The Scattering of Beams of Alkali Atoms in Various Gases. II. Sodium Atom Beam in Non-reactive and Reactive Gases

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In a previous paper(1), the scattering of atomic beams was discussed and the apparatus and the results obtained by scattering a sodium beam in argon were described. In this paper, rather simple molecules such as He, Ne, Ar, H_2, N_2 and CO, and molecules which might react with sodium atoms, such as NO, O_2 and CO_2 were used as scattering gases.

Experimental

Apparatus and Procedure.—The apparatus was the same as described in detail in the previous paper except the McLeod gauge. The gauge had not sufficient accuracy for the purpose so that it was replaced by a new one which had frosted capillary tubes to avoid sticking of mercury thread; it also had larger bulb volume (250 cc. instead of 120 cc. of the former gauge). To measure the pressure of scattering gases, the same Pirani gauge was used but its calibration was done during every experiment in the pressure range of $10^{-4}\sim10^{-5}$ mmHg and not in a high pressure range as before. Procedure of measurements was also the same as before, but more precaution was taken in the measurement of pressures of scattering gases in the detector and the oven chambers, because effusion rates of the gases and pumping speed for them vary with their molecular weights and, for reactive gases, reaction with sodium also affects the stationary pressure.

Materials. — Sodium used for the beam was purified by repeated vacuum distillation as described before.

Helium, Neon and Argon. Gases labeled extra pure or 99.9% were purchased on the market and used without further purification. They were examined by CEC type 401 mass-spectrometer and proved that they contained no detectable impurity.

Hydrogen was made by electrolysis of sodium hydroxide solution with nickel electrodes and passed through soda-lime, heated reduced copper, concentrated sulfuric acid, phosphorus pentoxide and a liquid oxygen trap.

Nitrogen was made by heating ammonium nitrite solution made by dropping sodium nitrite solution into ammonium sulfate solution in a flask. The gas evolved was passed through a mixture of concentrated sulfuric acid and potassium dichromate and over soda-lime, heated reduced copper, soda-lime and a liquid oxygen trap, successively. The gas was examined by the mass-spectrometer and proved to contain no detectable impurity.

Oxygen was made by electrolysis of sodium hydroxide solution and purified in a way similar to that of the hydrogen, except for the fact that heated reduced copper was replaced by heated cupric oxide.

Nitric oxide was made by dropping concentrated sodium nitrite solution into a heated mixture of concentrated ferrous sulfate solution and hydrochloric acid. The gas evolved was passed over solid potassium hydroxide and silica gel and then condensed by a liquid nitrogen trap. The solidified gas was distilled into another trap, and the procedure was repeated several times.

Carbon monoxide. Concentrated sulfuric acid was dropped on heated sodium formate. The evolved gas was passed over fused potassium hydroxide, silica gel and through a liquid nitrogen trap.

Carbon dioxide. Solid carbon dioxide was evaporated and passed through concentrated sulfuric acid, then over calcium chloride and phosphorus pentoxide. The gas was condensed by a liquid oxygen trap and distilled several times as in the case of nitric oxide.

Results

Weakening of sodium beams scattered in various gases are shown in Figs. 1 to 9. Calculated results are shown in Table I with other experimental data. In the table, p, p_1, p_3 represent relative pressures of scattering gas in the scattering-, the oven- and the detector-chambers, respectively. Mean free paths (λ)

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1) K. Kodera and T. Tamura, This Bulletin, **31**, 206 (1958).

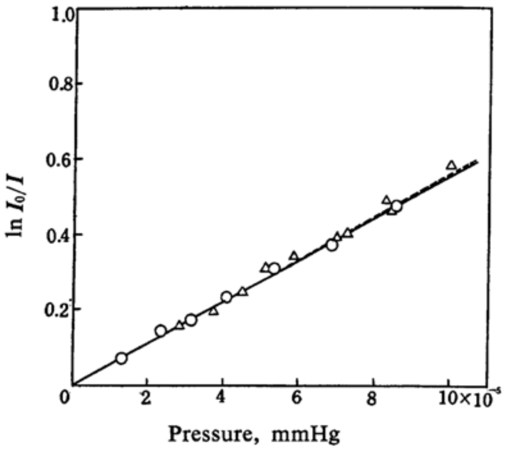

Fig. 1. Sodium beam in helium.

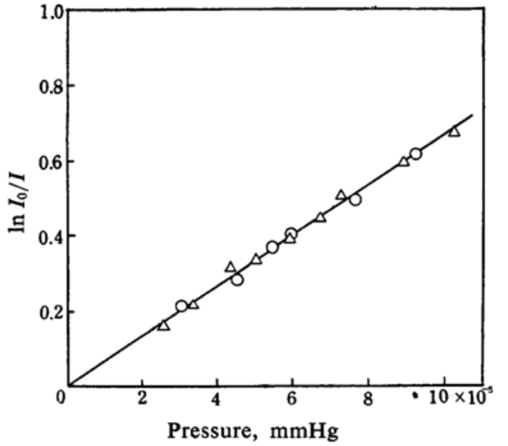

Fig. 2. Sodium beam in neon.

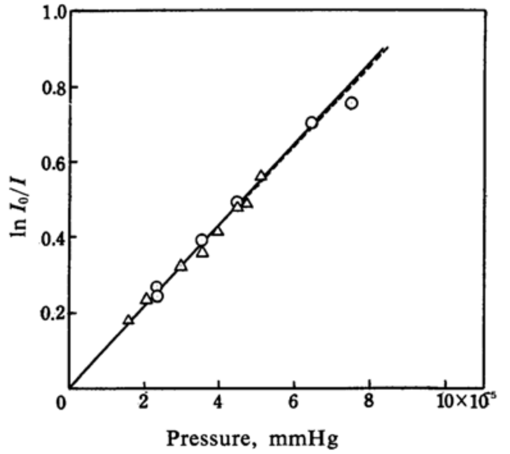

Fig. 3. Sodium beam in hydrogen.

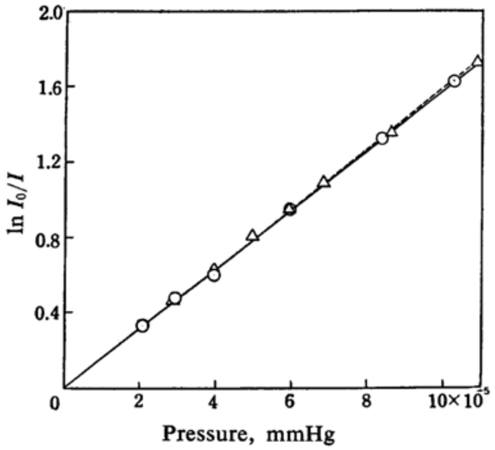

Fig. 4. Sodium beam in nitrogen.

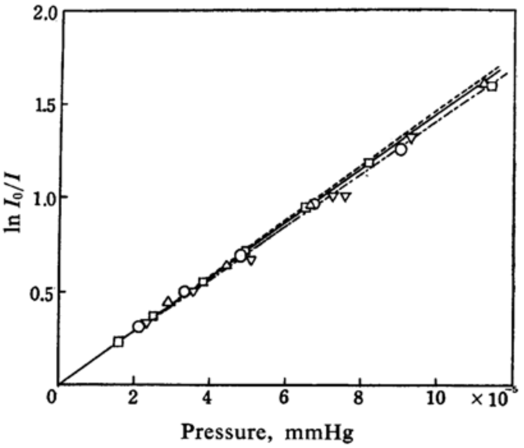

Fig. 5. Sodium beam in argon.

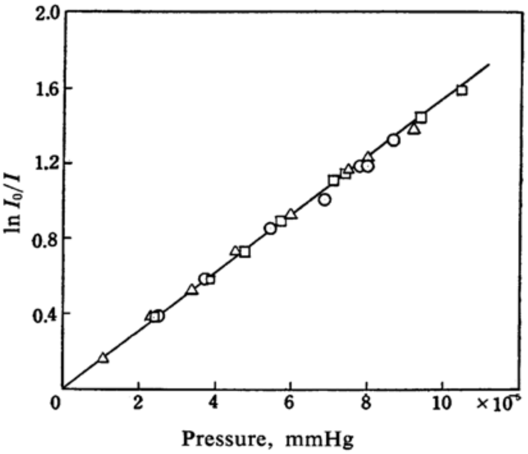

Fig. 6. Sodium beam in carbon monoxide.

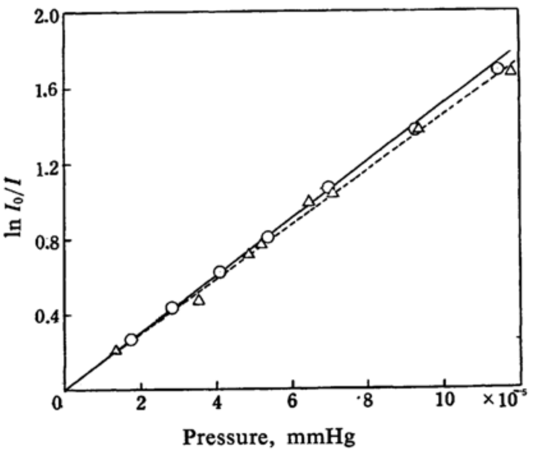

Fig. 7. Sodium beam in nitric oxide.

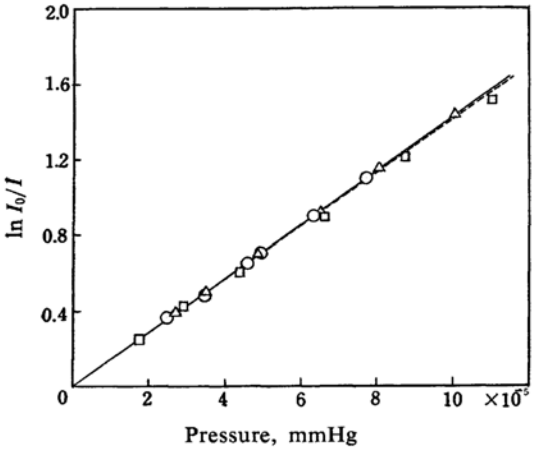

Fig. 8. Sodium beam in oxygen.

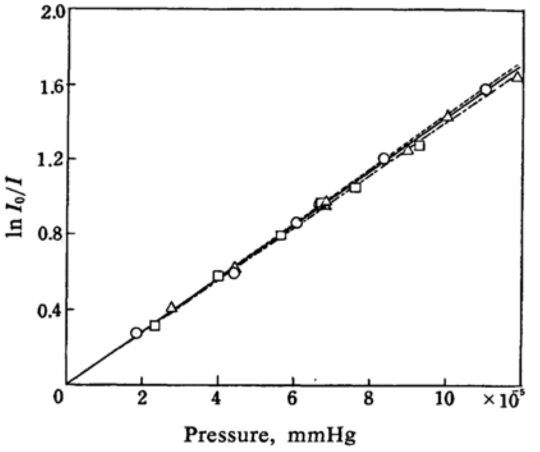

Fig. 9. Sodium beam in cabon dioxide.

are those of beam atoms in scattering gases at 10^{-4} mmHg. From these values, effective collision radii (σ) were calculated by Tait's equation using Rosenberg's table[2]. A detailed account of the calculation has been given in the previous paper. In Table II, average values of collision radii in Table I and collision cross sections are shown together with classical kinetic values (σ_K) for comparison. To evaluate these values, the radius of a sodium atom was assumed to be 3.0×10^{-8} cm. as in the previous paper, and for the radii of the scattering gas molecules, values obtained from the viscosity measurements[3] were used.

Discussion

The distributions of the scattering gases differ somewhat for each measurement. This fact may be attributable to the difference of pumping speeds as they were rather sensitive to the heating currents. For the detector chamber, the pressures were extremely low so that errors in the measurements were rather large but their contributions to l_e were small. For reacting gases, pressures in the oven chamber were extremely low, because the gases effused into the chamber reacted with sodium deposited on its wall or in the gas phase. In these cases the pressures might also be changed by the surface state of the deposit. Therefore, calculated l_e varied somewhat in some cases, but the values of collision radii which were obtained agreed satisfactorily.

Among scattering gases, rare gases, nitrogen and carbon monoxide will not react with sodium atoms. For hydrogen, there is a possibility of reaction with sodium atoms producing sodium hydride, but the pressure in the oven chamber indicates that, even if it is the case, the amount is negligible. On the other hand, pressures of oxygen, nitric oxide and carbon dioxide in the oven chamber were extremely low, indicating that the gases were consumed by the reactions with sodium deposited on the wall or in the gas phase. In the cases of oxygen and nitric oxide, the pressures were the same whether the oven was heated or not, so that the consumption of the gases should be considered to occur almost solely by the surface reaction. For carbon dioxide, when the oven was at room temperature, the pressure was intermediate between those of non-reactive gases and reactive gases. To see whether the reaction in the gas phase affects the stationary pressure of the scattering gas in this case,

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[2] P. Rosenberg, *Phys. Rev.*, **61**, 528 (1942).

[3] E. H. Kennard, "Kinetic Theory of Gases", McGraw-Hill, New York (1938), p. 149; L. B. Loeb, "Kinetic Theory of Gases", McGraw-Hill, New York (1927), p. 529.

TABLE I. MEAN FREE PATHS AND EFFECTIVE COLLISION RADII

Exp. No.	Gas	Press. dist.			Effective path l_e cm.	Mean free path λ cm.	Collision radius σ $\times 10^{-8}$ cm.	Temp. of Na °K	Temp. of Gas °K
		p	p_1	p_3					
1	He	1	0.28	0.017	5.04	9.16	6.69	569	106
2	He	1	0.30	0.014	5.01	8.93	6.83	577	109
3	Ne	1	0.28	0.012	4.99	7.45	8.35	599	108
4	Ne	1	0.27	0.016	5.01	7.49	8.34	596	109
5	Ar	1	0.36	0.013	5.06	3.50	12.46	567	109
6	Ar	1	0.30	0.014	5.04	3.47	12.36	553	104
7	Ar	1	0.30	0.025	5.10	3.49	12.46	592	109
8	H_2	1	0.30	0.038	5.21	4.79	8.46	576	101
9	H_2	1	0.33	0.021	5.08	4.72	8.52	576	103
10	N_2	1	0.36	0.016*	5.08	3.21	12.88	567	110
11	N_2	〃	〃	〃 *	〃	3.18	12.79	549	104
12	CO	1	0.36	0.014*	5.05	3.25	12.76	554	108
13	CO	〃	〃	〃	〃	3.19	12.97	567	112
14	CO	1	0.26	0.003	5.01	3.23	12.81	595	108
15	O_2	1	0.008	0.015*	4.88	3.41	12.55	572	110
16	O_2	〃	〃	〃 *	〃	3.37	12.47	550	105
17	O_2	1	0.001	0.003	4.77	3.39	12.59	593	110
18	NO	1	0.034	0.014	4.88	3.23	12.75	567	105
19	NO	1	0.054	0.012	4.88	3.35	12.77	592	114
20	CO_2	1	0.003	0.014	5.07	3.51	14.37	606	206
21	CO_2	1	0.006	0 *	4.96	3.49	14.39	556	201
22	CO_2	〃	〃	〃 *	〃	3.54	14.18	550	201

* These values are average values of several observations before the experiments.

TABLE II. EFFECTIVE COLLISION RADII AND CROSS SECTIONS

Gas	Temp. of Gas, °K	σ $\times 10^{-8}$ cm.	$\pi\sigma^2$ $\times 10^{-16}$ cm²	Classical kinetic value		
				r_G $\times 10^{-8}$ cm.	σ_K $\times 10^{-8}$ cm.	σ/σ_K
He	108	6.76	144	1.1	4.1	1.65
Ne	108	8.35	219	1.2	4.2	1.99
Ar	107	12.4	483	1.8	4.8	2.58
H_2	102	8.51	227	1.4	4.4	1.94
N_2	107	12.8	515	1.9	4.9	2.62
CO	109	12.8	515	1.8	4.8	2.67
O_2	108	12.5	491	1.8	4.8	2.62
NO	109	12.8	515	1.7	4.7	2.72
CO_2	201	14.3	642	2.3	5.3	2.70

number of carbon dioxide molecules which react with sodium atoms in the gas phase has been roughly calculated. The calculation revealed that, assuming reaction probability on collision to be unity, and assuming collision cross-section to be equal to the classical kinetic value, less than 4% of effusing molecules react with sodium atoms in the gas phase under the present experimental condition. Reaction probabilities of colliding molecules are in general far smaller than unity, so that the reaction cannot produce any detectable change upon the stationary pressure in the oven chamber. Thus, rather large pressure observed when the oven was at room temperature should be explained by the contamination of the deposit surface which retards the surface reaction. For the same reason, in the cases of oxygen and nitric oxide, the equal stationary pressures observed with or without sodium beams do not exclude the existence of the reaction in the gas phase.

As for reaction between these gases and sodium atoms in the gas phase no detailed investigations have been found in literatures, but Holt and Sims⁴⁾ found that sodium could be distilled in the atmosphere of completely dried oxygen without being oxidized. Therefore, it is reasonable to assume that the probability of reaction on collision is extremely small for oxygen and also for other gases, and the scattering can be treated as elastic, as in

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4) W. Holt and W. E. Sims, *J. Chem. Soc.*, **65**, 432 (1894).

the case of the non-reactive gases.

In Table II, it is seen that ratios of measured collision radii to those of classical kinetic values, i.e., σ/σ_K, for molecules of rather small molecular weight, such as hydrogen, helium and neon, are less than two, whereas for other gases they are about 2.7. Similar large collision radii have also been found in the scattering experiments of alkali beams carried out by Mais5), Rosin and Rabi6), Sasaki and Kodera7) and others8). As values of σ/σ_K, Sasaki and Kodera obtained 1.6 for hydrogen and 2.2 for oxygen, argon and chlorine with potassium beams. These values are smaller than the present ones. Measurements of Rosin and Rabi for sodium beams shown in Table III gave σ/σ_K for hydrogen, helium and neon smaller than 2 and for argon 2.4. The main difference in experimental conditions in these works are the geometric resolution, i.e., atoms deflected more than 25′ in average[*] in case of Sasaki and Kodera, 1.7′ in Rosin and Rabi, 41″ in present experiments fail to hit the detector filament and, therefore, measured as scattered. Estermann, Foner and Stern measured σ for cesium and helium by an apparatus with 5″ resolution and obtained more than 50% larger value than that which Rosin and Rabi obtained with the same pair. As an example of measurement with an apparatus of similar resolving power as in the present case, i.e., 45″, there are Rosenberg's results with a potassium beam. From his data collision radii with gases which were commonly used in both cases have been calculated and listed in Table IV. To estimate values for sodium a factor 0.9, which is an average ratio of σ for sodium and for potassium by Rosin and Rabi, was multiplied to these values and shown in the table. For argon and nitrogen, these values agree to ours fairly well, showing that measured radii increase with increasing resolving power, but will take same values by the same resolution. As described in the previous paper, the simplified quantum mechanical treatment of the colliding particles as hard spheres shows that the scattering intensity for small angles increase markedly below a certain angle θ_0. For the present work, the largest value for θ_0 is about 12° for hydrogen and the smallest value is about 1°40′ for carbon dioxide. The angles of resolution in the above-mentioned measurements are all far smaller than these values, therefore, contribution of the small angle scattering to the collision radius might be included almost completely in these experiments. Moreover, by this contribution the collision radius increases to the value only $\sqrt{2}$ times that of the classical one. Therefore, the change in collision radius with the resolving power and observed large values in the present experiment should be explained by the existence of considerable interaction between colliding particles. For molecules of rather small molecular weights such as hydrogen, helium and neon, values of σ/σ_K are smaller than 2 both in the present and in the other experiments cited above. However, while the value of helium in the present work is reasonable compared with the others', that of neon is rather small and that of hydrogen is considerably large. The difference in the experimental conditions other than the resolving power are temperatures of beams and gases, i.e., in the work of Rosin and Rabi the beam was at 700°K and though the temperature of gases was not described, it is considered to be at room temperatures, and in the work of Rosenberg, the beams and the gases were at 500°K and 300°K, while in the present work they were at 570°K and 110°K (except carbon dioxide), respectively. Therefore the temperature of gases was very low in the latter. The theoretical collision radius of $\sqrt{2}$ times that of classical value mentioned above is that for particles colliding with infinite relative velocity, but it increases with decreasing relative velocity until at the limit it becomes 2 times that of the classical value. Thus, lowering of the temperature of gas should cause increase of the collision radius, however, in the temperature range in these experiments the effect is too small for the molecules of large molecular weights. For hydrogen it may be possible to detect this effect, but the discrepancy observed

TABLE III. COLLISION RADII AND CROSS SECTIONS (Rosin and Rabi)

	σ $\times 10^{-8}$ cm.	$\pi\sigma^2$ $\times 10^{-16}$ cm^2	σ/σ_K
He	6.44	130	1.57
Ne	8.24	213	1.96
Ar	11.3	401	2.36
H_2	7.01	154	1.59

TABLE IV. COLLISION RADII FOR POTASSIUM BY ROSENBERG AND CALCULATED VALUES FOR SODIUM

	K $\times 10^{-8}$ cm.	Na(calcd.) $\times 10^{-8}$ cm.
He	7.39	6.65
Ar	13.7	12.3
H_2	7.94	7.15
N_2	14.0	12.7

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

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

7) N. Sasaki and K. Kodera, *Mem. Col. Sci., Univ. Kyoto*, **25**, 84 (1949).

8) P. Rosenberg, *Phys. Rev.*, **55**, 1267 (1939); I. Estermann, S. N. Foner and O. Sterm, ibid., **71**, 250 (1947).

[*] In this experiment, a detector filament was placed in the scattering gas, therefore, the angle of resolution differed from place to place.

is too large to be explained by this cause.

In Table II, it is seen that nitrogen and carbon monoxide have equal radii, this is reasonable that these molecules have nearly equal molecular weights and identical electronic structures. Oxygen has a slightly smaller radius than nitrogen; this slight difference in radii is also seen in the results of Sasaki and Kodera with sodium and potassium beams, and also in classical kinetic values. In the present work, since pressure distributions of nitrogen and oxygen differ considerably because of the reactivity of oxygen with sodium, it is difficult to decide whether this slight difference in the radii has any significance, but the measurements of Sasaki and Kodera were carried out under the same condition for the two gases; therefore, it is possible that the quantity of oxygen is smaller than that of nitrogen.

Summary

Collision radii considerably larger than those of classical kinetic values have been obtained. Among the measured values of collision radii, that for neon is rather smaller and that for hydrogen is considerably larger than those obtained by the other investigators. For molecules of rather large molecular weight, relative sizes among them are reasonable but they increase with the resolving power of the apparatus used. These large values of radii and their increase with the resolving power may be explained by the existence of considerable mutual interaction such as Van der Waals' force between colliding particles.

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