

A Slight Difference in the Isotopic Composition of Oxygen Made by the Fractionation of Liquid Air and Oxygen of Ordinary Air

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Citation: [The Journal of Chemical Physics](#) **2**, 298 (1934); doi: 10.1063/1.1749470

View online: <http://dx.doi.org/10.1063/1.1749470>

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TABLE II.

	Empirical			Beardsley C I
	C I	N II	O III	
G_1	2.18 (0.9)	3.35	4.25	3.44 volts
F_2	0.188(0.2)	0.290	0.400	0.29
W_0	13.7 (11.1)	20.2	26.1	14.6

that the energy of the "valence state" of carbon explained in section 2 of part III should range from 7.1 volts for the tetrahedral model $\mu = \frac{1}{2}$ to 8.5 volts for the model $\mu = 1$ without hybridization. The effect of the L , S structure is thus not quite as trivial as we previously estimated, and favors the tetrahedral modal model slightly. Because of

the successful application of Johnson's formulas to the new data, our estimate of 7 volts for the energy required to promote carbon to the tetravalent condition appropriate to CH_4 is now based on a much more certain calculation than formerly and is probably accurate to within half a volt. This estimate is fortuitously the same as that which we obtained in part III with the old values of the Johnson parameters. Hence sections 3 to 6 inclusive of part III, and so all the chemical applications in III, are mercifully unaltered.

J. H. VAN VLECK

Department of Physics,
University of Wisconsin,
Madison, Wisconsin,
March 21, 1934.

A Slight Difference in the Isotopic Composition of Oxygen Made by the Fractionation of Liquid Air and Oxygen of Ordinary Air¹

In an investigation of the fractionation of the isotopes of hydrogen and oxygen by the electrolysis of water, a series of measurements has been made on the difference in density of ordinary water and of the water formed by: (1) combining the electrolytic hydrogen with commercial oxygen; (2) combining the electrolytic oxygen with commercial hydrogen; (3) recombining the electrolytic gases as they come from the cell. The commercial oxygen, made from liquid air, was assumed at the start to have the isotopic composition of ordinary oxygen as it exists in air and water. The commercial hydrogen, made electrolytically in cells which have been in operation for years, was shown to be normal by combining it with ordinary atmospheric oxygen and comparing the density of the water thus formed with that of ordinary water. The difference in density was only 0.3 part per million.

However, in every case the sum of (1) and (2) failed to check with (3) by amounts ranging from 1 to 3 ppm and always of the same sign. The discrepancy was finally traced to the assumption that the commercial oxygen was the same as the oxygen in normal air and water. This assumption was tested by preparing two samples of water, one composed of the dried commercial oxygen combined with dried hydrogen from a given cylinder, and the other composed of ordinary atmospheric oxygen and dried hydrogen from the same cylinder. After purification by distillations from alkaline permanganate and from phosphoric acid followed by simple distillation, with the rejection in each case of small first and last portions, the water from commercial oxygen was found to be

heavier by 1.4 and 2.4 ppm. After an additional distillation the difference was 2.8 ppm, giving an average of 2.2 ± 0.5 ppm. Assuming adequate purification, this difference can result only from a difference in the two samples of oxygen.

The commercial oxygen was manufactured by the fractionation of liquid air in a column which produces nitrogen of 95.5 percent purity at the top, and apparently a slight fractionation of the oxygen isotopes occurs, so that the commercial oxygen has a density greater by about 2 ppm and therefore contains approximately 2 in 10^6 more atoms of O^{18} , than ordinary oxygen. This difference may vary somewhat with the efficiency of different fractionating columns and may be of significance in other investigations.

Before these measurements were completed Klar and Krauss² found differences in the isotopic composition of different fractions of technical oxygen. However, the results reported in this letter may be of some value since they confirm the results of Klar and Krauss and, in addition, show the magnitude of the change to be expected in the oxygen from an ordinary commercial cylinder.

EDGAR R. SMITH

Bureau of Standards,
Washington, D. C.,
March 27, 1934.

¹ Publication approved by the Director of the Bureau of Standards, U. S. Department of Commerce.

² R. Klar and A. Krauss, *Naturwissenschaften* **22**, 119 (1934).

The Magnetic Susceptibility of Ammonium Hexabromo-Hypoantimonate

At the suggestion of Professor Linus Pauling, I have determined the magnetic susceptibility of ammonium hexabromo-hypoantimonate, $(\text{NH}_4)_2\text{SbBr}_6$, in order to obtain some information about the valence of antimony in this compound.

The substance was prepared by the method of Ephraim and Weinberg.¹ It was dried by centrifuging. The product

was a deep black powder, apparently similar to Ephraim's compound.

The determination of the specific magnetic susceptibility by the Gouy method led to a value, $\chi = -0.036 \times 10^{-6}$ cg, the substance thus being shown to be diamagnetic.

¹ Ephraim and Weinberg, *Berichte* **42**, 4450 (1909).

Ammonium hexabromo-hypoantimonate, therefore, does not contain unpolymerized complexes involving a quadrivalent antimony atom, for such complexes would contain an odd number of electrons and hence give rise to strong paramagnetism. It is probable that the substance is a double salt containing one trivalent and one quinquivalent antimony atom corresponding to the formula $(\text{NH}_4)_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Br}_{12}$. The observed diamagnetism could be made compatible with the presence of quadrivalent antimony by assuming that the quadrivalent antimony

atoms occur in groups of two joined by shared electron-pair bonds, $\text{Sb} : \text{Sb}$, similar to the group $\text{Hg} : \text{Hg}^{++}$ in mercurous salts. This, however, seems improbable because the stoichiometric formula, $(\text{NH}_4)_2\text{SbBr}_6$, suggests that each antimony atom is surrounded by six bromine atoms which would prevent close approach of the antimony atoms.

NORMAN ELLIOTT

Pasadena, California,
April 11, 1934.

The Infrared Spectrum of Methyl Deuteride

As a consequence of its high degree of geometric symmetry the methane molecule, with nine degrees of freedom of vibration, has only two active fundamental absorption bands, each triply degenerate. While the character of these bands justifies the tetrahedral model, they yield very little information regarding the dimensions and elastic constants of the system. The replacement of one of the hydrogens by an atom of deuterium introduces a preferred axis, with respect to which the molecule is symmetrical, and increases the number of active vibrations from two to six. Of these, three are single, introducing electric moments parallel to the axis, and three are double, giving rise to perpendicular bands.

We have observed all of these fundamental bands, and have determined the rotational structure of one of them, the lowest frequency parallel vibration. This consists of a strong and narrow zero branch at approximately 1090 cm^{-1} , and the usual positive and negative branches, the intervals between rotation lines being about 4.5 cm^{-1} . From this interval the maximum moment of inertia may be computed at once, $I \sim 12.28 \times 10^{-40}$, and the H-H distances are about $2.51 \times 10^{-8} \text{ cm}$. More bands must be analyzed and the molecular constants evaluated before these dimensions can be given with precision. Assuming the atomic distances to be the same for ordinary methane, its moment of inertia comes out approximately 10.45×10^{-40} . As

would be expected, this value is about twice as large as that determined from the rotational Raman effect by Dickinson, Dillon and Rasetti,¹ since they assumed that the successive lines have J values differing by two. They found $I = 5.17 \times 10^{-40}$.

Methyl deuteride is of especial interest in the study of rotational and vibrational interaction in perpendicular bands, since it is the first molecule available in which both moments of inertia may be determined precisely. Because the bands lie rather close together and overlap considerably, their analysis must await further study, and will be reported later.

A very interesting test of the assumption that the atomic distances are the same for both isotopes of hydrogen will be provided by the study of the methane molecule with three hydrogen atoms replaced by deuterium. These measurements we hope to publish within a short time, as well as the fundamental frequencies of tetra-deutero methane.

E. F. BARKER
NATHAN GINSBURG

University of Michigan,
April 13, 1934.

¹ Dickinson, Dillon and Rasetti, *Phys. Rev.* **34**, 582 (1929).

Resolution of Crossed Bond Eigenfunctions in Terms of the Uncrossed Set

The method of repeatedly applying the theorem for uncrossing any pair of bonds expressed by the relation

$$\times = || + \equiv$$

is adequate for resolving every bond eigenfunction in terms of the linearly independent set. However, the labor of doing this rises rapidly as the number of bonds increases. Since in obtaining bases for irreducible representations¹ the resolution of crossed bond eigenfunctions is practically unavoidable, some simplification seems necessary. Very simple rules have been found for the cases usually encountered, i.e., those involving 5 bonds or fewer.

We assume we have a crossed bond eigenfunction A with $2n$ orbitals arranged symmetrically on a circle connected in pairs by n bonds.

Rule I

The number of times this process of uncrossing will yield a particular bond eigenfunction B with no crossed bonds equals the number of different ways a set of n continuous, entirely noncoincident (except perhaps at points), noncrossing paths may be drawn along the lines in A , such that they connect each pair of orbitals bound together in B . Ordinarily this rule enables one to determine coefficients 0 or 1 by inspection, but in any case the determination is very simple. A subsidiary rule is necessary in cases yielding larger coefficients. Such cases arise when there is a point common to more than three paths.

¹ Eyring, Frost and Turkevich, *J. Chem. Phys.* **1**, 777 (1933).