Simple Relations between Scattering Cross Sections and Molecular Diameters

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Empirical linear relations between the square roots of the electron-scattering cross sections for molecules and the cube roots of the van der Waals volumes for molecules due to Bondi are shown. The relations allow one to estimate, for example, the electron-impact ionization cross sections at 75 eV to within an error of ±15%. A dimensional analytic explanation of the relations is given.

It is a natural idea that the scattering cross section for a given collision process strongly depends on the size of the target. For example, in the case of electron collisions with molecules, Schmieder1) has shown that there is a positive correlation between the molecular size and the collision probability P_c (*i.e.*, the number of collisions, per unit electron flux, per unit path length, per unit pressure at 0 °C). However, since the method for the evaluation of the size of the molecule was not systematic, it has not been possible to render this idea quantitative. Recently, Christophorou *et al.*2) have shown that the cross section for the scattering of thermal electrons by normal alkanes is proportional to the mean square end-to-end distance, although the method for evaluating of the molecular size cannot be extended to molecules other than normal alkanes.

In this paper, it is shown that the following relation holds for several scattering processes involving molecules of molecular liquids:

$$\sigma^{1/2} = Av^{1/3} + B,$$

where σ is the scattering cross section, v the van der Waals volume of the molecule,3) and A and B are numerical constants independent of the target molecule. Since the van der Waals volume is a good measure of the molecular size, this linear relation is a quantitative version of the natural idea mentioned above. There exist other measures of the molecular size, but the van der Waals volume is convenient for small molecules. For large molecules (or molecules with melting points higher than 150 K), the method of evaluation using the effective hard-core size of the molecule, proposed by one of the present authors,4) can also be successfully used.

By using an empirical linear relation, rough estimations of the cross sections are possible. Such a relation reminds one of the Hammett rule, since the coefficients of the linear relation are independent of the target molecule and dependent only on the nature of process (or reaction).

A brief dimensional analytic account of the empirical relation will be given.

Empirical Relations

The van der Waals volumes for molecules, v, are calculated using the tables of Bondi.3) Van der Waals volumes for rare gas atoms and hydrogen chloride are calculated from their critical volumes, V_c, using the crude relation, $v \simeq 0.18\ V_c$.

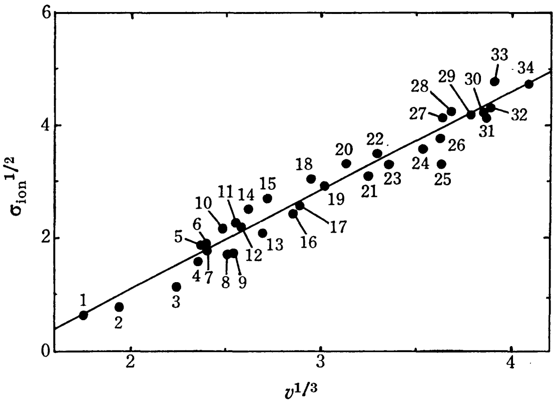

Fig. 1. The square root of the electron impact (75 eV) ionization cross section σ_{ion} (in Å^2)5) *vs.* the cubic root of the van der Waals volume v (in cm^3/mol). The line denotes Eq. 1.
1: Helium, 2: neon, 3: hydrogen, 4: oxygen, 5: argon, 6: ammonia, 7: nitrogen oxide, 8: nitrogen, 9: carbon monoxide, 10: hydrogen chloride, 11: krypton, 12: methane, 13: carbon dioxide, 14: hydrogen sulfide, 15: xenon, 16: acetylene, 17: ethylene, 18: chloromethane, 19: ethane, 20: cyclopropane, 21: propene, 22: chloroethane, 23: propane, 24: isobutylene, 25: isobutane, 26: butane, 27: benzene, 28: cyclopentane, 29: isopentene (probably a mixture), 30: isopentene, 31: neopentane, 32: pentane, 33: cyclohexane, 34: hexane.

The relation between the ionization cross sections for 75-eV electrons σ_{ion}5) and v is shown in Fig. 1. From Fig. 1 we get

$$\sigma_{ion}^{1/2} = 1.73v^{1/3} - 2.37, \tag{1}$$

where σ_{ion} is in Å^2 and v in cm^3/mol. Using Eq. 1, we can estimate σ_{ion}. The accuracy of the estimate is about ±15%, except for krypton, xenon, isobutane, and cyclohexane.

The linear relations between $P_c^{1/2}$ and $v^{1/3}$ for electron energies, E, of 49 and 25 eV are shown in Fig. 2. Even for E=4 eV this linear relation holds (Fig. 3). For 50 eV$\gtrsim E \gtrsim$15 eV these linear relations can be summarized as

$$P_c^{1/2} \simeq (5.56 - 0.22E^{1/2})(v^{1/3} - 1.0).$$

The linear relation between $P_c^{1/2}$ and $v^{1/3}$ also holds for much larger values of E, because the Born approximation is rather accurate for large E. However, the linear relation between $P_c^{1/2}$ and E$^{1/2}$ is crude and, for too large E, this linear relation ceases to hold.

For the case of monoatomic elements, it is known6) that P_c is inversely proportional to the ionization

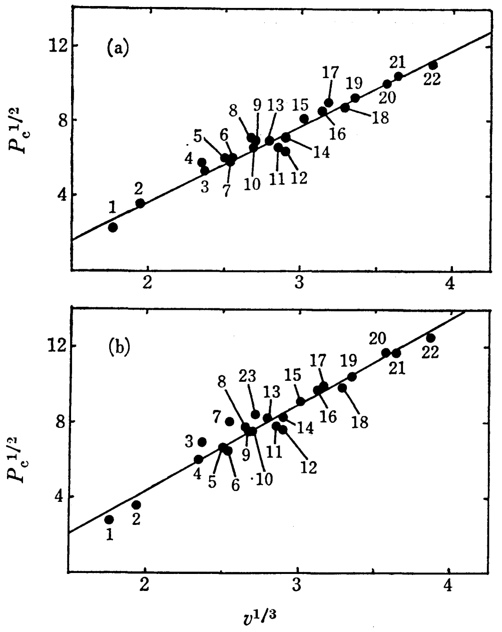

Fig. 2. The square root of the probability of collision P_c (in cm^2/cm^3 Torr)[1,6] *vs.* the cubic root of the van der Waals volume v (in cm^3/mol). (a) is for the electron energy 49 eV, and (b) for 25 eV. The line in (a) denotes $P_c^{1/2}=4.02v^{1/3}-4.31$ and that in (b) $P_c^{1/2}=4.26v^{1/3}-4.49$.

1: Helium, 2: neon, 3: argon, 4: oxygen, 5: nitrogen, 6: krypton, 7: carbon monoxide, 8: dinitrogen oxide, 9: carbon dioxide, 10: fluoromethane, 11: acetylene, 12: hydrogen chloride, 13: methanol, 14: methylamine, 15: ethane, 16: dimethyl ether, 17: ethanol, 18: dimethylamine, 19: propane, 20: trimethylamine, 21: isobutane, 22: pentane, 23: xenon.

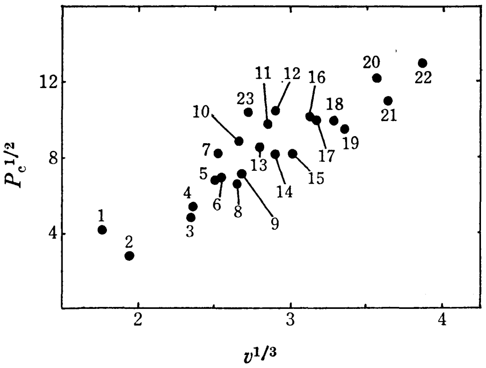

Fig. 3. The square root of the probability of collision P_c (in cm^2/cm^3 Torr) of electron[1,6] *vs.* the cubic root of the van der Waals volume v (in cm^3/mol) at electron energy 4 eV. The numbers in the figure are the same as in Fig. 2.

potential, I. Although there is some correlation between the ionization potential and σ_{ion}^{-1} or P_c^{-1}, no clear relation similar to that shown above exists between them. According to Morrison (cited in Ref. 3) the van der Waals radii of atoms are proportional to $I^{-1/2}$, but this relation does not hold as accurately as the empirical relations proposed here. Lampe *et al.*[5] have shown that σ_{ion} is proportional to the polarizability, α. It is also

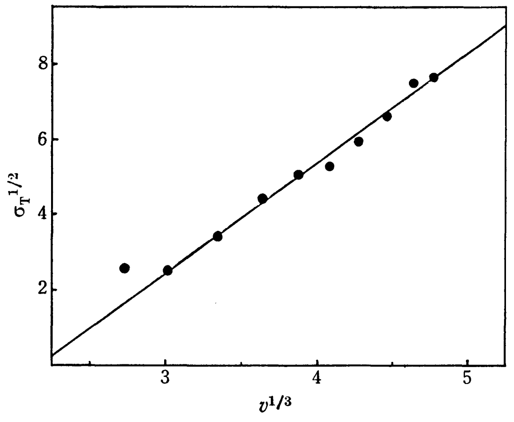

Fig. 4. The square root of the scattering cross section of thermal electrons with normal alkanes (methane to decane from left to right) σ_T (in Å^2)[2] *vs.* the cubic root of the van der Waals volume v (in cm^3/mol). The line denotes Eq. 2.

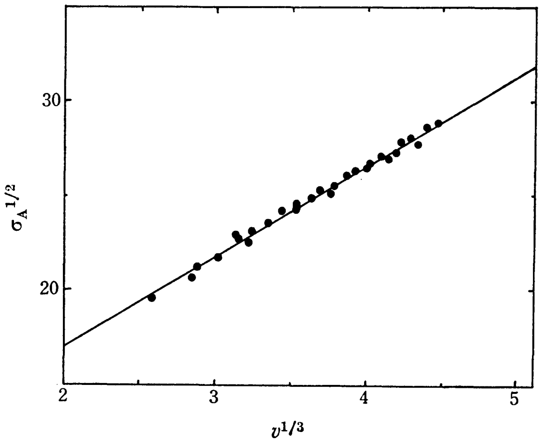

Fig. 5. The square root of the scattering cross section of thermal argon with hydrocarbons σ_A (in Å^2)[8] *vs.* the cubic root of the van der Waals volume v (in cm^3/mol). The line denotes Eq. 3.

known that P_c is proportional to α. However, it appears to be very difficult to explain these proportionalities. The explanation of Lampe *et al.* is based on the Born-approximation expression[7] of the cross sections, so that it is not conclusive.

The relation between the total cross section σ_T for the scattering of thermal electrons by normal alkanes[2] and v is shown in Fig. 4. The relation between the total cross section σ_A for the scattering of thermal argon atoms by hydrocarbons[8] and v is shown in Fig. 5. The empirical linear relations are as follows:

$$\sigma_T^{1/2} = 2.91v^{1/3} - 6.32 \tag{2}$$

and

$$\sigma_A^{1/2} = 4.79v^{1/3} + 7.38, \tag{3}$$

where σ_T and σ_A are in Å^2. For these very low-energy processes, the linear relations are valid only in a restricted group of compounds (*e.g.*, hydrocarbons), and hence are not very interesting, since we are interested in properties not strongly dependent on the electronic structure of the molecules.

Discussion

For higher-energy processes the Born approximation is valid, which suggests[7] that the cross sections are proportional to the geometrical cross sections of the target molecules. However, for lower-energy processes (for example, processes involving electrons having kinetic energy less than 100 eV), the Born approximation is not reliable. The theoretical calculation of the scattering cross sections for low-energy processes is very complicated. Thus, the derivation of the empirical relations above from scattering theory may be very difficult.

However, physical insight may be obtained from a dimensional analysis. All the relations obtained above are linear ones between $v^{1/3}+r_0$ and $\sigma^{1/2}$, where σ is the scattering cross section and r_0 is some constant. This suggests that the measure of the molecular diameter for collisional processes is not $v^{1/3}$, but $v^{1/3}+r_0$. The constant r_0 is considered, for example, to represent the Ramsauer-Townsend effect. Further considerations of r_0 are given below. Other relevant quantities with the dimension of length are σ, and the de Broglie wavelength of the projectile, λ. Hence we conclude that

$$\sigma^{1/2} = (v^{1/3}+r_0)f((v^{1/3}+r_0)/\lambda), \qquad (4)$$

where f is an appropriate function. In the high-energy limit, the scattering processes can be treated classically, so that $\lim_{\lambda\to 0} f((v^{1/3}+r_0)/\lambda)$ must be a finite constant. Therefore, for higher-energy scattering processes, f depends only slightly on $v^{1/3}+r_0$ and the empirical linear relation shown is obtained. As is seen in Figs. 1—5, r_0 is negative for σ_{ion}, P_c, and σ_T and is positive for σ_A. For the total cross sections for the scattering of positrons σ_P by rare gas atoms,[9] r_0 is also negative. Thus, we may concluded that r_0 is negative for charged particle scattering and positive for neutral particle scattering. For σ_T and σ_P, the negative r_0 can be explained by the Ramsauer-Townsend effect.[9] For impact ionization, an electron must strongly interact with the electron cloud of the target molecule, so that the length scale governing the cross section is not $v^{1/3}$ itself but the diameter of the electron cloud. Thus, the r_0 for σ_{ion} can be considered to represent the difference between the van der Waals diameter and the diameter of the electron cloud. For σ_{ion}, r_0 is *ca.* 1.8 Å and is about the twice the difference between the van der Waals radius and the covalent bond radius of Pauling. This may be a correct interpretation of r_0 for electron-impact ionization processes.

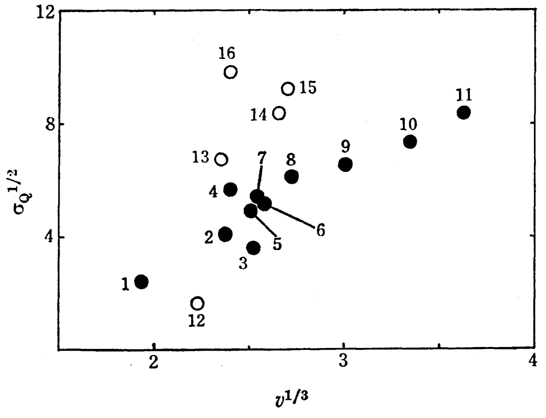

Fig. 6. The square root of the quenching cross section of He (2^1S) σ_Q (in Å^2)[10] *vs.* the cubic root of the van der Waals volume v (in cm^3/mol). ● Roughly satisfy a linear relation between $\sigma_Q^{1/2}$ and $v^{1/3}$, but ○ significantly deviate from this relation.
1: Neon, 2: argon, 3: nitrogen, 4: nitrogen oxide, 5: carbon monoxide, 6: methane, 7: krypton, 8: xenon, 9: ethane, 10: propane, 11: butane, 12: hydrogen, 13: oxygen, 14: dinitrogen oxide, 15: carbon dioxide, 16: ammonia.

The square root of the (scattering) cross section *vs.* $v^{1/3}$ plot may be used to extract the specificity of molecules, since it has been implicitly assumed in deriving Eq. 4 that the electronic structure of the target molecules is relevant only through the van der Waals diameter. For example, the quenching cross sections of He (2^1S) by atoms and molecules[10] are shown in Fig. 6. From this, it may be concluded that ammonia, carbon dioxide, dinitrogen oxide, oxygen, and hydrogen have chemically specific properties in this reaction.

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