Letters to the Editor

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The Influence of Binary Collisions on Molecular Gas Flow

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BINARY collisions occurring in a molecular gas flow (mean free path $\lambda \gg d$, d being the diameter or other characteristic dimension of cross section) cause a deviation from the limiting value of ideal free-molecule flow ($\lambda \rightarrow \infty$). The conductance or specific flow F (gas flow per unit difference of pressure) is therefore a function of the mean pressure $\bar{p}$, depending on the geometrical form of the flow resistance. Pollard and Present[1] have deduced an approximate function $F(\bar{p})$ for the case of a very long capillary tube. They employ a rigorous mathematical method but make use of the assumption that by mutual collisions the molecules are scattered isotropically, thus neglecting the "persistence of molecular velocities" (Jeans). A simple correction for persistence as in the case of the elementary treatment of gaseous self-diffusion is not possible here, because the distribution of molecule path directions in the flow resistance and its change by the collisions must be considered.

If the pressure drop $p_1 - p_2$ along the flow resistance is small relative to $\bar{p}$, one can reduce the kinetics of relatively rare binary collisions to the problem of single scattering of molecules in a gas with Maxwell velocity distribution. Recently we have deduced[2] an approximate distribution function of the directions of scattering, assuming the molecules to be rigid elastic spheres. Consistent insertion of this scattering distribution into the integral of Pollard and Present would lead to great mathematical difficulties; but by using graphical methods we have found approximate solutions of first order in d/λ, representing the pressure variation of molecular conductance for the most important flow resistances. The relations agree with experimental results.

For a long circular tube of radius a we find for the ratio between its conductance F and the limiting value F_0 (corresponding to $\bar{p} \rightarrow 0$, $\lambda \rightarrow \infty$):

$$F/F_0 = 1 - 0.75(a/\lambda)\ln(\lambda/3.56a). \tag{1}$$

By this equation F_0 can be calculated from experimental results at small pressures. From the best observations of Knudsen and Gaede on the conductance of capillary tubes, F_0 is found slightly larger than calculated by Knudsen's formula for free-molecule flow; we conclude that Maxwell's coefficient f (fraction of molecules reflected diffusely at the walls) for several gases at a glass wall has a mean value $f = 0.98 \pm 0.01$, and that the minimum which the F *vs* $\bar{p}$ curve reaches in the transition region to laminar flow (beyond the range of validity of our equation) lies nine percent below F_0, not five percent as Knudsen assumed.

For a narrow slit between two plane parallel plates we find a more complicated formula; two constants are adjusted by comparison with experiments of Gaede.[3] In such a slit, the binary collisions cause a much stronger decrease of specific flow with increasing pressure than in a circular tube.

With short tubes F becomes a linear function of $\bar{p}$. If $2a$ is the tube diameter, l the tube length (or mean length of straight sections of a tube with sharp corners), and if $l \ll \lambda$, then

$$F/F = 1 + \kappa \cdot 2a/\lambda. \tag{2}$$

For $l/2a \approx 4$, we find $\kappa = 0$. With longer tubes κ becomes negative, with shorter tubes positive. For a circular orifice we find $\kappa = 0.12$, in agreement with experimental observations of Knudsen.[4]

Equation (2) will also apply to a porous medium, as it resembles a network of short capillaries. Assuming a plausible mean ratio $l/2a \approx 3$, we find that in the molecular region κ has the same order of magnitude as the slope factor 0.0738 of the Poiseuille equation for laminar flow. This agrees with experiments of Carman[5] on the permeability of fine powders; the flattening of the curve in the molecular region observed by Barrer and Grove[6] may be caused by a different pore structure.

Detailed publication will appear in the *Zeitschrift für Naturforschung.*

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Spin-Spin Interaction in HD Nuclear Resonance

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THE existence of a nuclear spin-spin interaction has been postulated by Hahn and Maxwell[1] and McNeil, Slichter, and Gutowsky[2] to account for the slow-beat phenomenon in the spin-echo nuclear resonance technique. Ramsey and Purcell[3] have proposed a second-order perturbation arising from higher electronic triplet states of the molecule to account for the interaction. For the case of the HD molecule they have calculated the magnetic level shifts to be approximately 70 $I_H \cdot I_D$, which implies that the proton resonance in HD would consist of a triplet structure with a 70 cps separation between components.

We have completed a series of measurements on the resonance line structure of the proton in H_2 and in HD which are in agreement with the predictions of Ramsey and Purcell. The equipment used has been described elsewhere.[4] The proton resonance in HD was obtained in a sample of H_2-D_2 that had been allowed to equilibrate under 1200 lb/in.^{2} pressure for 18 months. A typical mass spectrometer analysis gave 2.4 percent H_2; 26.3 percent HD; 69.5 percent D_2 in good agreement with the assumption of a K_{eq} of 3.25. Resolution of the component lines was not feasible because of magnetic field homogeneity limitations, and thus resonance line widths were the criteria of structure. Since relaxation times can contribute to line broadening, line width measurements were made on pure H_2 at 1200 lb/in^2 and on a freshly prepared H_2-D_2 mixture where the H concentration was equal to that in the HD equilibrated sample. No significant difference in line width was detected. To insure that saturation broadening did not occur, the rf power was kept well below the saturation value. To insure the constancy of the field inhomogeneity over the gas sample volumes, interchange of the gas samples was made without moving the position of the gas chamber coil assembly in the magnet. The dc sweeping field rate was calibrated in terms of cycles per second by using a modulated radiofrequency source and by noting the separation of the resonances due to the sideband frequencies.

Operating at a radiofrequency of 30 Mc/sec, the results of 30 measurements on the H_2 proton resonance gave a line width (full width at $\frac{1}{2}$ maximum) at 109 ± 7 cps, while from 32 measurements of the H_2:HD proton resonances the average line width was found to be 138 ± 4 cps, the indicated error being the standard deviation of the mean. Obviously the triplet structure, revealed only in a broadening of the resonance line, cannot be deduced from the experimental evidence. However, with an *a priori* postulation of the structure one can deduce quite easily, by graphical analysis, the required separation of components to give agreement with experiment. Taking into account both the H_2 and HD contribution to the line width, the required separation of components is found to be 52±6 cps. The result can be considered in good agreement with the theoretical predictions, since relatively crude wave functions[5] were used in predicting the separation.

We are indebted to Dr. Ramsey and Dr. Purcell[6] for their invaluable suggestions and information and to Dr. O. C. Simpson of this laboratory who encouraged us to made these measurements.

[1] E. L. Hahn and D. E. Maxwell, Phys. Rev. **84**, 1246 (1951).
[2] McNeil, Slichter, and Gutowsky, Phys. Rev. **84**, 1245 (1951).
[3] N. F. Ramsey and E. M. Purcell, Phys. Rev. **85**, 143 (1952).
[4] B. Smaller, Phys. Rev. **83**, 812 (1951).
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[6] We have been informed recently that H. Y. Carr, using pulse echo techniques in HD, has obtained results in substantial agreement with our own.

The Probability of Internal Conversion of K Series Radiation of Au Arising from the Interaction of the L Subshells*

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If a vacancy is created in the K shell of an atom, for example, by a K capture event, an L electron can fall into this vacancy, losing energy either by emission of an x-ray photon or by transfer of energy to an outer electron (Auger effect). Calculations have been made by Massey and Burhop[1] for the probability of internal conversion of the K series radiation for gold arising from the interaction of the L_IL_I, L_IL_{II}, and L_IL_{III} shells. They used the Møller correspondence principle, employing Dirac wave functions, and treat the process as a transition between states of equal energy of the system comprised of the two electrons. Two approximations were made: (1) the treatment of the problem as a two-electron problem, neglecting the perturbation of the wave function of the atomic electrons due to the ionization of the atom; (2) the use of screened hydrogen-like wave functions for the atomic electrons. They obtained the probability of the Auger transitions $L_I,L_I \rightarrow K,\infty$, $L_IL_{,II}\rightarrow K,\infty$, and $L_I,L_{III}\rightarrow K,\infty$ for gold. These results for the relativistic theory were compared with those obtained in the nonrelativistic approximation of Burhop[2] (see Table I).

We have obtained an experimental value for the relative probability of the Auger transitions for which they made calculations, and in addition, we have obtained values for the transitions $L_{II},L_{II}\rightarrow K,\infty$, $L_{II},L_{III}\rightarrow K,\infty$, and $L_{III},L_{III}\rightarrow K,\infty$. The source, Hg^{197m}, which decays to Au^{197m} by K capture, was prepared by Dr. A. DeShalit by irradiating Au with protons in the Princeton cyclotron.[3] The Auger electrons were analyzed in a 180° permanent magnet photographic spectrograph. The measured energies of the lines, along with the energies expected using a recent compilation of x-ray level energies,[4] are listed in Table I. The measured intensities are compared with the two sets of theoretical calculations. It may be noted here that energy and intensity considerations eliminate the possibility of these Auger lines arising in Hg^{197m}. In addition, Ellis[5] has obtained similar data for Auger transitions in $Z=83$ [using Th(B+C)], which are listed in the table.

TABLE I. Experimental and theoretical energies and intensities for Auger transitions in Au involving two L electrons.

			Intensity			
					Measured	
	Energy (kev)		Theoretical		This	
Transition	Meas.	Calc.[a]	Nonrel.[b]	Rel.[c]	work	$Z=83$[d]
$L_IL_I\rightarrow K\ \infty$	51.87	52.00	1.0	1.0	1	1.0
$L_IL_{II}\rightarrow K\ \infty$	52.51	52.62	1.14	5.5	1.7	1.83
$L_IL_{III}\rightarrow K\ \infty$	54.26	54.43	2.28	5.3	1.2	1.33
$L_{II}L_{II}\rightarrow K\ \infty$	53.10	53.24			~0.3	<0.2
$L_{II}L_{III}\rightarrow K\ \infty$	54.89	55.05			1.4	2.33
$L_{III}L_{III}\rightarrow K\ \infty$	56.64	56.86			0.8	1.25

[a] Using x-ray critical absorption edge energies (see reference 4).
[b] See reference 2.
[c] See reference 1.
[d] See reference 5.

It is clear that the experimental data on intensities, which have an experimental uncertainty of about 25 percent, are incompatible with the relativistic results of Massey and Burhop, who suggested the experiment as a test for the extension of the Dirac equation to two bound electrons, believing it was not likely that the inaccuracies in the approximations discussed above would be great enough to mask the relativistic effect. However, it may be that a recalculation of this effect, using the Hartree self-consistent field method as suggested by Massey and Burhop, would modify the theoretical values. One would hesitate to question the validity of the Dirac equation on the basis of existing calculations for this Auger effect.

Two additional points are of interest. First, we observe the L_{II}, $L_{II}\rightarrow K,\infty$ transition which Ellis did not detect and for which he set an upper limit of 0.2 of the intensity of the other transition. Second, Ellis notes that the Auger electron energies were less (by ~0.2 kev) than the calculated values (E_K-2E_{LI}), etc., where E_K and E_{LI} are the x-ray absorption edge energies for the K and L_I shells. This is a measure of the additional energy required to remove an L electron from an atom ionized in the L shell. Robinson and Cassie[6] have noted a similar energy defect (~0.07 kev) for Cu, by directly comparing the energies of photoelectrons with the energies of Auger electrons. We also observe such an energy defect (~0.15 kev) which is just outside experimental error.

Thanks are due Dr. A. DeShalit, for preparation of the source, and Professor J. H. Bartlett, Dr. M. Goldhaber, and Dr. John Miskel for discussion.

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Interaction between Nuclear Spins in HD Gas*

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A number of nuclear resonance experiments have disclosed effects that could be explained only by an internuclear interaction of the form $\mathbf{I}_1\cdot\mathbf{I}_2$, I_1 and I_2 being the spins of the two nuclei involved.[1–3] Ramsey and Purcell[4] have pointed out that such an interaction can arise from the indirect coupling of one nuclear spin to another via the exchange-coupled electrons of the molecule and that an especially clear test of this theory would be afforded by the molecule HD. In this molecule the interaction should split both the H and the D resonances into multiplets. The separation of the multiplets is calculable and should be field independent.

Fine structure in both the H and D resonances of HD gas has now been observed. Furthermore, the fine structure has been observed in the H resonance at both 30 Mc/sec and 5 Mc/sec and found to be field independent. According to the theoretical prediction, the H resonance should consist of three equally intense lines, equally spaced in frequency, the separation between the central line and the satellites being denoted δ cps. The D resonance should consist of two equally intense lines, δ cps apart. This is the structure observed. An approximate calculation based on Heitler-London wave functions gave 70 cps as the order of magnitude of δ. The observed δ is 43.5±1 cps, which agrees with the theoretical prediction as well as one could expect.