Note on the sp 3 Configuration of Carbon, and Correction to Part III on CH4

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the imperfection cuts the surface of the fluorite.

The powder has been found to be insoluble in distilled water but soluble in dilute hydrochloric acid. It forms after a shorter period of time if the air is moist than if it has been carefully dried. It is possible that light of extremely short wave-length activates the oxygen of the air so that either (1) calcium oxy-fluoride (perhaps) is formed directly, or (2) hydrogen peroxide is produced first and then reacts with CaF_2 to form the deposit. In the latter case it might be expected that a very strong solution of H_2O_2 applied to the window would produce some effect upon it, but upon making this test not the slightest effect could be detected. As yet nothing further is known about the nature of the deposit or of the reaction which causes it.

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    March 20, 1934.

Note on the sp^3 Configuration of Carbon, and Correction to Part III on CH_4

In part III[1,2] of my recent series on CH_4, I overlooked Edlén's[3] new measurements and classifications for the spectra of C I, N II and O III, which appeared just as my article was being completed. The previously unknown sp^3 ^5S state has been found by Edlén in N II and O III, and may now be located in carbon I at approximately 4.1 volts above the ground state s^2p^2 ^3P by extrapolation from N II and O III with the aid of the irregular doublet law. A more accurate, in fact quite remarkable, method of extrapolation based on theoretical considerations has subsequently been developed by Bacher and Goudsmit.[4] It places ^5S at 4.3 volts in carbon. Thus ^5S is not quite as high above the ground state as my previous estimate 5–8 volts based on the Slater-Condon-Johnson F-G relations, but is much closer to this estimate than to the value 1.6 volts so often quoted in the literature. It is somewhat accidental that my estimate was as close as it is, for in applying these relations, I used the experimental values of the sp^3 ^1D and sp^3 ^1P terms, viz., 9.65 and 9.66 volts, usually listed in spectroscopic tables, such as for example Bacher and Goudsmit's book.

Edlén finds that the terms at these positions are certainly due to some other configuration, probably s^2pd. The true sp^3 ^1D and sp^3 ^1P levels have not yet been detected spectroscopically, but may be located by Bacher and Goudsmit's new method at 12.9 and 14 volts, respectively. (Because ^3S of N II was obviously out of line with ^1P and ^1D of C I in the old classification, I suggested in part III that ^3S was due to some other configuration than sp^3; it is now evident that the old ^1D, ^1P were the real culprits.) With the new classification and for more extensive data, the Johnson formulas fit experiment very much better than previously, in fact unusually well for F-G relations. The revised and extended version of Table I of part III is given in Table I.

TABLE I. Energies, in volts, relative to the ground state s^2p^2 ^3P.

	Observed			Calculated		
	C I	N II	O III	C I	N II	O III
sp^3 ^5S	[4.3]	5.8	7.4	(4.3	5.8	7.4)
sp^3 ^3S	13.0	19.2	24.4	(13.3	19.2	24.4)
sp^3 ^3D	7.9	11.4	14.8	8.2	11.8	15.2
sp^3 ^1D	[12.9]	17.8	23.1	12.6	18.5	23.7
sp^3 ^3P	9.3	13.5	17.6	(9.3	13.5	17.6)
sp^3 ^1P	[14.0]	20.6	26.0	13.7	20.2	26.1

The "observed" values in square brackets, unlike the others, are not really spectroscopic, but have been computed by Bacher and Goudsmit with their new extrapolation method. Their results are reliable to a few tenths of a volt, and better than the estimates 12.1 and 14.8 for ^1D, ^1P which Edlén obtained with the irregular doublet law. The calculated values have been obtained by the Johnson formulas given in part III, with the parameters chosen so as to yield the proper positions for ^5S, ^3S, ^3P. The corresponding magnitudes of the parameters are those labelled "empirical" in Table II; they would not be much altered if three other states were fitted instead of ^5S, ^3S, ^3P. We make this selection for the three because it makes the maximum deviation between the calculated and observed values in Table I less than with most other choices and so represents a closer approximation to the method of least squares. The Bacher-Goudsmit procedure is sufficiently accurate that it is not important that one of the three states fitted has been located in C I by this procedure rather than spectroscopically.

The values in parentheses are those obtained in part III for carbon by fitting ^1P, ^3D, ^3P with the old classification. We have also listed for comparison the results of Beardsley's theoretical calculations by means of approximate wave functions obtained by a variational method. It is seen that the new classification largely removes the previous qualitative disagreement between the empirical values of the Johnson parameters and those computed by Beardsley.

With the empirical values of the parameters listed in Table II, one calculates from Eqs. (7) and (8) of part III

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[1] J. H. Van Vleck, J. Chem. Phys. **2**, 20 (1934).

[2] The following minor errata may be noted in part II (ibid. **1**, 219, 1933): add $\frac{3}{2}(1-\cot^2\theta)\sin^2\theta N_{\pi\pi}+\cot^2\theta N_{ss}$ to the expression (41); in the line before (41) read $\mathfrak{R}=0$ for $N=0$.

[3] B. Edlén, Zeits. f. Physik **84**, 746 (1933); I am indebted to Professor Bowen for calling my attention to this reference and to the use of the irregular doublet law in connection with it.

[4] Bacher and Goudsmit have as yet published only a preliminary abstract on their method; Phys. Rev. **45**, 559 (1934). They have, however, very kindly informed me of the results of the application to carbon in advance of their detailed paper.

TABLE II.

| | Empirical | | | Beardsley |
	C I	N II	O III	C I
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 $\mu=\frac{1}{4}$ 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.

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March 21, 1934.

A Slight Difference in the Isotopic Composition of Oxygen Made by the Fractionation of Liquid Air and Oxygen of Ordinary Air[1]

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 10^5 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 Krauss[2] 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, $(NH_4)_2SbBr_6$, 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, $\chi=-0.036\times10^{-6}$ cg, the substance thus being shown to be diamagnetic.

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