

# Total Cross Sections for the Scattering of Potassium by Helium, Neon, Argon, Krypton, and Xenon

Isao KUSUNOKI

*Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto*

(Received June 15, 1966)

Total cross sections for the scattering of potassium by He, Ne, Ar, Kr, and Xe have been measured in the thermal energy range. The potassium beam and the scattering gases had Maxwellian velocity distributions. The angular resolution of the apparatus was 2.62 min of arc, so that quantum mechanical calculations could be applied. If a van der Waals potential,  $V = -C/r^6$ , is assumed for the long range intermolecular forces, the total cross section may be related to the constant,  $C$ , as follows;  $Q(v_r) = p \left[ \frac{C}{\hbar v_r} \right]^{2/5}$ , where  $p$  is a constant. In the present experiments care was taken to avoid the pumping effect of a McLeod gauge in the measurement of the pressure in the scattering chamber. The  $Ga_0$  function defined by Berkling *et al.* was used to derive an absolute total cross section from a measured effective total cross section. The van der Waals constants calculated from the measured total cross sections were compared with the theoretical values. The present values were about 25 percent smaller than the theoretical values for the Ar, Kr, and Xe systems. The differences for the He and Ne were considerably larger, with the theoretical values larger than the experimental by a factor of two or three.

A number of investigators<sup>1-3)</sup> have studied the total scattering cross sections of alkali atoms with rare gas atoms in the thermal energy range in order to obtain information concerning long range intermolecular forces or van der Waals constants. In this earlier work the values of the total cross sections and the van der Waals constants obtained by this method were considerably higher than those to be expected from the theory.

Alkali beams are often used in these experiments since the beams are easily obtained from a heated oven and since Langmuir-Taylor surface ionization detectors have a high sensitivity for measuring the intensity of such beams. On the other hand, rare gases are often used as scattering gases because their rather simple atomic structure makes both theoretical and experimental treatment easier than for other gases. In addition, their absolute pressures can be measured precisely with a McLeod gauge. However, the mercury drag effect in pressure measurements with a McLeod gauge has been reported by several authors<sup>4)</sup>

recently; this effect might have made the measured pressures too low and the total cross sections too high in some earlier investigations.

Bennewitz and Dohmann<sup>5)</sup> have shown that the discrepancies between van der Waals constants determined from beam experiments and theoretical calculations may be decreased by the following procedures; (1) by taking the mercury drag effect into consideration in measuring the scattering gas pressures with a McLeod gauge; (2) by using the function derived by Berkling *et al.*,<sup>6)</sup> instead of that of Rosin and Rabi, to calculate the total cross section; (3) by using the Schiff<sup>7)</sup> and Landau-Lifschitz<sup>8)</sup> approximate formula, instead of the Massey-Mohr formula,<sup>9)</sup> to estimate the van der Waals constant  $C$ .

In the present work, the experiments were carried out with the points mentioned above kept in mind, the results for the scattering of potassium beam by rare gases will be described

1) W. Mais, *Phys. Rev.*, **45**, 773 (1934); S. Rosin and I. Rabi, *ibid.*, **48**, 373 (1935); P. Rosenberg, *ibid.*, **55**, 1267 (1939); N. Sasaki and K. Koderu, *Proc. Imp. Acad. Tokyo*, **17**, 70 (1941); N. Sasaki and K. Koderu, *Memoirs of the College of Science, University of Kyoto, Series A*, **25**, 83 (1949); K. Koderu and T. Tamura, *This Bulletin*, **31**, 206 (1958); **34**, 566 (1961); K. Lulla, H. H. Brown and B. Bederson, *Phys. Rev.*, **136**, A 1233 (1964).

2) E. W. Rothe and R. B. Bernstein, *J. Chem. Phys.*, **31**, 1619 (1959).

3) R. Helbing and H. Pauly, *Z. Physik*, **179**, 16 (1964).

4) H. Ishii and K. Nakayama, Transactions of the Eighth National Vacuum Symposium, 1961 (Pergamon Press, Oxford, England, 1962), Vol. I, p. 519; Ch. Meinke and G. Reich, *Vakuum-Technik*, **11**, 86 (1962); E. W. Rothe, *J. Vac. Sci. Tech.*, **1**, 66 (1964).

5) H. G. Bennewitz and H. D. Dohmann, *Z. Physik*, **182**, 524 (1965).

6) K. Berkling, R. Helbing, K. Kramer, H. Pauly, Ch. Schilier, and P. Toschek, *ibid.*, **166**, 406 (1962).

7) L. I. Schiff, *Phys. Rev.*, **103**, 443 (1956).

8) L. D. Landau and E. M. Lifshitz, "Quantum Mechanics," Pergamon Press, Ltd., London (1959). p. 416.

9) H. S. W. Massey and C. B. O. Mohr, *Proc. Roy. Soc.*, **A144**, 188 (1934).

below, and the van der Waals constants deduced from the total cross sections will be compared with the theoretical values.

### Theoretical

For a theoretical analysis of the intermolecular force, it is convenient to divide it into two parts, one repulsive and the other attractive, as in the expressions for the Lennard-Jones or Buckingham potentials. The attractive terms in these expressions are dominant in the long-range region; they may be expressed by the van der Waals potential;

$$V = -\frac{C}{r^6}. \quad (1)$$

For the general case of a symmetrical attractive potential, the relation is;

$$V = -\frac{C^{(s)}}{r^s}. \quad (2)$$

The van der Waals constant,  $C$ , is related to the total cross section,  $Q$ , by;

$$Q(v_r) = p \left[ \frac{C}{\hbar v_r} \right]^{2/(s-1)}, \quad (3)$$

where  $v_r$  is the initial relative velocity of the colliding atoms. This formula has been derived by Massey and Mohr.<sup>9)</sup> According to their approximation,  $p$  in Eq. (3) is given by;

$$p_{MM} = \pi \left( \frac{2s-3}{s-2} \right) [2f(s)]^{2/(s-1)}, \quad (4)$$

where;

$$f(s) = \frac{\sqrt{\pi} \Gamma\left(\frac{s-1}{2}\right)}{2\Gamma\left(\frac{s}{2}\right)}.$$

For  $s=6$ ,  $p=7.547$ . Recently Bernstein and Kramer<sup>10)</sup> have shown that the Schiff and Landau-Lifschitz approximations lead to the same expression as Eq. (3). In this case, however,  $p$  is given by;

$$P_{SLL} = \frac{2^{2/(s-1)} \pi^2}{\sin[\pi/(s-1)] \Gamma(2/(s-1))} f(s)^{2/(s-1)} \\ = 8.083. \quad (\text{for } s=6) \quad (5)$$

They have also calculated the total cross section with an exact partial wave method and compared the results with the values obtained from Eqs. 3, (4) and (5). They have found that the SLL approximation,  $Q_{SLL}$ , is in good agreement with the more exact values which they calculated.

The experimental total cross section is given by;

$$S(\gamma) = 2\pi \int_0^\gamma \sigma(\theta) \sin \theta d\theta, \quad (6)$$

where  $\gamma$  is the angular aperture of the apparatus and where  $\sigma(\theta)$  is the differential cross section

in apparatus coordinates or in the center of mass coordinates.  $Q$  in Eq. (3) corresponds to  $S(0)$  which is obtained with an ideal apparatus of infinitesimal angular resolution.

Now, let us consider the differential cross section for small-angle elastic scattering and discuss the difference between  $Q$  and  $S(\gamma)$ . According to the Kennard<sup>11)</sup> approximation for small-angle scattering, the classical differential cross section can be written by;

$$\sigma(\theta) = \frac{(s-1)^{2/s}}{s} \left( \frac{2f(s)C}{\mu v_r} \right)^{2/s} \left( \frac{1}{\theta} \right)^{-2(s+1)/s} \quad (7)$$

and the total cross section, by;

$$S(\gamma) = \pi \left[ \frac{2\pi^{1/2} \Gamma\left(\frac{s+1}{2}\right) C}{\mu v_r^2 \Gamma\left(\frac{s}{2}\right) \gamma} \right]^{2/s} \quad (8)$$

Here, however,  $\sigma(\theta)$  and  $S(\gamma)$  increase infinitely as  $\theta$  and  $\gamma$  decrease to zero. Therefore, it is clear that these expressions will not be correct for very small-angle scattering. In these regions, a quantum mechanical treatment is necessary to estimate the differential cross section. According to a semiclassical theory,  $\sigma(\theta)$  is given approximately by:

$$\sigma(\theta) = \left[ \frac{kS(0)}{4\pi} \right]^2 \left( 1 + \tan^2 \frac{\pi}{s-1} \right) \\ \times \exp \left[ -\frac{g(s)k^2 S(0)\theta^2}{8\pi} \right], \quad (9)$$

where:

$$g(s) = \left[ \Gamma\left(\frac{2}{s-1}\right) \right]^2 \left[ 2\pi \Gamma\left(\frac{4}{s-1}\right) \right]^{-1} \\ \times \tan \left( \frac{2\pi}{s-1} \right),$$

$$k = \mu v / \hbar.$$

Helbing and Pauly<sup>12)</sup> have shown that their experimental results are in fairly good agreement with Eq. (9) for small angles and with Eq. (7) for larger angles. They combined Eq. (7) and Eq. (9) for small-angle scattering;

$$\sigma(\theta) = \frac{(s-1)^{2/s}}{s} f(s)^{2/s} \left( \frac{2C}{\mu v_r} \right)^{2/s} \theta^{-2(s+1)/s} \\ (1 - e^{-(\theta/\theta_0)^{s/2(s+1)}}), \quad (10)$$

where;

$$\theta_0 = \frac{\hbar \varphi_2}{\mu v_r} \sqrt{\frac{\pi}{Q}},$$

and;

$$\varphi_2 = \frac{(s-1)^{1/(s+1)}}{[F(s)]^{(s-1)/2(s+1)}} \left[ \frac{16}{s(1 + \tan^2 \pi/(s-1))} \right]^{s/2(s+1)}, \\ = 1.166 \quad (\text{for } s=6)$$

and;

$$F(s) = \frac{2\pi}{(s-1) \Gamma\left(\frac{s+1}{s-1}\right) \sin \frac{\pi}{s-1}}.$$

They estimated the experimental critical angle,  $\theta_0$ , as  $8.56'$  for the potassium-argon system at  $v_r \approx 600$  m/sec, at which angle the differential cross section deviates about 37% from the classical value. On the other hand, Mason *et al.*<sup>12)</sup> have found that the semiclassical expression of Eq. (9) is accurate for angles;

$$\theta < [\pi^2 F(s)/2]^{-1/2} \theta_c,$$

where  $\theta_c$  (the classical critical angle) is given by;

$$\theta_c > k^{-1}[2\pi/S(0)]^{1/2}.$$

In this investigation the lower limit of  $\theta_c$  for the potassium-argon system is given by;

$$\theta_c > 18.24',$$

while for  $s=6$ , in the present experiments;

$$\theta < 5.65'.$$

Thus, if the deflection angles are smaller than this angle, the differential cross section,  $\sigma(\theta)$ , will be almost constant, independent of the  $\theta$  value. The total cross sections measured with an apparatus of a few minutes angular resolution,  $S(\gamma)$ , will be expected to be almost the same as  $Q$ .

### Experimental

**The Principle of the Measurements.** The absolute total cross section,  $Q$ , for atom-atom scattering can be measured by means of the beam-gas attenuation method. If a molecular beam passes through a scattering chamber (the density of a scattering gas,  $n$ ; the length of the chamber;  $L$ ), the attenuated intensity of the molecular beam will be given by;

$$I = I_0 \exp(-nQL), \quad (11)$$

where  $I_0$  is the intensity of the primary beam. Equation (11) is only correct for the ideal case in which a monoenergetic molecular beam passes through a static target gas. In these experiments, however, a beam with a Maxwellian velocity distribution was used, and the target gases were not stationary. Therefore, it is necessary to replace Eq. (11) by;

$$I = I_0 \exp(-n\bar{Q}_{eff}L). \quad (12)$$

The effective total cross section,  $\bar{Q}_{eff}$ , has been related to the absolute total cross section,  $\bar{Q}_0(v_{iw})$ , by Berkling *et al.*<sup>10)</sup>;

$$\bar{Q}_{eff} = Q_0(v_{iw})Ga_0(s, y), \quad (13)$$

where;

$$y = v_{iw}/v_{kw},$$

$$Ga_0(s, y) = \Gamma\left(\frac{2s-3}{s-1}\right)\left(1 + \frac{1}{y^2}\right)^{s-3/2(s-1)},$$

and;

$$Q(v_r) = Q_0(v_{iw})(v_{iw}/v_r)^{2/s-1}, \quad (14)$$

$$v_r = \frac{2}{\sqrt{\pi}}(v_{iw}^2 + v_{kw}^2)^{1/2},$$

$v_{iw}$  and  $v_{kw}$  are the most probable velocities of atoms in the beam source and the scattering chamber respectively. For  $s=6$  and  $s=\infty$ , the values of  $Ga_0$  can be obtained from the tables of Berkling *et al.*

**Apparatus.** Figure 1 shows a schematic diagram of the apparatus, which is divided into two chambers, the oven chamber and the detector chamber, in which the scattering chamber is placed. The typical operating pressure in the oven and detector chambers when a liquid nitrogen trap was used was about  $2 \times 10^{-6}$  Torr; even with the highest gas pressures introduced in the scattering chamber, no pressure rise was observed in the detector chamber.

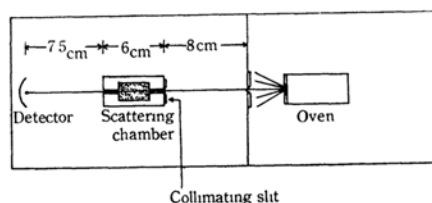


Fig. 1. Schematic diagram of the apparatus. The drawing is not to scale.

The potassium beam was effused from a single-chamber-type oven made of stainless steel. Thermal equilibrium in the oven was attained after two or three hours. The temperature was measured with a chromel-alumel thermo-couple. A cooled plate was placed between the oven slit and the collimating slit to remove surplus potassium atoms. The width of the collimating slit was 0.035 mm., and the height was 10 mm. In order to detect the beam, a tungsten filament (diameter; 0.035 mm, length; ca. 20 mm) was used as a Langmuir-Taylor surface ionization detector. The filament was heated by an electric current of about 230 mA d. c. and was biased by +68 V relative to the ion collector. The ion current was measured with a Takeda TR-84 vibrating-reed electrometer. The maximum ion current was about  $1 \times 10^{-9}$  A, which corresponds to a beam flux of  $6.25 \times 10^9$  atoms/sec.

The scattering chamber was of a type similar to that of Rothe *et al.*<sup>13)</sup> Its essential features are shown in Fig. 2. It has entrance and exit canals on both sides of the central volume, with a collimating slit at the end of the entrance canal. The estimation of the effective beam length in the chamber is very important because this length is inversely proportional to the absolute total cross section. By considering the gas conductances of the entrance and exit canals of the

10) R. B. Bernstein and K. H. Kramer, *J. Chem. Phys.*, **38**, 2507 (1963).

11) E. W. Kennard, "Kinetic Theory of Gases", McGraw Hill Book Company, Inc., New York (1938).

12) E. A. Mason, J. T. Vandersilce and C. J. G. Raw, *J. Chem. Phys.*, **46**, 2153 (1964).

13) E. W. Rothe, L. L. Marino, R. H. Neynaber, P. K. Rol and S. M. Trujillo, *Phys. Rev.*, **126**, 598 (1962).

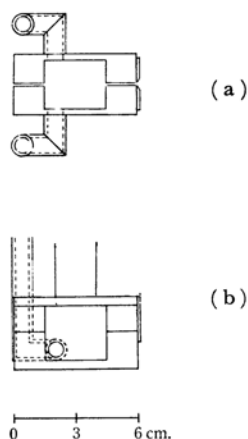


Fig. 2. Scattering chamber. (a), horizontal section of the chamber; (b), vertical section of the chamber.

scattering chamber, the following expression for the effective length was obtained;

$$L_{eff} = \frac{L_1}{2} \left( 1 + \frac{8Kab(a-c)}{8Ka^2b + 3(a+b)L_1c} \right) + L_2 + \frac{L_3}{2} \quad (15)$$

where  $L_1$  and  $L_3$  are the lengths of each canal (15 mm), and where  $L_2$  is the length of the central volume (30 mm). The quantity  $a$  is the width of each canal (0.5 mm), while  $b$  is the height (10 mm) and  $c$  is the width of the collimating slit (0.035 mm).  $K$  is the Clausing factor for the canals. The pressure outside the slit and the exit canal was assumed to be zero. Thus, an effective length of 4.91 cm was obtained from Eq. (15).

**The Measurement of Pressures.** The system used to introduce a gas into the scattering chamber is shown in Fig. 3. The stationary pressures in it were measured by an ionization gauge (Mitsubishi K-30). The emission currents of the gauge were precisely regulated to 1 or 0.1 mA by an emission regulator (Dan EMR-205), and the ion currents were read on a galvanometer (Yokogawa MPF-B,  $3 \mu A$ ). Then the gauge was calibrated against a standard McLeod gauge. In the present experiment the mercury drag effect was taken into consideration. The effect is caused by the streaming of mercury vapor from a McLeod gauge into a cold trap. The magnitude of the effect depends on the room temperature, the diffusion constant of the gas in mercury vapor, the radius of the connecting tube, and the pressure of the gas. Recently, Takaishi<sup>14</sup> has discussed the effect using a gas kinetic theory and has derived simple relations between these factors and the error in the measured pressure. In order to estimate this error the connecting tube between the McLeod gauge and the cold trap (at about  $-70^\circ C$ ) had a by-pass made of a small diameter tube (diameter, ca. 4 mm, length, ca. 150 mm), as is shown in Fig. 3. The pressure was measured through the by-pass by closing the main tube with a greaseless cock; it was also measured with both tubes

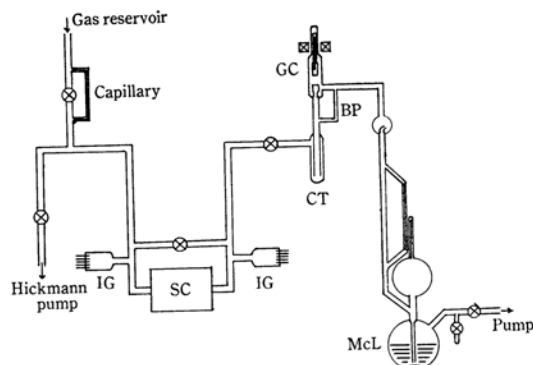


Fig. 3. Schematic diagram of the apparatus for introducing a gas into the scattering chamber and for measuring the absolute pressure in it. (SC), scattering chamber; (IG), ionization gauge; (CT), cold trap; (GC), greaseless cock; (BP), by-pass; (McL), McLeod gauge.

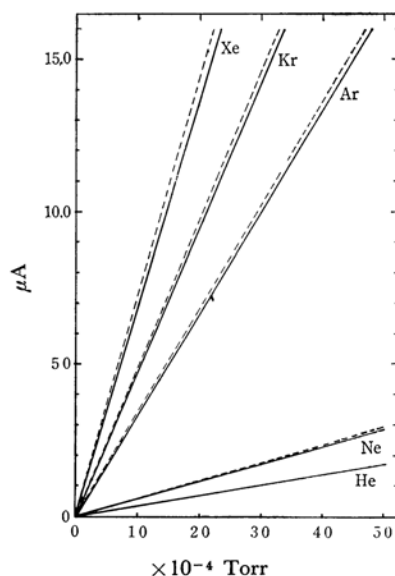


Fig. 4. Calibration curves for the ionization gauge. Ion currents in the ionization gauge (for an emission current of 1 mA) were plotted against absolute pressures measured with a McLeod gauge. Solid curves; measured through the by-pass; dashed curves; measured through both the tubes.

opened. A comparison of the pressures gives the mercury drag effect. An appreciable effect was observed for argon, krypton, and xenon, but for a lighter gas, such as helium and neon, the effect was very small or negligible, as was expected from theoretical considerations. The true pressures will be a little higher than those corresponding to the solid curves shown in Fig. 4. However, the largest error expected from Takaishi's theory would be less than 7% for xenon.

**Materials.**—The potassium was vacuum-distilled; the rare gases were more than 99% pure.

14) T. Takaishi, *Trans. Faraday Soc.*, **61**, 840 (1965).

TABLE 1. SUMMARY OF RESULTS

Gas	Temp. of gas	Temp. of beam source	$v_{iw}$	$\bar{Q}_{eff}$	$\bar{Q}_0(v_{iw})$	$\times 10^{-58} C_{SLL} \text{ erg cm}^6$	$\times 10^{-58} C_{MM} \text{ erg cm}^6$
He	19°C	134°C	423 m	361 Å <sup>2</sup>	205 Å <sup>2</sup>	0.145	0.172
	21	154	434	361	207	0.152	0.180
	20	182	447	342	199	0.142	0.167
					average	0.146	0.173
Ne	19	134	423	290	240	0.229	0.271
	17	193	452	292	248	0.248	0.294
	21	159	436	298	248	0.240	0.285
					average	0.239	0.283
Ar	19	135	424	635	581	1.95	2.31
	19	135	424	608	556	1.75	2.08
	17	192	452	607	562	1.92	2.28
					average	1.87	2.22
Kr	20	170	441	682	676	2.97	3.52
	20	203	458	647	646	2.75	3.26
	17	166	439	657	653	2.72	3.22
					average	2.81	3.33
Xe	17	165	439	765	780	4.33	5.14
	17	166	439	752	766	4.04	4.80
	20	179	446	751	766	4.10	4.86
					average	4.16	4.93

### Results

Figure 5 shows typical beam profiles obtained in the present work. Curve A corresponds to a "vacuum beam," and curve B, to a "scattered beam" attenuated by argon. At the detector, the half-width at the half intensity of the unscattered beam was 0.08 mm. According to the Kusch criterion,<sup>15)</sup> the angular resolution of the apparatus is estimated to be 2.62' of arc. Therefore we can treat the total cross sections, which are almost equal to  $Q$ , by means of the quantum theory.

A typical attenuation curve of a potassium beam scattered by xenon gas is shown in Fig. 6. In general, the beam intensity,  $I$ , was measured for about 7 to 13 values of the scattering gas pressure; a fairly straight line was obtained in each case. The results are listed in Table 1. Van der Waals constant,  $C$ , were calculated by Eq. (3).  $C_{SLL}$  represents the value calculated by the SLL approximation, and  $C_{MM}$ , that calculated by the MM approximation. These values were smaller than the previous experimental values and smaller than recent theoretically-calculated values. However, the values obtained by the MM approximation were rather close to the theoretical values for argon, krypton and xenon.

**Sources of Experimental Error.** There are three possible sources of error in the present work; 1) the calculation of the effective length of the

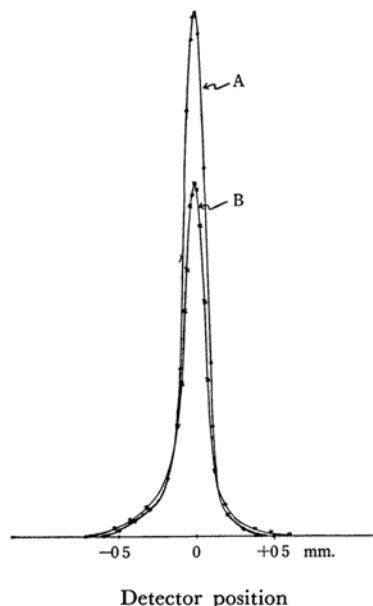


Fig. 5. Typical beam profiles. Curve A; vacuum beam; curve B, scattered beam by argon (pressure,  $6.4 \times 10^{-5}$  Torr).

scattering chamber; 2) the measurement of the pressure with the McLeod and ionization gauges, and 3) the measurement of the beam intensity. The effective length of the scattering chamber was the most uncertain value in the present work, because the apparatus has not an ideal structure for calculating the gas conductance. We are now

15) P. Kusch, *J. Chem. Phys.*, **40**, 1 (1964).

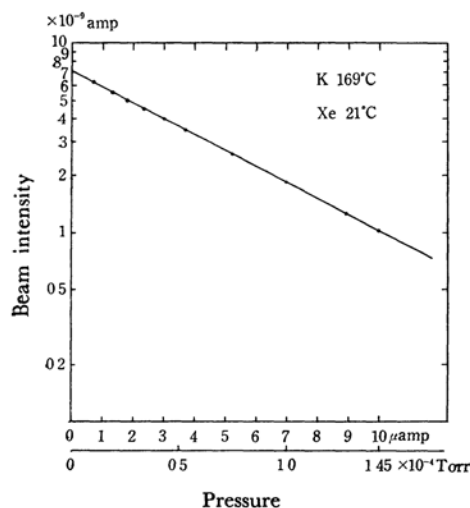


Fig. 6. The attenuated beam intensity versus the pressure of the scattering gas.

preparing a new scattering chamber with a variable length in order to avoid this source of error. The problems of pressure measurement have been discussed previously. In the present work the gases were kept at room temperature in order to avoid a possible error due to the thermal transpiration effect. Therefore, it is considered that correct pressures were obtained except for xenon, which still showed some mercury drag effect even with the smaller tube. During a run with different scattering gas pressures, the primary beam intensity should be constant, and the background of the beam must be small and stable. These conditions could be obtained by using liquid nitrogen traps in the present experiments.

### Discussion

The van der Waals constant,  $C$ , for the dispersion energy is related to the polarizabilities of each atom in the following way.

London<sup>16)</sup> used second-order perturbation theory to derive the expression;

$$C = \frac{3}{2} \frac{\Delta_1 \Delta_2}{\Delta_1 + \Delta_2} \alpha_1 \alpha_2 \quad (16)$$

Where  $\alpha$  is the static atomic polarizability and  $\Delta$  is an average excitation energy. The subscripts refer to the different atoms. The  $\Delta$  quantities are often set equal to the ionization energies of the atoms. Slater and Kirkwood<sup>17)</sup> have obtained a different expression for  $C$  by using a variation theory;

$$C = \frac{3e\hbar}{2m_e^{1/2}} \frac{\alpha_1 \alpha_2}{\left[ \left( \frac{\alpha_1}{N_1} \right)^{1/2} + \left( \frac{\alpha_2}{N_2} \right)^{1/2} \right]}, \quad (17)$$

where  $N$  is the number of outer shell electrons and where  $e$  and  $m_e$  are the electronic mass and the charge respectively. Recently, Mavroyannis and Stephen,<sup>18)</sup> and Salem<sup>19)</sup> have pointed out that the total number of electrons in the atom should be used for  $N_1$  and  $N_2$ . Dalgarno and Kingston<sup>20)</sup> calculated the van der Waals constants for the alkali metal - rare gas system. For these cases they used the approximate formula below, in which the assumption  $|\varepsilon_0^{(2)} - \varepsilon_n^{(2)}| \ll |\varepsilon_0^{(1)} - \varepsilon_n^{(1)}|$  was made;

$$C = \frac{3}{4} \alpha_1 \sum_n' \frac{f_n^{(2)}}{\varepsilon_0^{(2)} - \varepsilon_n^{(2)}} \quad (18)$$

where  $\varepsilon_0^{(2)}$  and  $\varepsilon_n^{(2)}$  are, respectively, the energies of a ground and  $n$ 'th excited state of an alkali atom, and  $f_n^{(2)}$  is an electric dipole oscillator strength between the ground state and the  $n$ 'th excited state.  $\varepsilon_0^{(1)}$  and  $\varepsilon_n^{(1)}$  are similar quantities of a rare gas atom, and  $n_1$  is the polarizability. Here, they used the theoretical values of the polarizabilities of the alkali metals, which were obtained from the oscillator strengths. In Fig. 7 the Dalgarno-Kingston values and the present experimental values are plotted against the polarizabilities of the rare gases. It is clear that the curve

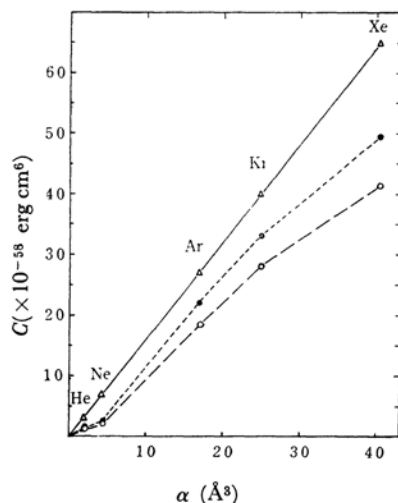


Fig. 7. Observed and calculated van der Waals constants versus the polarizabilities of rare gases.  $\triangle$ , calculated constants (Dalgarno and Kingston 1959);  $\circ$ ; experimental points calculated by SLL approximation;  $\bullet$ , experimental points calculated by MM approximation.

18) C. Mavroyannis and M. J. Stephen, *Mol. Phys.*, **5**, 629 (1962).

19) L. Salem, *ibid.*, **3**, 441 (1960).

20) A. Dalgarno and A. E. Kingston, *Proc. Phys. Soc.*, **73**, 455 (1959).

16) F. London, *Z. Physik Chem. (Leipzig)*, **B11**, 222 (1930); H. Margenau, *Rev. Mod. Phys.*, **11**, 1 (1939).

17) J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37**, 682 (1931).

TABLE 2. CALCULATED AND EXPERIMENTAL VAN DER WAALS CONSTANTS ( $10^{60}$ erg cm<sup>6</sup>)

Gas	London		Slater & Kirkwood $N \triangleq$ no. of outer shell electrons		Slater & Kirkwood $N \triangleq$ total no. of electrons		Dalgarno & Kingston	Present work		Previous experiments	
	a	b	a	b	a	b		$C_{SLL}$	$C_{MM}$	Rothe <i>et al.</i>	Others
He	62.5 (0.14)	83.7 (0.14)	28.7 (0.13)	33.4 (0.13)	99 (0.12)	126 (0.13)	31.4 (0.12)	16.6 (0.078)	17.3 (0.078)	53 (0.09)	40 <sup>21)</sup>
Ne	120 (0.27)	161 (0.27)	57.7 (0.26)	67.1 (0.25)	208 (0.26)	265 (0.27)	65 (0.24)	23.9 (0.13)	28.3 (0.13)	69 (0.11)	
Ar	453 (1.00)	609 (1.00)	223 (1.00)	265 (1.00)	797 (1.00)	1030 (1.00)	267 (1.00)	187 (1.00)	222 (1.00)	600 (1.00)	410 <sup>2)</sup> 300 $\pm$ 50 <sup>22)</sup>
Kr	672 (1.48)	906 (1.48)	333 (1.49)	384 (1.45)	1230 (1.54)	1570 (1.59)	400 (1.5)	281 (1.50)	333 (1.50)	990 (1.6)	550 <sup>23)</sup>
Xe	1040 (2.30)	1405 (2.30)	529 (2.36)	620 (2.34)	2000 (2.50)	2550 (2.59)	648 (2.4)	416 (2.22)	493 (2.22)	1360 (2.2)	1070 <sup>23)</sup> 740 <sup>24)</sup>

a) The value of  $46.0 \text{ \AA}^3$  was used for the polarizability of potassium atom, which was obtained from Stark effect measurement.

b) The value of  $34.1 \text{ \AA}^3$  was used for the the polarizability of potassium atom, which was obtained from molecular beam method.

of the experimental values is not linear, as was expected from Eq. (18). However, the relative experimental values referred to the potassium-argon interaction constant are in fair agreement with the results of Rothe *et al.*<sup>2)</sup> (Table 2). This fact suggests that some systematic errors exist between the theory and the experiment.

The discrepancies for helium and neon are particularly large. In these cases perhaps the repulsive terms in the intermolecular forces partially weaken the attractive dispersion forces, so that Eq. (1) cannot be applied.

The plotted curve of the measured values deviates downward from a straight line for xenon; this may be expected from London's formula. However, the London approximation gives values of  $C$

which are too large. On the other hand, the values calculated from the Slater-Kirkwood formula are fairly close to the present values, while the modification by Mavroyannis *et al.*<sup>18)</sup> makes the situation worse.

The authors wishes to thank Professor Kumasaburo Koderu and Professor Isadore Amdur for their valuable advice and guidance on the experiment. The valuable assistance of Mr. Akira Doi during the course of the experiment is also acknowledged. The author is grateful for financial support from The Sakkokai Foundation. It is a pleasure to acknowledge the advice of Dr. Katsuya Nakayama on the pressure measurements.

21) R. Helbing and H. Pauly, "Advances in Atomic and Molecular Physics," Vol. I, Academic Press, Inc., New York (1965), p. 195.

22) E. W. Rothe and R. H. Neynaber, *J. Chem. Phys.*, **42**, 4178 (1965).

23) E. W. Rothe and R. H. Neynaber, *ibid.*, **42**, 3306 (1965).

24) H. Florin, "Advances in Atomic and Molecular Physics," Vol. I, Academic Press, Inc., New York (1965), p. 195.