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Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the first of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($4.00 per page) will not be made and no reprints will be furnished free.

A Comparison of the Ionization Cross Sections of H₂ and D₂

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$\mathbf{W}$E wish to correct an impression given in the opening sentences of a recent note by R. E. Honig[1] on "A comparison of the ionization cross sections of H_2 and D_2" which referred to our note on "Differences in mass spectra of H_2 and D_2."[2] We did not report a significant difference between the sensitivities for H_2^+ and D_2^+. Rather the difference observed (about 10 percent) was interpreted as being within the probable limit of mass spectrometer discrimination for the two masses. The difference observed (presumably caused by discrimination) was reported as about 10 percent—not 10 to 40 percent. Our note was not concerned with the question of correcting sensitivities by $M^{\frac{1}{2}}$, and the data were not obtained or discussed with that question in view.

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[1] Richard E. Honig, J. Chem. Phys. 16, 837 (1948).
[2] Norman Bauer and J. Y. Beach, J. Chem. Phys. 15, 150 (1947).

Calculation of Transport Properties of Gases

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$\mathbf{H}$IRSCHFELDER, Bird, and Spotz[1] have recently reported a method for calculating transport properties of non-polar gases which leads to excellent correlation of experimental results. Since they did not compare their procedure with that previously used by Amdur[2] in calculating low temperature transport properties of the rare gases, it seems desirable to point out briefly the similarities and differences in the two approaches. The discussion will be limited to viscosity and self-diffusion, which should suffice to illustrate the major steps in the two treatments.

The classical, velocity dependent cross section for viscosity and thermal conductivity, $S_{\eta,K}$, may be defined as

$$S_{\eta,K} = 2\pi \int_0^\pi G(\theta) \sin^3\theta d\theta, \tag{1}$$

and the classical, velocity dependent cross section for self-diffusion, $S_{D(1,1)}$, as

$$S_{D(1,1)} = 2\pi \int_0^\pi G(\theta) \sin^2\frac{\theta}{2} \sin\theta d\theta, \tag{2}$$

where $G(\theta)$ is the solid angle scattering coefficient, and θ, the angle through which the direction of the relative initial velocity, v, of two colliding particles is turned by a collision. $G(\theta)$ may be defined by the statement that $2\pi N G(\theta) \sin\theta d\theta$ is the number of atoms deflected per second between θ and $\theta + d\theta$ from a stream of N atoms per unit area per second impinging upon a single scattering atom. The scattering angle, θ, may be calculated from classical treatment of the two-body collision problem if the potential energy of interaction as a function of distance is known, and, for a given value of the initial relative velocity, $G(\theta)$ may be evaluated from the known dependence of θ on r_0, the distance of closest approach of the two particles.[3]

The method of Hirschfelder, Bird, and Spotz consists, in effect, of evaluating functions such as $S_{\eta,K}$ and $S_{D(1,1)}$ from fundamental relations such as Eqs. (1) or (2). (They actually calculated reduced cross sections which are the ratios of velocity dependent cross sections to the hard sphere cross section, πr_0^2, which is independent of velocity.) Their method is direct and should give excellent results within the limitations imposed by their choice of a single analytical form for the interaction potential of all the non-polar gases which they consider, and by the validity of classical mechanics in treating the transport phenomena.

Amdur used an indirect approach in calculating $S_{\eta,K}$ and $S_{D(1,1)}$ by assuming that, at any given value of v, the *ratio* of these cross sections to the classical total collision cross section, S, is the same for a real gas as for a gas of hard spheres. In the latter case, $G(\theta) = r_0^2/4$, and since

$$S = 2\pi \int_0^\pi G(\theta) \sin\theta d\theta, \tag{3}$$

the desired ratios are $S_{\eta,K}/S = \frac{2}{3}$ and $S_{D(1,1)}/S = \frac{1}{2}$. For real gases, S, as calculated from Eq. (3), is infinite if $G(\theta)$ is calculated from classical mechanics which does not allow for the diffraction effects which predominate at sufficiently small angles of scattering. Massey and Mohr[4] have shown, however, that classical mechanics may be used to calculate proper classical values of S by limiting the integration in Eq. (3) to angles greater than the "critical scattering angle, θ_c." This angle, above which diffraction effects are negligible, is equal to $\lambda/(2r_0)$ where λ is the deBroglie wavelength of the colliding system. Amdur's method reduces to calculation of total classical collision cross sections for real gases from

$$S = 2\pi \int_{\theta_c}^\pi G(\theta) \sin\theta d\theta \tag{4}$$

on the basis of classical two-body collision theory, and use of the hard sphere ratios of $\frac{2}{3}$ and $\frac{1}{2}$ to obtain values of $S_{\eta,K}$ and $S_{D(1,1)}$ appropriate to the real gas.

The manner in which values of the velocity dependent cross sections are used to obtain actual transport properties does not differ in the two approaches. Both methods calculate transport cross sections which are functions of *temperature* by averaging over the Maxwellian distribution of ve-

locities, and then substitute these temperature dependent cross sections into the classical transport equations of Chapman[5] and Enskog.[6]

One would not expect Amdur's indirect approach to be capable of the same accuracy as that of Hirschfelder, Bird, and Spotz. The method does seem, however, to permit greater flexibility in the choice of forms for the potential energy function and does not require numerical integrations. The good agreement between calculated and experimental values for the transport properties of the five rare gases (for example, for viscosities in the range 14°–550°K the average absolute deviation is 4.8 percent) would appear to justify the assumptions used to obtain quantities such as $S_{\eta, K}$ and $S_{D(1, 1)}$ as functions of v. This seems particularly likely since care was taken to use potential energy functions whose constants were not evaluated from experimental values of the transport properties which were being calculated.

[1] J. O. Hirschfelder, R. G. Bird, and E. L. Spotz, J. Chem. Phys. 16, 968 (1948).
[2] I. Amdur. J. Chem. Phys. 15, 482 (1947); 16, 190 (1948).
[3] E. H. Kennard, Kinetic Theory of Gases (McGraw-Hill Book Company, Inc., New York, 1938), Chapter III.
[4] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. A141, 434 (1933).
[5] S. Chapman, Phil. Trans. Roy. Soc. A211, 433 (1912); A216, 279 (1915); A217, 115 (1917).
[6] D. Enskog, Kinetische Theorie der Vorgange in massig verdunnten Gasen, (Inaug. Diss., Upsala, 1917).

The Transport Properties of Non-Polar Gases

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IN the October issue of this Journal, Hirschfelder, Bird, and Spotz[1] (HBS) have published extensive tables for calculating the viscosity and thermal conductivity of gases whose molecules have a van der Waal's interaction potential of the form $E(r) = Ar^{-12} - Br^{-6}$. Their tables now enable such data to be analyzed with almost the same precision as has been applied to second virial coefficient data since 1924. The purpose of this note is to report an independent and almost simultaneous investigation of the same problem which, although different approximation methods were used, confirms the results of these authors.

The dynamics of an encounter were treated by a method similar to that of Burnett.[2] His treatment could not be followed exactly as some of his substitutions are valid for repulsive force-fields only. χ, the angle of deflection, was computed as a function of two variables α and q. In the notation of HBS, α is given by

$$\alpha = 1 + (1 + K)^{\frac{1}{2}} \quad \text{(cf. HBS Eq. (43))},$$

where K is the ratio of the relative kinetic energy to the maximum energy of interaction. q is a measure of $1/b$, where b would be the distance of closest approach if $E(r)$ were everywhere zero, and is given by

$$y_m = q(\alpha/2)^{1/6}.$$

For head-on collisions, $q = 1$, and when molecules pass at infinite distance $q = 0$. For each value of α and q, χ was computed by Gauss' method of approximate quadrature,

using 6 ordinates. To avoid the complications of incipient "orbiting," the viscosity was only found for $kT/\epsilon \geqslant 0.5$ (HBS $kT/\epsilon \geqslant 0.3$). The largest value of χ was 475°. A function of $\sin^2 \chi$, denoted by J (as in Eq. (6) of Burnett and corresponding to $S^{(1)}(K)$ of Eq. (53) of HBS) was then found by integration by Gauss' method, using 5 ordinates in each of the following ranges of q, 1.00–0.95, 0.95–0.90, 0.90–0.40, and 3 ordinates in the range 0.40–0.00. Finally the J terms were summed by the most accurate of Burnett's formulae (4-terms). Empirical formulae were used to give J as $f(\alpha)$ and interpolation was used at many of the temperatures. It is readily seen that $\frac{1}{2}\Sigma n_s J_s$ should be identical with $W^2(2)$ of HBS. The two are compared in Table I.

kT/ϵ	0.5	0.6	0.7	0.8	0.9	1.0	1.2	1.4	1.6
$\frac{1}{2}\Sigma n_s J_s$	2.300	2.085	1.916	1.773	1.651	1.554	1.410	1.312	1.241
$W^2(2)$	2.257	2.065	1.908	1.780	1.675	1.587	1.452	1.353	1.279

kT/ϵ	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.5	4.0
$\frac{1}{2}\Sigma n_s J_s$	1.190	1.105	1.118	1.083	1.064	1.042	1.022	0.9864	0.9547
$W^2(2)$	1.221	1.175	1.138	1.107	1.081	1.058	1.039	0.9999	0.9700

kT/ϵ	4.5	5.0	5.5	6.0	7.0	8.0	9.0	10.0
$\frac{1}{2}\Sigma n_s J_s$	0.9403	0.9262	0.9074	0.8950	0.8740	0.8562	0.8406	0.8265
$W^2(2)$	0.9464	0.9269	—	0.8963	0.8727	0.8538	0.8379	0.8242

The viscosity may be calculated from either of these functions by using Eq. (7) of HBS. No attempt was made to compute the small correction factor V, as $(V - 1/V)$ is less than the probable error in $W^2(2)$.

In view of the length and complexity of these calculations, and the different methods used in each laboratory, the agreement is very satisfactory. The differences are small and irregular, and are almost certainly due to inaccuracy in the interpolation formulae used in this work and to the use of methods which were essential in a single-handed computation.

[1] J. O. Hirschfelder, R. B. Bird, and E. L. Spotz, J. Chem. Phys. 16, 968 (1948).
[2] D. Burnett, Proc. Camb. Phil. Soc. 33, 363 (1937).

Effect of Temperature on Mass Spectra

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IN a recent communication with a title similar to that of the present one, Fox and Hipple[1] describe the effect of temperature on the mass spectrum of isobutane. It is the object of this note to indicate the nature and origin of their observations.

An increase of temperature has two observable effects on the mass spectra of the substances thus far studied. These are:

1. The specific intensity of all ions decrease with increasing temperature.

2. The specific intensities of the "parent ion" decrease more rapidly with temperature than do the specific intensities of fragmentary ions, and within the accessible temperature range (75–350°C) this effect is more pro-