The Scattering of Beams of Alkali Atoms in Various Gases. I. Sodium and Argon

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The collision between gaseous molecules is the fundamental process in various phenomena which occur in the gas phase. By means of the molecular beam, it is possible to observe directly the process, which enables us to evaluate the effective collision radii and to get information about the mutual interaction between the molecules.

When the atoms in a molecular beam are scattered by an atom which is at rest in the co-ordinate system, the scattering cross-section Q is expressed by

$$Q=2\pi\int_0^\pi I(\theta)\sin\theta d\theta \qquad (1)$$

where $I(\theta)$ is the scattering intensity per unit solid angle of the beam atoms scattered through the angle θ from the direction of the incident beam. From the classical kinetic theory, it is easy to show, for a hard sphere model, that $I(\theta)$ is independent of θ and expressed as

$$I(\theta)=\frac{1}{4}\sigma^2, \qquad (2)$$

where σ is the sum of the radii of colliding molecules; hence Q is equal to $\pi\sigma^2$. On the other hand, from the quantum mechanical calculation for the hard sphere model, $I(\theta)$ is approximately given by the curve A in Fig. 1[1]. The curve shows that $I(\theta)$ becomes larger than the classical value when θ is smaller than $\theta_0=\pi/k\sigma$.

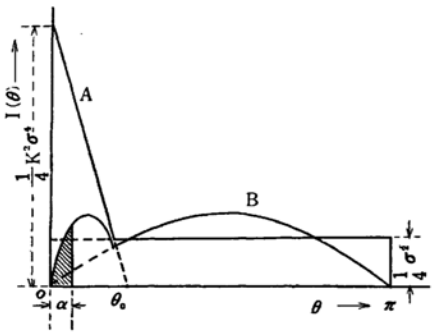

Fig. 1.

In this case, the collision cross-section given by equation (1) is equal to the area between the curve B and the abscissa multiplied by 2π, and therefore, is larger than the classical value. Q varies with $k\sigma$ in such a way that it becomes $2\pi\sigma^2$ when $k\sigma$ is very large, and approaches $4\pi\sigma^2$ when $k\sigma$ is zero. k is equal to $2\pi/\lambda$, where λ is the de Broglie wave length $\lambda=h/\mu v_r$, $\mu=m_A m_G/(m_A+m_G)$ is the reduced mass, and v_r is the relative velocity of the colliding molecules.

Since in actual experiments, both the molecular beam and its detector have definite widths, e. g., α in Fig. 1, the atoms scattered inside this region, i. e., the shaded region, are counted as unscattered, hence giving smaller Q. To minimize this error the resolving power of the apparatus should be increased by making α much smaller than θ_0.

The existence of van der Waals' force should be considered between the actual molecules. In this case, the classical kinetic theory predicts also the marked increase of $I(\theta)$ in the region of small θ, and gives infinite cross-section Q. On the other hand, quantum mechanical treatment with molecules having intermolecular potential of the type

$$V(r)=-Cr^{-s} \qquad (3)$$

gives a finite $I(\theta)$ at θ equal to zero, provided that s is larger than 3, thus giving a finite Q. Therefore, it is necessary to make the widths of the beam and its detector small compared with θ_0. If it were not the case, i. e., if the resolving power of the apparatus were small, the measured cross-section and hence the collision radius would be too small. This can be ascertained from the values presented by several authors. For instance, Mais[2] with the apparatus which excludes the atoms scattered more than 4.5′, obtained the collision radius of 6.91 Å for potassium and helium, Rosin and Rabi[3] with the angle of exclusion 1.7′, gave the values

1) H. S. M. Massey and C. B. O. Mohr, *Proc. Roy. Soc.*, **A141**, 454 (1933).

2) W. H. Mais, *Phys. Rev.*, **45**, 773 (1933).

3) S. Rosin and I. I. Rabi, ibid., **48**, 373 (1935).

7.25 Å for the same pair and 7.18 Å for cesium and helium. Estermann, Foner and Stern[4] obtained the value 12.5 Å for cesium and helium by reducing the angle to 5′. Further, Jawstusch, Schuster and Jaeckel[5], using potassium beams, have shown that the collision radii increase markedly with the resolving power of the apparatus. Since in these instances angles of exclusion α were very small compared with θ_0, it was inferred that an appreciable interaction exists between colliding atoms, and the increase in $I(\theta)$ is greater than for hard spheres. Therefore, in order to measure the effective collision radii, it is essential to make the resolving power of the apparatus as great as possible, and the comparision of the values for various molecules should be done with the apparatus of the same dimensions.

In the works cited above, the collision radii of alkali atoms with, mainly, rare gases were measured to verify the quantum mechanical collision theory. One of the present authors[6] carried out the experiments with potassium beam and various gases including chlorine. In the experiments described below, the apparatus was improved and, in addition to simpler molecules, more complex ones were measured, giving information of chemical interest. In this report, the details of the apparatus and the result with sodium and argon will be mentioned.

Apparatus

The methods to measure the scattering of a molecular beam by gases are roughly classified into the following two. In the first method, the scattering gas is confined in a small region in the path of the beam, while in the second, the gas fills the whole region behind the collimating slit. The former method was employed by Rosin and Rabi, Estermann, Foner and Stern; the crossing beam method of Jawtusch, Schuster and Jaeckel can also be classified into this type. In this method, the angle of scattering of beam atoms and their angular distribution can definitely be determined; since the beam path in the scattering region is short, it is possible to make use of a high pressure, which makes the measurement easier and more accurate. On the other hand, the accuracy in the measurement of the length of the scattering region decreases and the effect of escaping gas molecules from the region increases.

Mais and one of the present authors employed the second method. Although the apparatus can be simplified by this method, the beam detector placed in the scattering gas detects atoms scattered in large angles from points directly in front of it, making the overall resolving power decrease. The determination of the pressure of scattering gas, in this case, is rather difficult because the pressure must be kept low to avoid multiple collisions. These points being considered, in the experiments described below, the first method was employed to raise the resolving power, but a rather large region of scattering gas was taken to facilitate precise determination of its length. The pressure of the scattering gas, which should be low in this case, was measured by a sensitive Pirani gauge calibrated carefully by a McLeod gauge.

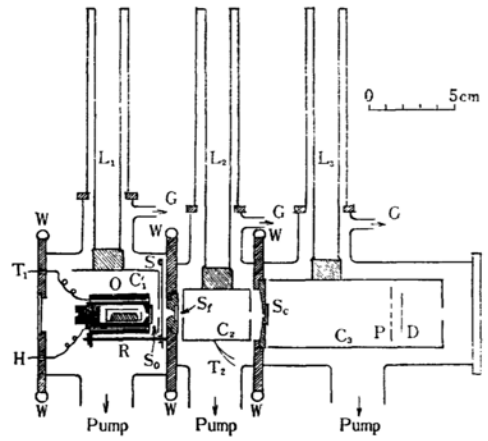

Fig. 2. Apparatus.
O, oven; S_o, oven slit; S_f, fore slit; S_c, collimating slit, S, shutter; D, detector; P, ion collector; T_1 T_2, thermocouples; H, heater; L_1 L_2 L_3, traps; C_1 C_2 C_3, cooling plates; G, to Pirani gauge; W, cooling water; R, supporting rod.

The vertical section of the apparatus is shown in Fig. 2. It consists of three chambers, i. e., the oven chamber I, the scattering gas chamber II and the detector chamber III. The source of the beam was the small oven O made of a single piece of nickel-chromium steel. It had six holes inside the side wall, in five of which were inserted tungsten heater filaments coated with alumina; the last hole contained a copper-constantan thermocouple. The junction was placed near the front wall of the oven to measure the temperature near the oven slit. The oven was joined by three thin iron rods R to the wall separating I and II. S shows a magnetically operated shutter to screen the beam. The beam path was surrounded by plates C_1, C_2 and C_3 which were cooled by liquid air or carbon dioxide snow contained in traps, L_1, L_2 and L_3, respectively. The temperature of C_2 was

4) J. Estermann, S. N. Foner and O. Stern, ibid., **71**, 250 (1949).
5) W. Jawstusch, G. Schuster and R. Jaeckel, *Z. Physik*, **141**, 146 (1955).
6) K. Kodera, *J. Chem. Soc. Japan, Pure Chem. Sect.*, (*Nippon Kagaku Zassi*), **65**, 645 (1944); **66**, 52 (1945); **67**, 80 (1946); N. Sasaki and K. Kodera, *Mem. Col. Science, Univ. Kyoto*, **A**, **25**, 83 (1949).

measured by a copper-constantan thermocouple T_2 fastened to it.

The beam was formed by an oven slit S_o, a fore slit S_f and a collimating slit S_c. The widths of the slits were 0.019 mm., 0.5 mm. and 0.015 mm., for the oven slit, fore slit and collimating slit, respectively; all of them were 3 mm. high and the fore slit had a thickness of 1.5 mm. to form a canal. The length of the beam was 1.55 cm. in the chamber I, 5.06 cm. in II of which 4.10 cm. was inside C_2, and 7.91 cm. in III. The beam atoms (sodium) were detected by a Langmuir Taylor surface ionization gauge[7], D, made of a tungsten filament of a diameter 0.016 mm. The filament could be moved across the beam from outside by a screw device. Sodium ions emitted from the filament were collected on a negatively charged plate P and measured by a Lindemann electrometer connected to it. The detector filament subtended an angle 2.0×10^{-4} radian $= 41''$ at the collimating slit. This angle was low compared with θ_0, which was estimated to be about 2° for sodium and argon under the experimental conditions.

The chambers I, II and III were separately evacuated by three Hickman oil diffusion pumps, which in turn were connected to a one stage mercury diffusion pump and then to a mechanical fore pump. The scattering gas was introduced into the chamber II from a reservoir through a glass capillary tube. The inlet of the gas was provided on the evacuation tube of the chamber II and during the introduction of the gas the pump was kept working. After the pressure in the chamber reached a stationary value, the measurements were carried out.

The sodium which was used was melted in vacuo to remove oxide coating, distilled three times and poured into a glass tube in high vacuum. Just before the experiment, it was cut into a suitable length and put into a stainless steel sheath and introduced into the oven; then, the apparatus was evacuated as fast as possible. Argon (99.9 %) was purchased on the market.

Experimental Procedure

As described above, it is necessary to measure the beam intensity in vacuo I_0 and the weakened intensity in the scattering gas I, along with the pressure and temperature. The experimental procedure was as follows:

The apparatus was evacuated until the McLeod gauge registered "sticking" for both the scattering and the detector chamber. The trap L_1 was cooled by a mixture of carbon dioxide snow and ethanol, L_2 and L_3 by liquid oxygen. The oven was heated to about 250°C by a constant current supplied through a current stabilizer. The detector was then traversed across the beam and its intensity distribution was measured to find the position of maximum intensity. All the measurements described below were carried out with the detector fixed at that position. The intensity in vacuo I_0 was measured, then the scattering gas, argon, was introduced into the scattering chamber. After the pressure of the gas reached the stationary value, the weakened intensity I and the pressure were measured. The vacuum intensity I_0 was measured again and this value was averaged with the former I_0 and taken as the beam intensity at the instant of measurement of I. These processes were repeated for different pressures of the scattering gas.

Since the pressure range was below about 10^{-4}mmHg, its precise measurement was rather difficult. The McLeod gauge could not be used as it showed a rather large margin of error in this pressure range. For this purpose, a Pirani gauge improved by Yoshida[8] was employed. Since the deflections of the gauge were linear with respect to the pressures below 2×10^{-2}mmHg, it was calibrated by the McLeod gauge at relatively high pressures where high precisions were expected. The sensitivity was tested every time after the measurement to confirm its constancy. It was found that in certain cases a slight change in sensitivity did occur at long intervals but not during the measurements.

The probability that a beam atom will pass 1 cm. through the scattering gas without collision is given by the equation,

$$P=\exp(-l/\lambda) \tag{3}$$

where λ is the mean free path of the atom. If the scattering gas were confined within the chamber II, and the temperature of the gas were homogeneous, then l would be equal to 5.06 cm. In practice, however, some of the scattering gas would flow out of the chamber through the slits S_f and S_c into the chambers I and III, respectively. Moreover, the temperature of the gas in II was low inside C_2 and high outside it. From the pressure and the widths of the slits, the flows could be assumed as molecular effusions. The collision of the beam atoms with the effusing molecules might be ignored, as the density of the effusing molecules just outside the slit is half that inside and decreases rapidly with the distance. But these effusing molecules, although they were evacuated continuously, produced certain stationary pressures in the chambers so that the scattering of the beam atoms could not be ignored. Taking into consideration these effects, equation (3) can be written as follows;

$$P=\exp\left\{-\left(\frac{l_1}{\lambda_1}+\frac{l}{\lambda}+\frac{l_2}{\lambda_2}+\frac{l_3}{\lambda_3}\right)\right\} \tag{4}$$

where λ and l are mean free path and beam length inside C_2, respectively, and λ_2 and l_2 those outside C_2 in the chamber II. Suffixes 1 and 3 show the corresponding values in the chamber I and III, respectively. When the distribution of the pressure and temperature for each chamber is assumed to be independent of the pressure introduced into II, the equation (4) can be rewritten by using an effective path length l_e, as follows:

7) J. B. Taylor, *Z. Physik*, **57**, 242 (1929).

8) S. Yoshida, *J. Chem. Soc. Japan, Pure Chem. Sect.*, (*Nippon Kagaku Zassi*), **63**, 383, 391, 520, 527 (1942).

$$P=\exp -l_e/\lambda \tag{5}$$

where l_e can be evaluated from the knowledge of the pressure and temperature distribution in each chamber. If the beam atoms experienced no multiple collision, P should be equal to I/I_0, where I_0 and I are the beam intensities in vacuo and with scattering gas, respectively. Then,

$$I/I_0=\exp -l_e/\lambda \tag{6}$$

Therefore,

$$\lambda=l_e/\ln(I_0/I) \tag{7}$$

From the λ obtained by Eq. (7) the collision radius can be calculated by the equation of Taits' mean free path[9], i. e.,

$$\left.\begin{aligned}\lambda&=\frac{2}{\pi^{1/2}\nu_G\sigma^2}\left(\frac{T_GM_A}{T_AM_G}\right)^2\\&\quad\int_0^\infty\frac{x^5e^{-(T_GM_A/T_AM_G)x^2}dx}{\phi(x)}\\\phi(x)&=xe^{-x^2}+(2x^2+1)\int_0^\infty e^{-y^2}dy\end{aligned}\right\} \tag{8}$$

where ν_G is the number of scattering molecules per cc., T_A, T_G, M_A and M_G are the temperatures and molecular weights of beam atoms and scattering molecules. x is equal to v/α_G, in which v is the velocity of beam atoms and $\alpha_G=\sqrt{2KT_G/M_G}$, Numerical values of $\phi(x)$ have already been calculated by Rosin and Rabi.

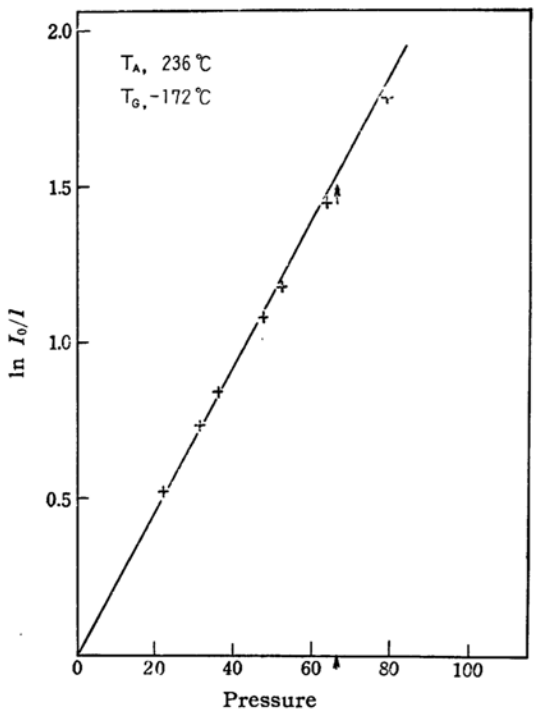

Fig. 3. Weakening of sodium beam scattered by argon.

9) J. H. Jeans, "Dynamical Theory of Gases", Combridge, 4th ed. (1916) p. 255; N. F. Ramsey, "Molecular Beams", Oxford, (1956), p. 24.

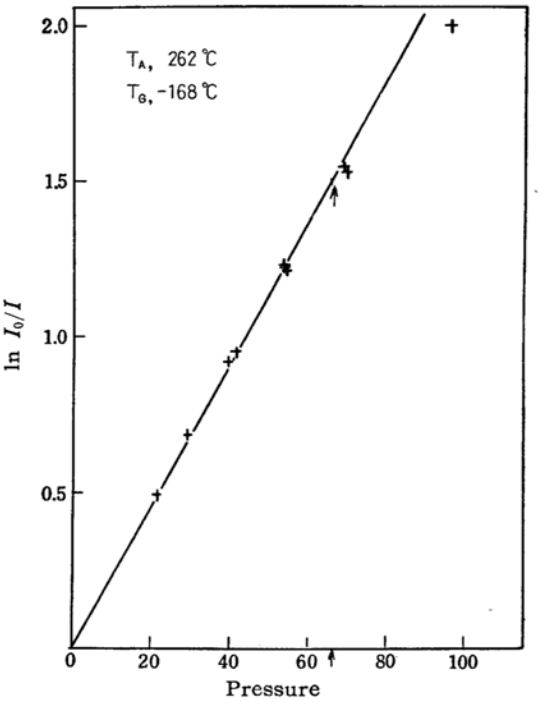

Fig. 4. Weakening of sodium beam scattered by argon.

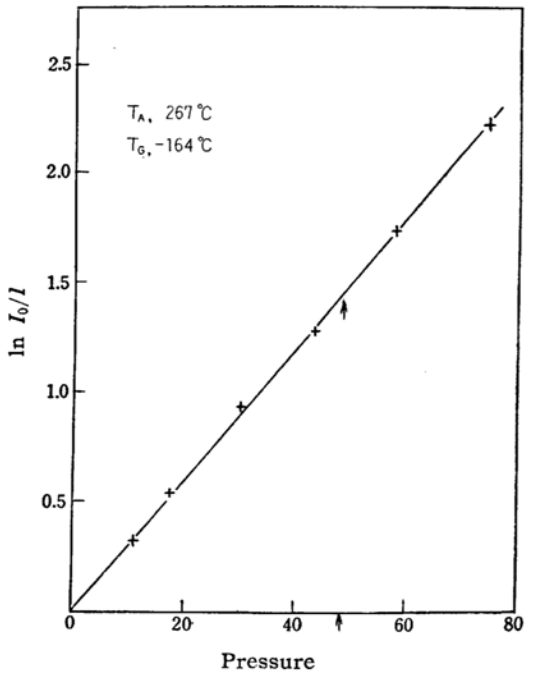

Fig. 5. Weakening of sodium beam scattered by argon.

It should be remarked here that the Pirani gauge was kept at 0°C but the temperature of the chamber whose pressure had to be known differed from 0°C, so that the effect of the thermal transpiration must be taken into account to evaluate the true pressure.

Results

Three series of measurements were carried out on different days and the results are shown in Figs. 3, 4 and 5. In these figures the values of $\ln I_0/I$ are plotted against the pressure of the scattering gas. The pressure are shown by the readings of the Pirani gauge, and arrows in the figures show the pressure in the unit of 10^{-4}mmHg in the gauge. The plots coincide with straight lines below 10^{-4}mmHg, which show that Eq. (6) is satisfied, in this pressure region. For higher pressures, trends are seen to deviate downwards from the straight lines; this fact may be explained by the multiple collisions experienced by the beam atoms.

The measured pressure distribution of the scattering gas in each chamber, collected with the thermal transpiration effect was as follows:

$$p : p_1 : p_3 = 1 : 0.34 : 0.013$$

where p, p_1 and p_3 represent the pressure in the chamber II, I and III, respectively. From these values, together with the temperature distribution in the scattering chamber and the beam length in each chamber, the effective beam length l_e was evaluated as 5.06 cm., i. e., the same value as the beam length in the scattering chamber. It means that the scattering in chambers I and III was compensated by its decrease in the low density region in chamber II outside C_2, where the temperature of the gas was higher than that inside of C_2.

Results calculated from Figs. 3 to 5 are listed in Table I. λ is the mean free path of the beam atoms when the Pirani gauge registered 10^{-4}mmHg. σ is the collision radius between sodium and argon.

TABLE I

COLLISION RADIUS BETWEEN SODIUM AND ARGON

T_A	T_G	λ	σ
236°C	−172°C	3.36 cm.	$12.4^7\times10^{-8}$ cm.
262	−168	3.36	$12.3^8\times10^{-8}$
267	−164	3.47	$12.3^6\times10^{-8}$
	average		12.4×10^{-8} cm.

Discussion

As mentioned above, the quantum mechanical theory for the collision of hard spheres without interaction predicts that $I(\theta)$ increases in the region of small θ; hence, when $k\sigma$ is large, cross-section Q assumes the value twice as great as the classical theory value, consequently σ becomes $\sqrt{2}$ times the classical value. When $k\sigma$ approaches zero, i.e., the relative velocity of colliding particles approaches zero, Q increases four times and σ twice the classical value. In the present experiment σ should be about $\sqrt{2}$ times that of classical theory. When the classical theory radius of argon is assumed to be 1.8×10^{-8}cm. as evaluated from the viscosity of the gas[10], and the radius of sodium in the gas phase to be 3.0×10^{-8}cm.*, the collision radius will be evaluated to be 4.8×10^{-8} cm. The measured value 12.4×10^{-8}cm. is 2.6 times as great as this value, thus much greater than the value given by multiplying 4.8×10^{-8}cm. by $\sqrt{2}$. This discrepancy can be ascribed to the presence of an appreciable van der Waals' force between the colliding particles.

The value 11.3×10^{-8}cm. presented by Rosin and Rabi for sodium and argon is slightly lower than the present value. The difference may be attributed to the smaller resolving power in the former case, i. e., 1.7′ in the former whereas 41″ in the latter. That is, the shaded area in Fig. 1 seems to be appreciable in these small regions of θ. This is also explained by the attractive force between coolliding particles.

The authors take this opportunity to thank Professor N. Sasaki of Kyoto University for permitting them to use the Lindemann electrometer in his laboratory.

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10) E. H. Kennard, "Kinetic Theory of Gases", McGraw-Hill, (1938), p. 149.

* This value is assumed by the similar consideration as Mais. See also Ref. 6.