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The Scattering of a Beam of Potassium Atoms in Various Gases[1]

WALTER H. MAIS, *Columbia University*

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A narrow beam of neutral K atoms was scattered in H_2, He, Ne, N_2, A and CO_2 at low pressures. The distribution of the scattered K atoms about the original beam was measured by the Langmuir-Taylor surface ionization detector. The experimental conditions were sufficiently refined that K atoms suffering very small angular deviations (down to about 4.5′ of arc) were counted as scattered atoms. The computed "effective collision radii" when compared with the values expected from the quantum theory of elastic sphere collisions show good agreement for H_2 and He. For the other gases, the experimental values are much larger, indicating the existence of considerable interatomic attractive forces even for Ne and A.

INTRODUCTION

THE kinetic theory of the collision of molecules treated as elastic spheres predicts a scattering function $I(\theta)$ which gives a uniform scattering per unit solid angle with respect to the centroid of the system composed of the two colliding molecules. In other words, all angles of scattering are equally probable. By the angle of scattering we mean the angle through which the relative velocity vector of the colliding molecules is turned. If the simple elastic sphere model is improved by the addition of a force field the scattering function will no longer be uniform but will give preference to scattering in the forward direction. This model will thus increase the probability of small angle scattering. However, if we attempt to use this revised model for computing collision cross sections it turns out that, as we define smaller and smaller deviations as collisions, the mean free path tends to zero and the collision cross section tends to become infinitely great.

The quantum theory[2,3] for the collision of elastic spheres at velocities corresponding to ordinary thermal agitation gives a marked preference for small angle scattering, in many respects similar to that of the classical theory of the scattering of elastic spheres, plus an attractive field of force. (See Fig. 1.) However, in the quantum theory, the total scattering even down to the smallest angles still remains finite. This is also true if we add an attractive field of force to the quantum theory of elastic spheres provided the interaction energy $V(r)$ vanishes at infinity faster than r^{-3}. Furthermore, since the large angle scattering is practically the same on both theories the extra scattering comes almost entirely from the small angle region. Small angles are defined as those for which $\theta \ll \pi/k\sigma_{12}$ where $k=2\pi\mu v/h$; μ being the reduced mass and v the relative velocity of the colliding molecules. Another result is that the total scattering on the basis of the quantum theory of elastic spheres is about twice the

[1] Mais and Rabi, Phys. Rev. **43**, 378 (1933).

[2] Mizushima, Phys. Zeits. **32**, 798 (1931).

[3] Massey and Mohr, Proc. Roy. Soc. **A141**, 434 (1933).

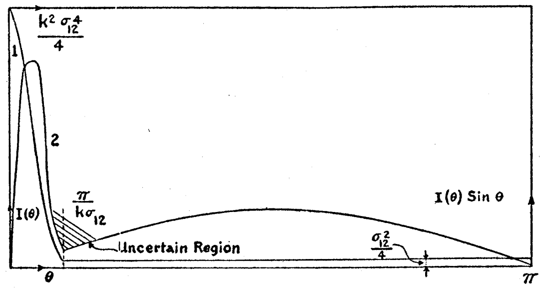

FIG. 1. Curve 1 is a modified form of the curve given by Massey and Mohr (Fig. 2), obtained by using a more exact expression for $I(\theta)$ which was worked out by Dr. Harvey Hall. The expression is: $I(\theta)=(x^4/k^2)[J_1(x \tan\theta)/x \tan\theta]^2$ where $x=k\sigma_{12}$. I wish to thank Dr. Hall for permitting me to use his results before publication. Curve 2 is $I(\theta)\sin\theta$ plotted on a different scale.

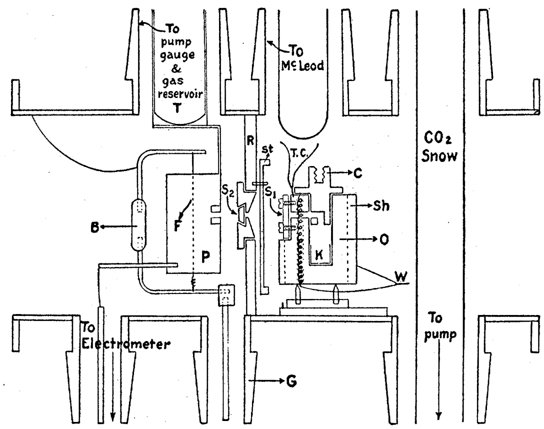

FIG. 2. Diagram of apparatus.

classical theory result for elastic spheres, provided $k\sigma_{12}$ is about 20 or greater. For very small relative velocities, $k\sigma_{12}$ approaches zero and the total scattering is then four times what it is on the classical theory. The larger values of $k\sigma_{12}$ thus give an effective collision radius of $\sigma_{\text{eff.}}=1.5\sigma_{12}$, which increases to $\sigma_{\text{eff.}}=2\sigma_{12}$ for the smaller values of $k\sigma_{12}$.

The object of the experiments which are to be described was to obtain data on the scattering of a narrow beam of potassium atoms in a variety of gases. The gases chosen were: firstly, the more available inert gases namely helium, neon and argon; and secondly, as examples of more complex gases, hydrogen, nitrogen and carbon dioxide. These six gases give a considerable range in mass and consequently considerable variation in the value of the important quantity k. The experiments were designed to investigate the scattering down to about 4.5′ of arc, which is well within the interesting angular region from 0 to $\pi/k\sigma_{12}$. The theoretical scattering curves presented in Fig. 1 show the kind of scattering to be expected in this region from pure hard sphere scattering.

A number of investigators have used the molecular ray method to determine mean free paths and collision radii.[4–12] In none of these experiments were measurements made at angles as small as those used in the experiments to be described.

[4] Born, Phys. Zeits. **21**, 578 (1920).
[5] Bielz, Zeits. f. Physik **32**, 81 (1925).
[6] Knauer and Stern, Zeits. f. Physik **53**, 766 (1929).
[7] Ellett and Zabel, Phys. Rev. **37**, 1112 (1931).
[8] Knauer, Zeits. f. Physik **80**, 80 (1933).
[9] Knauer, Naturwiss. **21**, 366 (1933).
[10] Zabel, Bull. Am. Phys. Soc. Vol. 8, No. 7, page 10.
[11] Zabel, Phys. Rev. **44**, 53 (1933).
[12] Fraser and Broadway, Proc. Roy. Soc. **A141**, 626–641 (1933).

APPARATUS

The source of the beam was the oven O (Fig. 2) which contained a small quantity of potassium K. The potassium was cleaned under petroleum ether by cutting off the hydroxide coating and was then introduced into the oven in a small nickel cup filled with the petroleum ether. The oven was constructed of a single piece of nickel which could be closed at the top, after the introduction of the potassium, by means of a close fitting cylinder of monel metal C. The coefficient of expansion of nickel is less than that of monel metal and therefore when the oven was heated the two metals formed a very tight joint. The oven was mounted on three pointed nickel pegs, fixed in a dove-tailed slide, so that it could be removed from the apparatus after being lined up and then subsequently replaced without any difficulty. The sharply pointed pegs also served to prevent the conduction of heat away from the oven. The oven was heated by two 10 mil tungsten spirals W which were contained in quartz tubes embedded in the copper shield Sh, which surrounded the oven. One end of these heating filaments was grounded. The temperature of the oven and potassium beam was determined by a chromel-alumel thermocouple $T.C.$ located near the oven slit S_1. The temperature was kept constant by two rheostats connected in parallel. Changes in temperature amounting to 0.1°C were easily observed and the oven was usually kept constant within these limits. The height of the oven slit was limited to 2 mm by a hole drilled in the body of the oven. The width of the oven slit was limited to 0.01 mm by two nickel slit jaws which were screwed on the face of the oven. The beam was then defined by a collimating slit S_2 which was also limited to 2 mm in height. These slit jaws ran in a dove-tailed slide, were made of phosphor bronze and were set to a width of 0.013 mm. The beam could be screened by the magnetically operated shutter (*St*). The collimating slit holder was kept cool by a large water jacket on the outside of the tube.

The potassium beam formed by this slit system was detected[13] by the tungsten line filament (F) of diameter 0.01 mm, which could be rotated by means of the ground joint (G) about an axis passing through the collimating slit in the direction of its length. The filament was mounted on a rigid nickel frame, the two halves of which were insulated by the glass bead (B). A two mil tungsten spiral served to keep the 0.01 mm filament taut. This detecting filament rotated inside the semi-cylindrical sheet nickel plate (P) which was cooled by carbon dioxide snow contained in the trap (T). The potassium positive ion current was measured by an FP-54 vacuum tube electrometer (sensitivity 3×10^{-14} amp./mm). A potential of 45 volts applied between the filament and plate was more than sufficient to give saturation. The position of the filament with respect to the beam was then determined by a glass micrometer stage mounted on the ground joint G and a microscope focussed on this scale. This 0.01 mm filament subtended an angle of about 3′ at the collimating slit.

After the oven had reached equilibrium the procedure adopted was to investigate the "vacuum beam"; that is the beam obtained when the McLeod gauge registered "flat" for both the oven and detecting chambers. A typical "vacuum curve" is shown in Fig. 3 where intensity is plotted against scale-divisions. (1 scale division $=2.17'$.) Before running through a curve the residual positive-ion current, due to the filament itself, was measured by cutting off the beam with the shutter. This residual current was then subtracted from the observed beam intensity. It never amounted to more than a few millimeters deflection. The absence of any considerable tails close to the "vacuum beam" indicates that the residual pressure was negligible as far as this experiment is concerned. The small tails close to the beam itself are due chiefly to the finite width of the detecting filament. The "vacuum beam" background further out is due to K atoms scattered from various parts of the apparatus.

[13] Taylor, Zeits. f. Physik **57**, 242 (1929).

The scattering gas was stored in a 5 liter bulb as a reservoir and admitted to the detecting chamber through a stopcock plugged with plaster of paris. The pressure of gas in the detecting chamber was then varied by changing the pressure of gas in the reservoir and was maintained at a given pressure by the diffusion pump. The pressure of the scattering gas was measured by a carefully calibrated McLeod gauge connected at a point such that a considerable pressure gradient could not occur. Under the above conditions the pressure in the oven chamber was always 10^{-5} mm or lower. The intensity distribution in the scattered beam was then obtained by moving the detector on its ground joint. Typical experimental curves for the different gases are given in Figs. 3–8. In each case the upper curve represents the "vacuum" beam, the lower the "gas" beam.

At low pressures it becomes difficult to distinguish between residual gases and vapors and the scattering gas. It therefore became advisable in the interest of accuracy to work with relatively high pressures (10^{-4} mm to 5×10^{-4} mm). The dimensions of the beam were made small so as to reduce the possibility of multiple collisions, the distance from collimating slit to detector being 1.3 cm.

Results

A total of 30 sets of runs were made on the various gases yielding scattering curves of which those shown in Figs. 3–8 are typical. A convenient and instructive way of expressing results of scattering experiments is by means of an effective collision radius. This gives a measure of the total scattering per atom under the defined conditions. The relation

$$I=I_0e^{-d/\lambda} \tag{1}$$

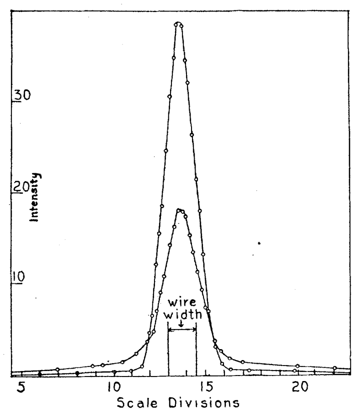

FIG. 3.

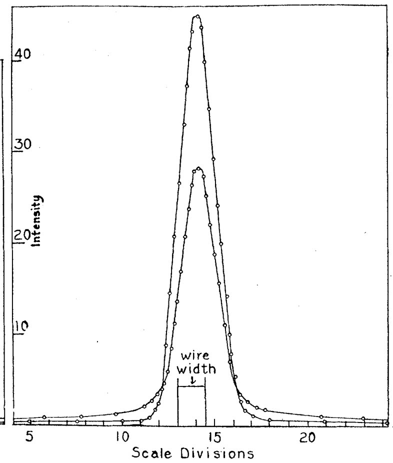

FIG. 4.

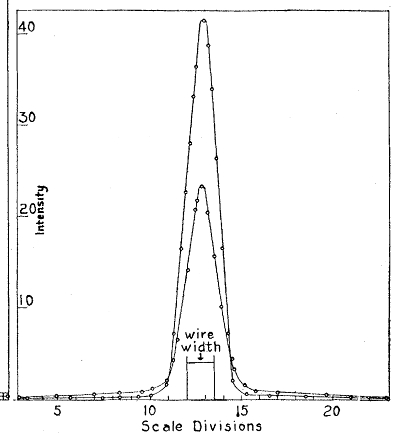

FIG. 5.

FIG. 3. CO_2, pressure -2.59×10^{-4} mm, oven temperature 443°K, wire width 0.01 mm, one scale division is 2.17′.
FIG. 4. Neon, pressure 2.85×10^{-4} mm, oven temperature 436°K.

FIG. 5. Helium, pressure 3.76×10^{-4} mm, oven temperature 446°K.

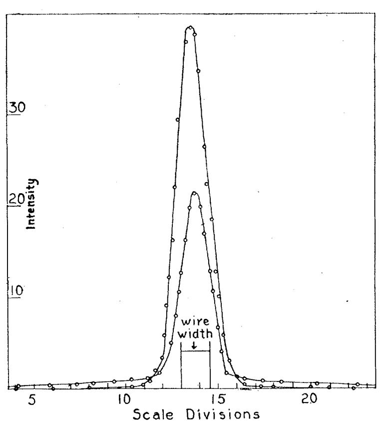

FIG. 6.

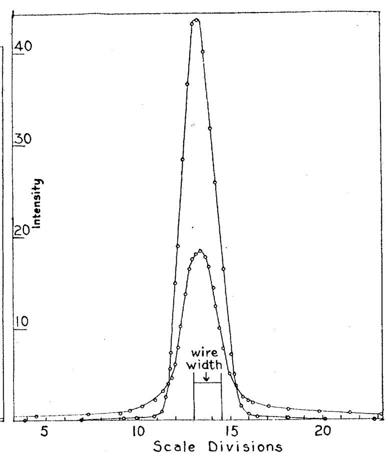

FIG. 7.

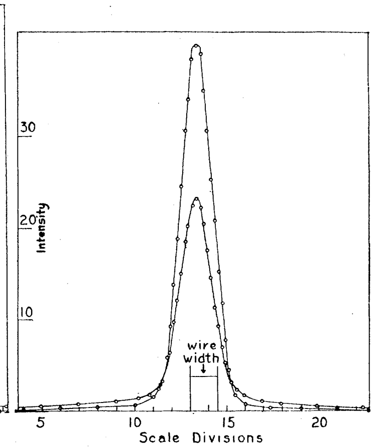

FIG. 8.

FIG. 6. Hydrogen, pressure 2.46×10^{-4} mm, oven temperature 445°K.
FIG. 7. Nitrogen, pressure 2.55×10^{-4} mm, oven temperature 444°K.
FIG. 8. Argon, pressure 1.70×10^{-4} mm, oven temperature 430°K.

defines an effective mean free path λ. Here d is the distance from the collimating slit to the detector expressed in cm, I_0 is the integrated intensity of the vacuum beam within certain angular limits (in arbitrary units), and I the integrated intensity of the scattered beam within the same angular limits. We will thus obtain values for λ depending on the angular limits we choose in the calculation of I and I_0 or in other words depending on what deviation we define as constituting a collision. We will consider two extreme cases.

Case I

We take I to be the peak reading of the "gas curve." The corresponding value of I_0 is the peak reading of the "vacuum curve." Using the ratio I/I_0 and Eq. (1) one can then compute an effective mean free path.

Case II

We take I to be the integrated intensity under the "gas curve" out to 10.5 detector wire-widths (0.105 mm) from the peak; and then get the corresponding value of I_0 from the integrated intensity under the "vacuum curve." We then compute another λ corresponding to these larger angular deviations.

The λ's obtained in this way are shown in sections I and II of Table I; together with the product $(p\lambda)$, p being the pressure of the scattering gas expressed in mm of mercury. If multiple collisions are infrequent this product should be constant for any one gas. It is evident that this is very nearly the case. The deviations from constancy are not greater than the errors in the pressure measurements.

From these λ's we obtain the effective collision cross sections or collision radii. The mean free paths obtained in experiments of this type are obviously analogous to Tait's mean free path, except that the colliding atoms have different masses, and that the potassium beam and scattering gases are at different temperatures. Account must also be taken of the fact that the detecting wire measures a quantity which is proportional to the number of potassium atoms received per sq. cm per sec., instead of the number present in unit volume. The distribution to be used for the K atoms is therefore not the ordinary Maxwellian distribution of velocities, but:

$$Ae^{-mc^2/2kT}c^3dc. \tag{2}$$

We then obtain[14]

$$\sigma_{12}^2=\frac{2}{\pi^{\frac{1}{2}}\nu\lambda}\left(\frac{T_xm_k}{T_km_x}\right)^2\int_0^\infty xe^{x^2(1-T_xm_k/T_km_x)}\frac{x^4e^{-x^2}}{\psi(x)}dx, \tag{3}$$

where ν is the number of molecules per cc of the scattering gas, T_k, T_x, m_k, m_x, are the temperatures and masses of the potassium and the scattering gases, and

$$\psi(x)=xe^{-x^2}+(2x^2+1)\int_0^x e^{-y^2}dy.$$

The integral in the above expression was evaluated by the method of quadratures by using Tait's tables for values of x from 0.1 to 3.0. For the heavier gases it became necessary to extend his tables to $x=5.0$ before the integral became sufficiently convergent.

The effective collision radii computed in this way are given in sections I and II of Table I. If the detecting wire and beam had been infinitesimally thin, the σ_{12} values obtained from the peak readings would have represented the total effective collision radius. In any actual experiment, however, both beam and detector must have a finite width and the σ_{12} values in section I therefore represent minimum values; because some of the atoms which are scattered through small angles can still reach the detector due to its finite angular width. The difference between the σ_{12}'s listed in sections I and II is due to the fact that the angular width in case II is 21 times as great as in case I. In order to determine the angular limits for cases I and II we must remember that the beam is being scattered along its entire length and therefore the detecting wire subtends different angles at different scattering points. However, if we weight all parts of the length of the beam equally we can compute an average angle of scattering. For case I this average angle is about 4.5′ and for case II it is about 1.5°.

Since the only theory of atomic scattering which has been worked out in any detail is the "hard sphere theory," we shall proceed to discuss the experimental data in the light of that theory. As previously stated, an important quantity in the theory is $k\sigma_{12}$. The k used was obtained by averaging over the distributions of relative velocities of the colliding particles. The radii of the scattering gases were computed from Chapman's viscosity formula[15] derived from an elastic sphere model; but since no viscosity or diffusion measurements exist for potassium we are forced to estimate the size of its radius from other considerations. The packing radius of potassium in the solid state is known to be about 2.3A.[16] Hartree[17] finds that the radius at which the ψ function for the series electron has its large maximum is 2.01A and the radius at which $|r\psi|^2$ has its maximum is 2.66A. This last value would correspond on the old Bohr theory to the radius

[14] Jeans, *Dynamical Theory of Gases*, 4th Ed., p. 255.
[15] Chapman, Phil. Trans. Roy. Soc. Ser. **A216**, 279 (1915).
[16] Neuberger, Zeits. f. Kryst. **80**, 103 (1931).
[17] Hartree, Proc. Roy. Soc. **A141**, 282 (1933).

TABLE I. *Mean free paths and effective collision radii.*

	I CASE I				II CASE II				III	IV	V	VI
Gas	λ	λp	σ_{12}	Aver. σ_{12}	λ	λp	σ_{12}	Aver. σ_{12}	$\sigma_{12}=\sigma_K+\sigma_g$	Effect quantum σ_{12}	$k\sigma_{12}$	θ
H_2	1.52	5.88	7.08	7.20	2.64	10.2	5.36	5.67	5.0	7.4	20	8.5°
	2.12	5.43	7.37		4.86	10.6	5.27					
	2.49	5.43	7.36		3.29	8.43	5.91					
	3.83	5.75	7.16		9.29	8.64	5.84					
	4.23	5.92	7.06		9.22	9.32	5.62					
	5.42	5.48	7.34		8.10	12.2	4.93					
	6.40	5.95	7.03		4.58	6.43	6.78					
He	2.04	8.52	6.98	6.91	4.21	17.6	4.86	4.96	4.7	6.9	27	6.8°
	2.24	8.42	6.84		3.84	14.5	5.22					
	2.46	8.56	6.76									
	2.89	8.65	6.80									
	5.89	8.25	6.92		12.2	17.1	4.81					
	5.92	7.70	7.16									
Ne	2.85	8.55	8.80	8.74	6.70	17.3	6.19	5.98	4.8	6.9	56	3.2°
	2.69	8.07	9.06		7.22	21.6	5.53					
	3.10	8.84	8.66		8.04	22.9	5.37					
	3.33	8.60	8.78		5.61	16.9	6.28					
	12.1	9.43	8.38		20.0	15.6	6.52					
N_2	1.68	4.54	12.5	12.6	5.11	13.8	7.19	7.30	5.5	7.8	72	2.5°
	1.74	4.56	12.5		5.51	14.5	7.04					
	3.70	4.58	12.5		12.5	12.4	7.60					
	4.45	4.41	12.7		10.6	13.2	7.36					
A	3.14	5.90	11.3	11.3	5.07	9.55	8.92	8.78	5.4	7.7	79	2.3°
	2.95	5.28	12.0		4.78	8.56	9.41					
	5.28	6.03	11.0		9.96	11.8	8.01					
	6.07	6.68	10.7									
CO_2	1.59	4.08	13.7	13.3	3.37	8.66	9.44	9.63	5.9	8.4	89	2.0°
	1.64	4.25	13.5		3.11	8.06	9.80					
	3.80	4.37	13.3		7.40	8.52	9.53					
	4.25	4.80	12.7		7.23	8.16	9.73					

In the above table λ values are given in cm, σ_{12} values in A units, and the λp values should be multiplied by 10^{-4} when p is in mm of mercury.

of the orbit of the series electron. The quantity $|r\psi|^2$ drops to one-third of its maximum value at a distance of about 3.5A. If we make the very plausible assumption that the collision of a potassium and a helium atom is most like a hard sphere collision because of the symmetry and small polarizability of the helium atom, we can obtain an upper limit for the potassium radius from our data on helium. In case II most of the "extra classical" forward scattering is included in the integrated I. (See Fig. 1.) The correction to be made for classical hard sphere scattering at small angles is less than 1 percent. The σ_{12} value for He and K as given in section II of Table I is about 5A and it should be approximately equal to the kinetic theory value for σ_{12}. If we take the kinetic theory radius of helium to be 1.1A this would give us 3.9A for the potassium radius. This value of 3.9A is probably too high. In all future discussions we shall use the value 3.6A which represents a mean between the values 3.9 and 2.66. It is then possible to compute the kinetic theory values for σ_{12}. They are given in section III of Table I. The computed values of $k\sigma_{12}$ are shown in section V.

A comparison of the σ_{12} values presented in sections I and III shows that the σ_{12} values computed from the small angle scattering (case I) are much larger than the classical kinetic theory values; but when we compute these values from the large angle scattering (case II) they approach the classical kinetic theory values more closely, especially in the case of H_2 and He. This diminution in the "effective collision radius" would be quite large even if we did not go out to angles as large as 1.5°; and it indicates the predominance of small angle scattering. Multiplying the classical kinetic theory radii by the appropriate factor[2] (approximately 1.5) gives the "effective quantum collision radii." They are presented in section IV of Table I. A comparison of sections I and IV then shows that in the case of H_2 and He the quantum theory values agree with the experimental small angle σ_{12} values within the limit of experimental error.

Accuracy

The accuracy of the σ_{12}^2 values depends on the reliability of the λ's and the pressure measurements. The average error of the pressure measurements amounted to about 2.6 percent; but it should be mentioned that the σ_{12}^2 values obtained from the long mean free paths are not as reliable as the others since their accuracy depends on the accurate determination of small pressures. It is also evident that the σ_{12} values computed from case II show more dispersion than the values obtained from case I. This dispersion arises because the integrated intensities I and I_0 depend on readings along the steep part of the curve, where the intensity varies rapidly over the distance of a wire-width.

In case I the detecting wire covers only a portion of the beam, approximately equal to the width of the central part, which in a "vacuum beam" contains 2/3 of the total beam intensity. It is therefore desirable to find out what the probability is of having atoms from the rest of the beam scattered into this region and being counted as undeviated atoms. It can easily be seen that this probability is small on the hard sphere model. The quantum theory[2] shows that, for the values of $k\sigma_{12}$ under consideration, the "extra scattering" (beyond the amount predicted by classical theory) occurs almost entirely in the region $\theta=0$ to $\theta=\pi/k\sigma_{12}$ and is about equal in amount to the total classical scattering, namely that resulting from an effective collision cross section $\pi\sigma_{12}^2$. The values of $\theta=\pi/k\sigma_{12}$ are tabulated in section VI of Table I. This extra scattering has a form such that the fraction scattered within an angle θ_1 is given quite closely by:

$$\frac{6k^2\sigma_{12}^2}{\pi^2}\left(\frac{\theta_1^2}{2}-\frac{k\sigma_{12}}{\pi}\cdot\frac{\theta_1^3}{3}\right). \tag{4}$$

The filament and beam used were narrow enough that about 95 percent of the atoms scattered in this extra classical region were scattered through angles sufficiently large to miss the detecting wire entirely. This still holds true when account is taken of the circumstance that the angle θ defines the change in direction of the relative velocity and not the actual change in direction of the K atoms. It is easily shown that for small values of θ, such as occur in this experiment, an angular change θ gives rise to an angular deviation ϕ of the K atoms expressed by: $\phi\geqq\theta k/2k'$ where $k'=2\pi m_k\bar{v}_k/h$. This results in an effective contraction of the critical region where the extra quantum scattering takes place; but the wire-width chosen is narrow enough so that 95 percent of the extra scattering is beyond the filament. Of the total scattering on the hard sphere model only 2.5 percent can reach the wire when it is at the central position. This results in a possible 1.6 percent error in calculating the σ_{12}. This is less than the errors due to other causes. No such discussion can be given for the case where the hard sphere model does not seem to fit the data (CO_2, N_2, A, etc.). The values of the σ_{12} in this case are to be regarded as minimum values or as a graphic means of expressing the experimental results.

Conclusions

The experimental results, as is evident from a comparison between cases I and II, show that there is in all gases in question a very striking predominance of small angle scattering. This is better shown by a comparison of the σ_{12}^2's rather than the σ_{12}'s. In the past this effect would have been interpreted as due to attractive forces. However, since the diffraction effects of molecules have been well verified experimentally, this strong forward scattering must be ascribed in part at least to such effects. The agreement of the σ_{12} values for He and H_2 with the hard sphere theory is then something rather to be expected. This agreement is not forced by the choice of the radius for the K atom since we have obtained an experimental upper limit to this quantity. A fair agreement would remain if we made any reasonable assumption. It is then a rather striking fact that this agreement is not maintained for the other gases, not even for neon and argon. The excess in the σ_{12} values for these cases must be ascribed to an interatomic interaction of considerable range.

Although the σ_{12} values presented are really lower limits for this quantity, in view of the finite total scattering predicted by the quantum theory it is rather likely that they are quite close to the real values.

ACKNOWLEDGMENT

In conclusion I wish to express my appreciation for the guidance and advice provided by Professor I. I. Rabi, under whose direction this investigation was carried out. I also wish to thank Mr. Seymour Rosin for his valuable assistance during the course of the experiments.