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On the Direct Measurement of the Effective Collision Radii of Potassium with Chlorine and Other Gases.

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In the chemical kinetics the problem of the effective collision radii between the chemically reactive molecules is of special interest. By means of their "highly diluted flame" Polanyi and his collaborators[1] claimed to have shown chlorine and sodium to react at a distance greater than the classical collision radius.

By more direct method of molecular beam, we have examined if there be any influence of chemical reactivity on the effective collision radii. The scattering of an atomic beam of potassium was measured in reactive molecules (Cl_2) and in non-reactive molecules (H_2, N_2, O_2 and A) for the sake of comparison. The atomic beam had the cross section 0.01 mm × 1 mm. Its intensity was measured by the Langmuir-Taylor method of surface ionization using a tungsten filament of diameter 0.022 mm. The thinest beam and the finest filament were used to minimize the scattered atoms striking the filament. The intensities of the beam in vacuum I_{o1} and in a gas I_{p1} at a distance l_1 (1.4 cm) from the collimating slit and the corresponding values I_{o2} and I_{p2} at a distance l_2 (4.3 cm) from the slit give the mean free path λ of potassium atom by

$$\lambda = \frac{l_2 - l_1}{\ln\left(\dfrac{I_{o2}I_{p1}}{I_{o1}I_{p2}}\right)},$$

from which the effective collision radius σ may be calculated by the Tait's expression[2] for the mean free path. The results are shown in

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[1] M. Polanyi and his collaborators: Z. physik. Chem., **B 1**, 3, (1928) et seq., "Atomic Reactions," London (1932) If we use, instead of their seemingly too small value, that estimated by Mais' method for the radius of sodium atom, the said difference disappears. Cf. Table 2, last column.

[2] J. H. Jeans, "Dynamical Theory of Gases", 2nd Ed., p. 271 (1916).

Table 1, where T_G represents the temperatures of the scattering gases and σ_K the sums of r_B and r_G in Table 2.

Table 1.

No.	H_2	N_2	O_2	A	Cl_2	T_G
1	7.79Å		12.1Å	12.0Å		112°K
2				11.8Å		112°K
3*	(7.57Å)	(11.5Å)	(11.6Å)			112°K
4	7.32Å	12.2Å	12.0Å	12.3Å		210°K
5					13.5Å	112°K
6					13.4Å	112°K
σ_K	5.0Å	5.5Å	5.4Å	5.4Å	6.1Å	

* The results obtained with a filament of a larger diameter 0.036 mm.

In Table 2, the mean values from Table 1 together with those previously obtained in our laboratory by a different method (No. 1) and by the same method with a beam and a measuring filament of larger dimensions (No. 2 and 3) are given, where r_B means the radii of the beam atoms estimated by Mais[3], r_G the kinetic radii of the scattering gas molecules.

Table 2.

No.	Atomic beam.	Scattering gas.	Observed value σ	Classical kinetic value			Ratio σ/σ_K	Other σ
				γ_B	γ_G	σ_K		
1[4]	Na	Cl_2	5.01	3.0	2.5	5.5	0.91	5.5(Magee) 5.25 (Polanyi)
2[5]	Na	N_2	6.48	3.0	1.9	4.9	1.3	
3[5]	Na	O_2	6.13	3.0	1.8	4.8	1.3	
4[6]	K	N_2	12.2	3.6	1.9	5.5	2.2	
5[6]	K	O_2	12.1	3.6	1.8	5.4	2.2	
6[6]	K	A	12.0	3.6	1.8	5.4	2.2	
7[6]	K	Cl_2	13.5	3.6	2.5	6.1	2.2	8.0(Magee)

Values of σ and γ are in Å unit.

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[3] W. H. Mais: Phys. Rev., **45**, 773, (1934). The value for sodium was not given by Mais. We estimated it by his own method.

[4] N. Sasaki, E. Nishibori and H. Uchida: Journ. Chem. Soc. Japan, **57**, 1277, (1936).

[5] N. Sasaki, E. Nishibori, G. Kondo and K. Kodera: ibid., **57**, 1284, (1936).

[6] The present report. Also cf. K. Kodera: ibid., **65**, 645, (1944); **66**, 52, (1945); **67**, 80, (1946).

[7] J. L. Magee: J. Chem. Phys., **8.**, 687, (1940).

Magee[7] estimated the collision (end-on) radii of sodium and the halogen molecules. His theoretical values together with the Polanyi's σ are given in the last column. The collision radius between sodium atom and chlorine molecule (σ_s) was determined by measuring the intensities[8] of the resonance radiation at two spots (9.5 mm apart) along a sodium atomic beam of 2 mm diameter.

In order to consider the meanings of the various kinds of collision radii now at our disposal, a brief account of a result of the quantum mechanical theory of atomic collisions[9] must be introduced. In the case of a rigid body scattering of an atomic beam in a gas, the probability, or more precisely, the "differential" cross section, for the scattering into unit solid angle decreases rapidly, as the angle of scattering increases from zero, from a large value to attain the relatively very small classical cross section at a certain critical angle of scattering (1.4° for potassium and chlorine, and 1.9° for sodium and chlorine) and retains that value for larger angles. Due to this predominance of the small angle scattering the "total" cross section taken all over the scattering angle surpasses the classical value by a factor of 2 to 4.

Putting the angle of demarcation between the large and the small angle scattering at this critical angle, let us compare the various collision radii mentioned above. Beam atoms scattered in large angles (S) may be divided into three parts: (1) those chemically reacted (S_c), (2) those straggled before arriving at the second point of measurement (S_s) and (3) those arriving at the second point (S_a). Beam atoms scattered in small angles may also be divided into three corresponding parts (R_c, R_s and R_a). The letters in parentheses denote qualitatively the portions of the collision radius (σ), which the respective divisions of the scattered atoms may contribute as the manner of measurement varies, so that we have a general formal expression:

$$\sigma = S + R = S_c + S_s + S_a + R_c + R_s + R_a.$$

The classical collision radius σ_k can be given by

$$\sigma_k = S = S_c + S_s + S_a,$$

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[8] To be correct, these must be multiplied by the atomic velocities to give the beam intensities I's. This correction will reduce the value of σ_s, for the faster atoms are less liable to scattering. On the other hand the pressure of chlorine near the beam must be smaller than the value indicated by the manometer, because the gas is consumed rather vigorously by sodium abundantly depositing on the slits. This correction will increase the value of σ_s.

[9] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc., A **141**, 434, (1932).

neglecting its very small classical portion in R; the Polanyi's collision radius σ_p by

$$\sigma_p = S_c + R_c,$$

and our σ_s by

$$\sigma_s = S_c + S_s + R_c.$$

By the way it is to be noted here that, since the cross section of the beam and the second spot of measurement are large, R_s part of the scattered atoms comes to be included in R_a and ceases to contribute to σ. If measured with a very fine beam and a very fine filament as in the case of potassium and chlorine, the radius thus obtained (σ_f) will coincide with the general expression above mentioned:

$$\sigma_f = S + R,$$

S_a and R_a parts being nearly zero.

In the case of potassium the ratios σ_f/σ_k in Table 2 are the same for all gases investigated, irrespective of their chemical reactivity and this will certainly be the case with sodium also. This fact excludes the possibility that σ in any way be increased by the existence of chemical reactivity between the colliding particles. The large value 2.2 of σ_f/σ_k may be explained quantum mechanically if some interaction such as van der Waals force exists between the colliding particles. The small value 1.3 is due to the larger measuring tungsten filament which receives larger number of atoms scattered in small angles.

In the case of sodium, if we may assume $\sigma_p = \sigma_s$, then $S_s = 0$, from which necessarily follows $S_a = 0$, so that $\sigma_k = S_c$, finally, if we may put $\sigma_k = \sigma_s$, then $R_c = 0$. The conclusion is approximately: The large angle ($>1.9^\circ$) classical kinetic scattering is all effective in bringing about the chemical reaction between sodium atom and chlorine molecule, while the small angle scattering, or largely quantal scattering, though dominant, is all ineffective.

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