Size of the Mercury Metastable Atom

M. L. Pool has reported measurements (Phys. Rev. **38,** 955, 1931) of the diffusion of the 2^3P_0 metastable atom of mercury in nitrogen, in which he finds for the distance between centers of the metastable atom and the nitrogen molecule at impact, the value $\sigma=3.2\times10^{-8}$ cm. This agrees closely with the value given by kinetic theory for the normal mercury atom, and is of special interest, since previous measurements indicated that the metastable atom was somewhat larger than the normal atom.

The method used by Pool is subject to an important criticism. The metastable atoms were produced in a cylindrical absorption cell containing nitrogen at several millimeters pressure, and the problem of determining the diffusion constant of these atoms in the nitrogen, here involves the solution of the diffusion equation in a cylindrical vessel, with zero concentration at the walls as boundary conditions. This solution involves a series of time exponential terms, with the exponential constants proportional to the squares of the roots of the Bessel's function of zero degree. The coefficients of these terms depend upon the initial distribution of the metastable atoms in the absorption cell, which is usually not known. The exact solution is therefore impracticable. However, if observations be made only when sufficient time has elapsed after the cut-off of the exciting radiation, all the terms with the exception of the one having the smallest exponential constant will have fallen to negligible values and we can deal with this single exponential term, from which the diffusion constant can be found. Apparently Pool has used only this single term, but has applied it to measurements made so soon after the cut-off of the excitation, that the other terms were not negligible. To what extent his conclusions are affected can not be calculated without more detailed data. In the light of the above criticism they should be examined with great care.

The value given by Pool for the effective cross-section of the metastable mercury atom when diffusing through nitrogen is, however, in fair agreement with measurements made by the undersigned using a method not subject to the above criticism. The apparatus employed was similar to that used by Zemansky (Phys. Rev. **29,** 513, 1927). The mercury and nitrogen contained in a quartz cell, were irradiated intermittently by a mercury arc in front of a slit behind which rotated a toothed wheel. On the same shaft, behind the cell was a disk which passed very close to a photographic plate. In this disk was a series of small holes all at the same distance from the center of the shaft, each hole corresponding to a tooth in such a way that on the photographic plate was recorded the radiation emitted by the cell after the exciting radiation was cut off. Except for a short interval after the cut-off, this radiation consisted only of $\lambda2537$ resulting from metastable atoms which had been raised to the 2^3P_1 state by impact and was therefore a measure of the concentration of these atoms. The fluorescence of the quartz walls of the cell (Phys. Rev. **34,** 1463–1465, 1929) was eliminated by a calcite filter in front of the cell, cutting out that part of the arc radiation which produced the fluorescence.

Of the curves obtained for the decay of the concentration of metastable atoms, only those parts were used in computation for which sufficient time had elapsed to make only the first term in the solution of the diffusion equation of importance, so that the decay followed a simple exponential relation. In addition to the diffusion, the decay constant depended also on the rate of loss of metastable atoms by impacts of the first and second kind with nitrogen molecules. This part decreased as the pressure of the nitrogen was decreased, so that at low pressures the decay was determined primarily by the diffusion. From such measurements the diffusion constant was calculated and σ, the distance between centers of metastable mercury atoms and nitrogen molecules at impact was found to be 3.7×10^{-8} cm. This value lies very close to the kinetic theory value, $\sigma=3.35\times10^{-8}$ cm, indicating that under these circumstances the metastable mercury atom is not very different in size from the normal atom.

The effect of some gases other than nitrogen on the life of the metastable mercury atom is very marked and much care must be taken in purifying the nitrogen for dependable results. Merely heating a prebaked quartz cell to 150°C has been found to free enough gas

to shorten the life of the metastable atom many hundreds of times. Since with the cells used in these experiments the decay constant of the metastable atoms was of the order of 100 sec.$^{-1}$ for pressures of nitrogen in the neighborhood of 4 mm it may be readily seen why minute quantities of other gases cause appreciable quenching.

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Isotope Displacements in the Hyperfine Structure of Lead

Isotope displacements much larger than those expected from the Bohr mass correction to the Rydberg constant have been observed by H. Schüler and J. E. Keyston[1] for Tl and Hg. With Aston's data for the relative abundance of isotopes of Hg and the relative intensities of the hyperfine structure components of several lines of Hg, they found that the terms due to different isotopes fell in the order of the masses. This appears remarkable since the suggestion so far is that the large isotope displacements must be due to nuclear fields. There is no obvious reason, however, why these fields should vary in the order of the nuclear masses.

In the study of isotope displacements there are special advantages in working with lead since isotopes 206 and 208 give single lines and can be obtained fairly pure from uranium and thorium ores, respectively. It is the object of this letter to report isotope displacements of Pb^{206}, Pb^{207} and Pb^{208} in the order of their masses similar to those found by Schüler and Keyston for Hg.

Kopfermann[2] using uranium lead has identified the next to the strongest components for λλ5372, 4245, 4242 and 4058 of ordinary lead to be due to Pb^{206}. The strongest components of these lines were found by him, when thorium lead was used, to belong to Pb^{208}. We have verified his observations for uranium lead in the visible and extended them into the ultraviolet. The next to the strongest components of λλ4168, 4062, 4019, 3739, 3683, 3671, 3639, 3572 and 2833 of Pb I and λλ4386, 3786, 3016 and 2948 of Pb II were all found to be due to Pb^{206}. With this result and that of Kopfermann for Pb^{208} in the visible, it is definitely established without using thorium lead that the strongest component of each of these lines is due to Pb^{208}. Although the isotope displacement for Pb^{208} I and Pb^{206} I was found to be as large as 0.093 cm^{-1}, values for the displacement of Pb^{208} II and Pb^{206} II ranged from 0.086 cm^{-1} for λ4386 to 0.415 cm^{-1} for λ3786.

From the line patterns of λλ4058, 3683, 3639, and 2833 the hyperfine splittings, shown in the second column of Table I, of $s^3P_{0,1}$ and $p^3P_{0,1,2}$ of Pb^{207} I have been calculated by using a nuclear spin, $i=\frac{1}{2}$. In the last two columns of the same table are the term displacements of the center of gravity (with $2f+1$ as

TABLE I.

Term	Pb^{207} term separation $\Delta\nu$(cm^{-1})	Nature of term	Term displacement with respect to Pb^{208}* C.G.Pb^{207} $\Delta\nu$(cm^{-1})	Pb^{206} $\Delta\nu$(cm^{-1})
s^3P_0	0.000	———	(?)	−0.003
s^3P_1	.436	regular	0.000	.000
p^3P_0	.000	———	−.048	−.079
p^3P_1	.125	inverted	−.052	−.088
p^3P_2	.864	regular	−.016	−.093

* The last figure in these tables, 0.001 cm^{-1} is subject to doubt. The estimated accuracy of the measurement is ±0.005 cm^{-1}.

[1] Schüler and Keyston, Zeits. f. Physik **70,** 1 (1931); **72,** 433 (1931).

[2] Kopfermann, Naturwiss. **19,** 400 (1931); **19,** 675 (1931). See also Aronberg, Astrophy. Jour. **39,** 185 (1918) and Merton, Proc. Roy. Soc. **A96,** 388 (1920); **100,** 1921 (1922) for qualitative agreement.