collision cross-section for elastic spheres tends to twice the classical cross-section as the wave-length decreases (*i.e.*, increasing temperature). This may be proved as follows.

When the wave-length is sufficiently small a large number of terms of the series (17) is required and nearly all the important phases are large. We have

$$Q = \frac{4\pi}{k^2} \sum_n (2n + 1) \sin^2 \delta_n,$$

and under the conditions stated we may replace the sum by an integral to give

$$Q = \frac{8\pi}{k^2} \int_0^X x \sin^2 \{f(x)\} dx.$$

Owing to the magnitude of $f(x)$ we may replace $\sin^2 \{f(x)\}$ by its mean value of $\frac{1}{2}$ giving

$$Q = \frac{2\pi X^2}{k^2}.$$

If the field falls off very sharply at a point $r = r_0$ we have from (33)

$$X = kr_0,$$

so that

$$Q = 2\pi r_0^2. \quad (37)$$

Actually the cross-section may be slightly greater than this owing to the assumption of a definite limit for X . It is clear from this result that the quantum collision area for even, say, billiard balls is still twice the classical, but the difference between classical and quantum theory is confined to such small angles of deviation that the difference is of no practical value in such cases. It is just as if the rigid spheres can, owing to their wave nature, affect each other without interacting in the ordinary sense. With gas kinetic collisions, the angles at which the deviations from classical theory are important, are sufficiently large (of the order of several degrees for light atoms) to be

within the reach of experiment, and the evidence in this direction will be discussed below. These conclusions will not be affected by the existence of a weak attractive field, when $r = r_0$ will refer to the distance at which the repulsive field becomes important, Q having the perfectly definite value above. If the attractive field is strong enough to introduce additional phases in the series (17), the cross-section Q may be considerably greater than $2\pi r_0^2$ if r_0 is taken as the distance at which the repulsive field begins to predominate.

From the point of view of the experimentalist it is important to be able to determine the angular resolution necessary in any experiment in order to measure free paths accurately. In particular we need some knowledge of the distribution at small angles where quantum and classical theory differ so markedly. We have

$$I(\theta) = \frac{1}{4k^2} \left| \sum_n (e^{2i\delta_n} - 1) (2n + 1) P_n(\cos \theta) \right|^2, \quad (38)$$

$$= \frac{1}{4k^2} \left\{ \left| \sum_n 2 \sin^2 \delta_n (2n + 1) P_n(\cos \theta) \right|^2 + \left| \sum_n \sin 2\delta_n (2n + 1) P_n(\cos \theta) \right|^2 \right\}. \quad (39)$$

In the limit of small angles

$$P_n(\cos \theta) = 1,$$

and under the conditions of experiment a large number of terms of the series in expression (39) are required, and the δ_n oscillate rapidly with n . Hence

$$\sum_n 2 \sin^2 \delta_n (2n + 1) \gg \sum_n \sin 2\delta_n (2n + 1),$$

and so

$$I(\theta) \simeq k^{-2} \left| \sum_n (2n + 1) \sin^2 \delta_n \right|^2, \\ = \frac{k^2 Q^2}{16\pi^2} \quad (40)$$

or, in the special case of rigid spheres of radius r_0 ,

$$Q \simeq 2\pi r_0^2,$$

so that

$$I(\theta) \simeq \frac{1}{4} k^2 r_0^4, \quad (41)$$

giving the value at the origin.

At large angles the scattering is classical and we have for a sphere of radius r_0 ,

$$I(\theta) = \frac{1}{4} r_0^2. \quad (42)$$

This classical formula fails at angles less than the first zero of $P_n(\cos \theta)$ (which is nearly at π/n) where n is the harmonic of highest order effective in the scattering. n is approximately equal to kr_0 . To obtain a sufficiently accurate

form for $I(\theta)$ it is only necessary to assume a linear variation at small angles between the value $\frac{1}{4}k^2r_0^4$ at $\theta = 0$ and the classical value which is taken to fail at an angle θ equal to π/kr_0 . By multiplying this angular distribution by $\sin \theta$, the error made in counting only deviations greater than a certain

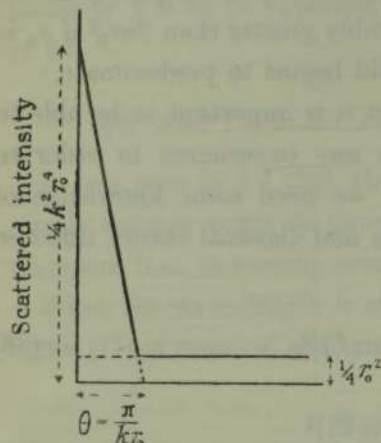


FIG. 2.—Illustrating a simple approximate method of obtaining the form of the angular distribution of the scattering of hard spheres of radius r_0 and velocity $kh/2\pi M$, M being the “reduced mass.”

angle as indicating collisions can be easily estimated. Fig. 2 illustrates the procedure to be adopted.

In fig. 3 two angular distributions are illustrated for the collision of hard spheres when the wave-length is approximately one-third of the diameter. Curve A is for dissimilar atoms, and curve B for the collision of similar atoms. Comparison with the classical curve reveals the behaviour discussed above. Direct experimental test of the form of these curves would be difficult, as any inhomogeneity in the colliding atomic beams would certainly obscure the maxima and minima of curve A. For collisions between similar atoms, there is more hope of experimental verification, as the maximum at 90° (45° when measured relative to the direction of incidence)

does not vary in position with relative velocity of the gas atoms. It should therefore be possible to detect it experimentally by scattering one atomic beam by another. Such measurements offer a means of direct proof of the applicability of the Bose-Einstein statistics, for the maximum at 90° is a consequence of these statistics.

§ 6. *The Viscosity of Helium and Hydrogen with the Rigid Sphere Model.*

Owing to the independence of temperature exhibited by the classical expression for Q_η , the rigid sphere model predicts on classical theory a variation of viscosity with temperature of the form

$$\eta \propto T^{-\frac{1}{2}}, \quad (43)$$

whereas the experimental evidence* indicates a variation of the form

$$\eta \propto T^{-0.647} \text{ for helium,} \quad (44)$$

$$\propto T^{-0.695} \text{ for hydrogen.} \quad (45)$$

* ‘International Critical Tables,’ vol. 5, p. 2 (1929).

The difference of these exponents from 0.5 was then explained by Lennard-Jones* as caused by deviations from the rigid sphere model, and from them he determined the repulsive field of force between the molecules concerned. If, however, we refer to fig. 1, we see that the quantum theoretical formula gives a

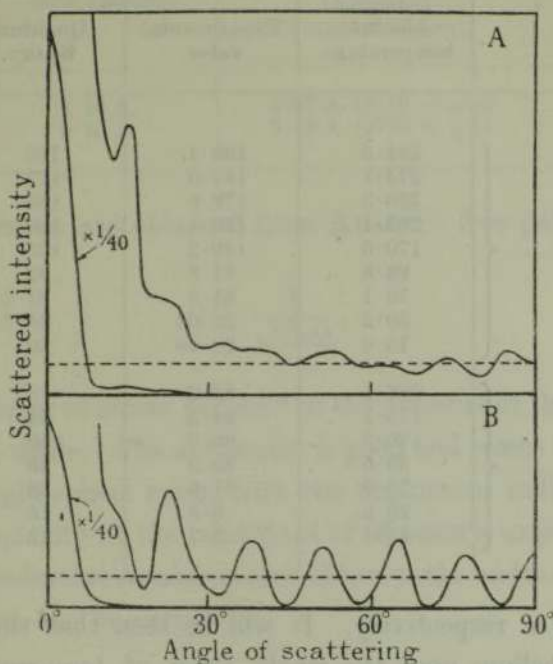


FIG. 3.—Angular distributions (in relative co-ordinates) of helium atoms scattered in helium for the case of $kr_0 = 2\pi r_0/\lambda = 20$. --- denotes the classical value. A, dissimilar atoms; B, identical atoms.

variation of η with temperature more rapid than that given by a $T^{-\frac{1}{2}}$ law, and in Table III and fig. 4 the viscosity of helium and hydrogen is shown as calculated on the assumption that the molecules are rigid spheres of diameter

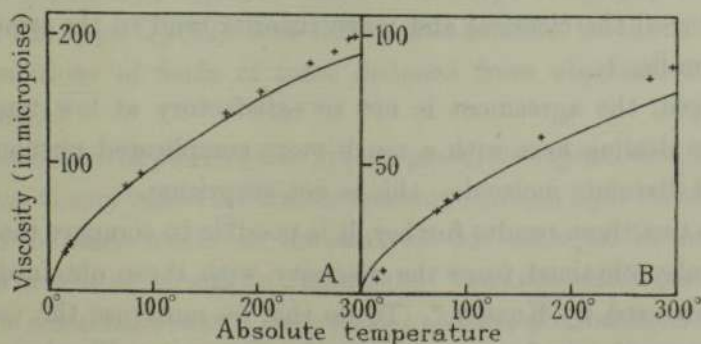


FIG. 4.—Comparison of calculated and observed viscosity of helium and hydrogen at different temperatures. — calculated curve; $\times \times \times \times$ observed values. A, helium; B, hydrogen.

* Vide Fowler. *loc. cit.*

Table III.—Comparison of the experimental values of the viscosity of helium and hydrogen at different temperatures with the values calculated on quantum and classical theory using the hard sphere model. (Values of the viscosity are in micropoise.)

	Absolute temperature.	Experimental value.	Quantum theory.	Classical theory.
Helium	294·5	199·4	185	200
	273·1	187·0	177	193
	250·3	178·8	169	184
	203·1	156·4	150	167
	170·5	139·2	135	152
	88·8	91·8	92	110
	75·1	81·5	81·5	101
	20·2	35·03	35·5	52
	15·0	29·46	30	45
	Hydrogen	296·1	88·2	78
273·1		84·2	74	84
170·2		60·9	56	66
89·6		39·2	38	48
70·9		31·9	33	43
20·6		8·5	15	23
15·4		5·7	12	20

2·10 Å. and 2·75 Å. respectively. It will be seen that this model fits the observations for helium over the whole range of temperature within 7%, as contrasted with the classical rigid sphere model which is in error by 50% over this range. This result is very surprising, and seems to indicate that the rigid sphere model is very near the truth, or that viscosity phenomena are not sensitive to the actual fields of force between molecules in collisions when they are properly treated on a wave mechanical theory—at least so far as light atoms are concerned. For heavy atoms (except at very low temperatures) the classical and wave theories tend to the same result, as is evident from fig. 1.

For hydrogen, the agreement is not so satisfactory at low temperatures, but as we are dealing here with a much more complicated phenomenon, the interaction of diatomic molecules, this is not surprising.

In order to test these results further, it is possible to compare the diameters of the molecules obtained from the viscosity with those obtained from the free paths measured by Knauer.* To do this we must use the value of the quantum cross-section in formula (13) for the free path. We then obtain the following comparison between theory and experiment.

* 'Z. Physik,' vol. 80, p. 80 (1932).

Table IV.

	Diameter of molecule from viscosity.	Effective diameter in collisions.	
		Calculated (quantum theory).	Observed (from free paths).
Helium	2.10 A.	2.97 A. (2.10 × √2)	2.74 A.
Hydrogen.....	2.75 A.	3.89 A. (2.75 × √2)	3.54 A.

The observed values are obtained from Knauer's free path l by using the expression

$$l = \frac{1}{\sqrt{2\nu Q}}, \quad (46)$$

where ν is the number of atoms per cm.³ at the pressure of the gas in which the measurements are made. The agreement is good and seems to provide further support for the rigid sphere model with the dimensions indicated. However, owing to the complexity of the conditions of Knauer's experiment, it will be necessary to obtain further measurements of free paths under definite conditions before any decision can be arrived at.

§ 7. Diffusion and Thermal Diffusion.

Referring to fig. 1, we expect little deviation from classical theories of diffusion except at very low temperatures. For self-diffusion the identity of the colliding atoms would reduce the classical result by a factor of nearly 2. Although this phenomenon is not observable, the same effect will appear in the thermal diffusion in which integrals of the type of Q_D (11) occur as well as integrals of the type Q_D (12), and this must therefore be taken into account in all calculations of fields of force deduced from observations of thermal diffusion effects.

For the mobilities of positive ions in pure gases, we expect, then, no deviations from classical theory unless the ions are passing through a gas containing neutral atoms with the same nuclei as the ions, as, for example, in the mobility of helium ions in helium. Owing to "umladung"* an appreciable percentage of the ions may be scattered towards large angles and the phenomenon then becomes comparable with self-diffusion. One would thus expect appreciable deviations from classical theory. The calculations for this case are in progress.

* *Vide*, Kallman and Rosen, 'Z. Physik,' vol. 64, p. 808 (1930).

It is clear, however, that the most interesting field for investigation, both experimental and theoretical, lies in the comparison of observed and calculated mean free paths, and it is to be hoped that accurate measurements will soon be obtainable for various gases.

APPENDIX.

Calculation of the Zero Velocity Limit of the Collision Cross-Section for an Exponential Field of Force.

We take the mutual potential energy of the two particles as

$$V = De^{-2ar},$$

The equation for the zero order scattered wave, which alone differs from a Bessel function at the low velocity limit, is in relative co-ordinates

$$\frac{d^2u}{dr^2} + \frac{4\pi^2M}{h^2} (E - De^{-2ar}) u = 0, \quad (47)$$

where u must satisfy the boundary conditions

$$\begin{aligned} u &= 0 \text{ at } r = 0, \\ u &\sim \sin(kr + \delta), \quad r \rightarrow \infty. \end{aligned} \quad (48)$$

Using the substitution $y = e^{-ar}$ reduces the equation (47) to

$$\frac{d^2u}{dy^2} + \frac{1}{y} \frac{du}{dy} + \left(\frac{4\pi^2M}{a^2h^2} \frac{E}{y^2} - \frac{4\pi^2MD}{a^2h^2} \right) u = 0. \quad (49)$$

The solutions of this equation are the Bessel functions

$$J_{\pm ik}(imy),$$

where

$$k = \sqrt{\frac{\pi^2ME}{a^2h^2}}, \quad m = \sqrt{\frac{4\pi^2MD}{a^2h^2}}.$$

In order to satisfy the boundary conditions at the origin we must have

$$u = AJ_{ik}(imy) + BJ_{-ik}(imy),$$

where

$$AJ_{ik}(im) + BJ_{-ik}(im) = 0,$$

giving

$$\frac{A}{B} = -\frac{J_{-ik}(im)}{J_{ik}(im)}. \quad (50)$$

We have further to break this solution into an incident and a scattered wave.

The asymptotic expansion of u for large r will be obtained from the series expansion of the Bessel functions, which gives

$$u \sim \frac{A (\frac{1}{2}ime^{-ar})^{ik}}{\Gamma(1+ik)} + \frac{B (-\frac{1}{2}ime^{-ar})^{-ik}}{\Gamma(1-ik)}. \quad (51)$$

This must be equivalent to

$$C \left\{ \frac{\sin kr}{k} + \alpha e^{ikr} \right\}, \quad (52)$$

where $4\pi|\alpha|^2$ gives the scattering cross-section. Equating the expressions (51) and (52) we find

$$4\pi|\alpha|^2 = \frac{\pi}{a^2k^2} \left| \frac{(\frac{1}{2}im)^{-ik}\Gamma(1+ik)J_{ik}(im)}{(\frac{1}{2}im)^{ik}\Gamma(1-ik)J_{-ik}(im)} - 1 \right|^2. \quad (53)$$

For a repulsive field m is real and the above expression tends to a finite limit under all conditions. When m is large (as with gas atoms) we obtain, using the asymptotic expressions for the Bessel functions,

$$4\pi|\alpha|^2 = \frac{4\pi}{a^2} (\log \frac{1}{2}m + \gamma)^2, \quad (54)$$

where $\gamma = 0.5771$. For an attractive field the cross-section becomes infinite when m is approximately equal to $(n + \frac{3}{4})\pi$, where n is integral. When m is small it is easy to see, using the series expansions for the Bessel functions, that the cross-sections for both the attractive and the repulsive field become equal to $\pi m^4 a^{-2}$, the result obtained by the use of Born's formula (21).

Summary.

The quantum theory of collisions is applied to the motion of gas atoms. Using the rigid sphere model, the range of validity of the classical theory of free paths, viscosity, and diffusion is determined. The use of quantum mechanics greatly improves the applicability of this model to the viscosity of helium. The scattering of atoms is considered in detail, and the possibility of experimental proof of the Bose-Einstein statistics is discussed.