

COMMUNICATIONS TO THE EDITOR

OPTICAL ROTATION AND ATOMIC DIMENSION. IX. HALOGENO-TETRA-ACETYL DERIVATIVES OF MANNOSE. THEIR CONFIGURATIONAL PECULIARITIES

Sir:

In continuation of my investigations on Optical Rotation and Atomic Dimension [last publication, VIII, THIS JOURNAL, 51, 1820 (1929)], there have been prepared the pure crystalline substances α -fluorotetraacetylmannose and α -iodotetraacetylmannose and their specific rotations measured. Further, we have revised the value for crystalline α -bromotetraacetylmannose as first measured by Micheel [*Ber.*, 63, 390 (1930)] and later by Levene and Tipson [*J. Biol. Chem.*, 90, 93 (1931)]. As I prepared several years ago crystalline α -chlorotetraacetylmannose and measured its rotation, a series of values is available for comparison with the atomic dimension values.

It has been established in my former investigations on this subject that for all the investigated halogen derivatives of the monosaccharides (glucose, fructose, xylose and arabinose) the differences in specific rotation, Cl-F, Br-Cl and I-Br, are proportional to the corresponding differences in atomic diameters. These differences in the specific rotations have the same ratio to each other as the corresponding differences in the atomic diameters, namely, 41:17:21. By using the values for the neutral atomic diameters of Goldschmidt [see Wherry, *Am. Mineralogist*, 14, 54 (1929)], the proportionality existing between the differences of specific rotation and atomic diameter values holds very accurately for the derivatives of these four monosaccharides. However, the values for the mannose derivatives give the ratio 41:25:35. These experimental results point to the explanation that for the mannose derivatives the halogens on the one hand and the atoms of the second carbon on the other influence each other, as will be discussed in detail in the forthcoming paper. The results of Freudenberg [*Naturwissenschaften*, 18, 393 (1930)] and Haworth [*J. Chem. Soc.*, 1395 (1930)] are of interest in this connection. They found for the structure of some mannose derivatives that even ring formation occurs between the adjacent groups of the first and second carbon atoms. An explanation of the different behavior of the mannose derivatives in comparison with the other monosaccharide derivatives could be obtained by model studies (detailed in the forthcoming article) which show that for the α -halogen derivatives of mannose the acetyl group of the second carbon is directed through its CH₃ group to the halogens of the first carbon with a resulting influence; whereas for the α -halogen derivatives of glucose, arabinose and xylose, the acetyl group of the second carbon is directed through its CH₃ group to the ring or another oxygen atom and also that the detailed structure of the halogen derivatives of fructose (β -derivatives) does not show a similar influence on the halogen atoms.

If we consider the consequences of this explanation it is seen that for the α - and β -mannose pentaacetates the acetyl group of the second carbon atom has a different position for the α -compound in comparison with the β -derivative, as its CH_3 group is directed by the respective places of the oxygen atoms of the first carbon acetyl group, whereas such a difference does not exist (or is of another nature) for the other discussed monosaccharides. Hence the testing of the principle of optical superposition in the mannose and rhamnose series should be taken up with caution, taking into account these configurational peculiarities.

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D. H. BRAUNS

THE VARIATION OF ELECTRIC MOMENT WITH TEMPERATURE

Sir:

Because of the uncertainty which has recently arisen in regard to the possible temperature variation of the moments of molecules in which two dipoles may rotate relative to one another, it has seemed of immediate importance to investigate this effect in such molecules. Ethyl acetate, the moment of which should depend, to a considerable extent, upon the position of the moment of the $\text{O}-\text{C}_2\text{H}_5$ bond relative to that of the $\text{C}=\text{O}$ group, is found to show no significant variation of moment with temperature between -70 and $+30^\circ$ when measured in dilute solution in heptane. The moment of ethylene chloride in solution in heptane is found to increase uniformly from 1.07×10^{-18} at -70° to 1.41×10^{-18} at $+30^\circ$ in satisfactory agreement with the measurements of Meyer [*Z. physik. Chem.*, [B] 8, 27 (1930)]. In similar fashion the moment of ethylene chlorobromide in heptane solution is found to increase from 0.92×10^{-18} at -50° to 1.19×10^{-18} at $+30^\circ$. This change is in accord with Meyer's idea that the mutual potential energies of the doublets in the two halves of the molecule cause these halves to occupy such positions relative to one another that the moments are partially canceled. The increase in rotational energy with rising temperature tends to overcome this effect of the mutual potential energies and so increase the moment.

Diethyl succinate which was found to have a moment lower than those of the other dicarboxylic acid esters and, apparently, increasing with temperature [Smyth and Walls, *THIS JOURNAL*, 53, 527 (1931)], has been measured over a wide range of temperature in solution in kerosene. The moment increases regularly from 2.01×10^{-18} at 0° to 2.47×10^{-18} at 180° , the latter value being practically identical with the moments of the higher members of the series. The tendency of the succinate molecule to bend in such a way that the doublets partially oppose and cancel one

another at the lower temperatures is evidently overcome by the increased vibrational and rotational energy acquired within the molecule as the temperature rises.

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CHARLES P. SMYTH
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THE ENTROPY OF POLYATOMIC MOLECULES

Sir:

The theoretical entropy of diatomic molecules has been calculated and discussed quite extensively,¹ but so far as I am aware, no one has as yet tackled the problem presented by the polyatomic molecule. I have recently computed the entropies (at 298.1°K.) of ammonia and of methane and find quite good agreement with the experimental thermochemical values. As such an agreement represents one of the few possibilities of actual check on the conclusions of band spectra as applied to chemistry, I am writing up the calculation in detail for publication, probably in the *Physical Review*.

The same formulas that were used for diatomic molecules² are applicable here but a double summation is necessary, corresponding to the two rotational quantum numbers, j and τ , in the symmetrical top type of rotator. When plausible assumptions are made for converting these summations to integrals, the absolute rotational entropy of each symmetry³ modification (nuclear quartet and doublet forms in the ratio of 1:2, respectively, at high temperatures for ammonia and nuclear quintet, triplet and singlet forms in the ratio of 5:27:4, respectively, at high temperatures for methane) may be calculated. From this was subtracted the "zero point" entropy which is the correction term necessary on account of the experimental difficulties of reaching temperatures sufficiently near the absolute zero and in measuring the extremely small heat effects.

Using the moments of inertia of ammonia as given by Badger and Mecke,⁴ the total effective entropy of ammonia is 44.0 E. U. and compares very favorably with the value derivable from the data in Lewis and Randall (p. 557), 43.5.

¹ Fowler, *Proc. Roy. Soc. (London)*, A118, 52 (1928); Giaque and Johnston, *THIS JOURNAL*, 50, 3221 (1928); Rodebush, *Proc. Nat. Acad. Sci.*, 15, 678 (1929); Villars, *ibid.*, 15, 705 (1929); 16, 396 (1930); Giaque and Johnston, *Phys. Rev.*, 36, 1592 (1930); Giaque, *THIS JOURNAL*, 52, 4816 (1930); Rodebush, *Phys. Rev.*, 37, 221 (1931); Giaque, *THIS JOURNAL*, 53, 507 (1931); MacGillavry, *Phys. Rev.*, 36, 1398 (1930).

² Villars, *loc. cit.*, or Giaque, *THIS JOURNAL*, 52, 4816 (1930).

³ Cf. Hund, *Z. Physik*, 43, 805 (1927), for NH₃; Elert, *ibid.*, 51, 6 (1928), for CH₄.

⁴ Badger and Mecke, *Z. physik. Chem.*, B5, 333 (1929).

For methane, three values were computed, depending on which line spacing one assumes to be representative of the moment of inertia. They are 44.1, 42.3 and 42.0; for $I = 10.2, 5.66$ and 5.17×10^{-40} . The last corresponds to the spacing most accurately measured (Raman effect)⁵ and, for various reasons, is probably the correct one. In fact, the agreement with the observed entropy⁶ 42.5 may be adduced as additional evidence for the reliability of this choice.

These results indicate that the actual calculation of thermodynamic equilibria⁷ from band spectra data is not to be much longer limited to reactions between molecules having a maximum of two atoms.

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2,4,5-TRIMETHOXYBENZOIC ACID: A DERIVATIVE OF DEHYDRODEGUELIN

Sir:

It has been shown by LaForge and Smith¹ that, through a series of reactions, the rotenone molecule may be ruptured in a manner which yields derric acid, $C_{12}H_{14}O_7$. Derric acid represents the half of the rotenone molecule which contains the methoxyl groups, but as yet the exact nature of the acid is unknown.

Recently three other insecticides of the same type as rotenone, namely, deguelin, tephrosin and toxicarol, have been described.² It has also been shown that structural relationships exist common to the entire molecule of rotenone, deguelin and tephrosin;³ but the fact which is of immediate interest is that the derric acid portion of the molecule is common to all three substances.

It is desired at this time to report in a preliminary way the results of some experiments which clarify to a considerable degree the problem of the derric acid portion of rotenone and allied materials.

Permanganate oxidation of dehydrodeguelin in acetone solution yields two hydroxy acids, one of which contains the two methoxyl groups present in the starting material and thus represents the derric acid portion of the molecule. This acid crystallizes in plates which may be roughly described as rectangular with notched ends and with constrictions in the center of their long axis. It melts at 210° with decomposition and gives an intense blue color with ferric chloride.

⁵ Dickinson, Dillon and Rasetti, *Phys. Rev.*, **34**, 582 (1929).

⁶ Randall and Mohammad, *Ind. Eng. Chem.*, **21**, 1048 (1929).

⁷ Cf. Ludloff, *Z. Physik*, **57**, 227 (1929), for a general discussion of this problem.

¹ LaForge and Smith, *THIS JOURNAL*, **52**, 1091 (1930).

² Clark, *ibid.*, **52**, 2461 (1930); **53**, 313 (1931); **53**, 729 (1931).

³ Clark, *Science*, **73**, 17 (1931); also a paper now being submitted to *THIS JOURNAL* for publication.

Analysis proved the material to be an hydroxydimethoxybenzoic acid. Methylation of the free hydroxyl group gave a trimethoxybenzoic acid which was shown by its melting point and derivatives obtained by bromination and nitration to be asaronic acid, 2,4,5-trimethoxybenzoic acid.

The hydroxydimethoxybenzoic acids which could give this acid are 2-hydroxy-4,5-dimethoxy-, 5-hydroxy-2,4-dimethoxy- or 4-hydroxy-2,5-dimethoxybenzoic acid. It is thought that because of the ferric chloride reaction given by the acid from dehydrodeguelin it is 2-hydroxy-4,5-dimethoxybenzoic acid. Work upon its synthesis is in progress, and it is hoped that a report upon its structure can be made shortly.

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E. P. CLARK

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SYNTHESIS OF GAS-METAL COMPOUNDS BY SPUTTERING

Sir:

In connection with a somewhat extensive study of cathodic sputtering [see *Phys. Rev.*, **32**, 649 (1928); **34**, 972 (1929); *Nature*, **126**, 204 (1930)], the writer has recently found that this process has remarkable possibilities as a method of chemical synthesis. This applies particularly to the formation of metal-gas compounds such as nickel and similar metals with hydrogen, nitrogen, etc. Nickel sputtered in nitrogen under rather special conditions of current, voltage and gas pressure gives a dark, somewhat metallic-looking film which shows on x-ray examination a crystal structure distinctly different from that of the pure metal. Heating to about 350° decomposes this compound, which gives off its gas and reduces to metallic nickel. Upon heating such a nitride film to 150° in hydrogen, ammonia is formed and in an amount which agrees reasonably well with the quantity of nitrogen absorbed in sputtering. Compounds of cobalt and iron with nitrogen have likewise been produced, as well as of nickel and hydrogen—this latter showing on crystal structure examination a lattice spacing some 6% larger than for pure nickel.

It seems certain then that we are dealing here with such unusual compounds as nitrides and hydrides of these metals. Moreover, they are formed, not at the expense of a difficult and special technique of synthesis [see A. C. Vournasos, *Compt. rend.*, **168**, 889 (1919)] but by a simple process of wide applicability, for the conditions encountered in sputtering, with the metal in the vapor state and the gas largely excited by the discharge, would seem to be ideal for the formation of a compound if this is chemically possible. Indeed one series of experiments yielded considerable evidence for the formation of compounds with even helium and

argon, and, while this evidence was later vitiated by the discovery of impurities, the question is by no means as yet settled in the negative. Compounds with excited helium or argon are at least not unthinkable, and this is probably the most promising way of forming them.

A word of caution may not be out of place as to the use of this method of synthesis. Metals ordinarily contain a great deal of absorbed gas and while the usual baking (at say 500°) may remove the bulk of such impurity adsorbed on the surface, it will probably take little from the interior. Then as layer after layer of atoms is removed from the cathode in the sputtering process, fresh supplies of gaseous impurity are released, so when purity of product is a main factor some provision must be made to eliminate this source of trouble. It may be possible to secure nearly gas-free metal for the cathode, or to outgas it effectively by having it in the form of a thin strip which can be heated electrically to a high temperature, but probably the most feasible method is to dilute the impurity to a point where it becomes negligible by a continuous flow of fresh gas through the chamber during the sputtering.

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L. R. INGERSOLL

A RELATION CONCERNING ATOMIC NUCLEI

Sir:

An interesting numerical relation of known atomic species is to be found in the helium-thorium series. The atomic nuclei of this series have a composition represented by the general equation

$$a_{(Z/2+n/4)} + (e_2)_{n/4}$$

in which e is an electron, a represents a group of 4 protons and 2 electrons, Z is the atomic, and n , the isotopic number. For thorium Z is 90 and n is 26, so the specific formula is $a_{58}e_{26}$. In a recent paper Latimer develops a model for the nuclei of this series. He bases his model not only on the general hydrogen-helium theory¹ developed in 1915 by the writer, but he also makes use of the very specific features of this theory, such as the pairing of the nuclear electrons,² the introduction of the first pair of extra or cementing electrons in the argon nucleus³ of mass 40, and the later addition of still other pairs of electrons as the atomic number increases.⁴

Latimer also uses the idea that the abundance of an atomic species is

¹ Harkins and Wilson, *THIS JOURNAL*, **37**, 1367-1396 (1915).

² Harkins, *ibid.*, **39**, 859 (1917); **42**, 1958, 1963-1964, 1991-1993 (1920).

³ Harkins, *ibid.*, **39**, 859, Table II (1917); *Phil. Mag.*, **43**, 305 (1921).

⁴ Harkins, *Phil. Mag.*, **42**, 1976 (1920).

related to its stability,⁵ and considers that the stability is related to the intranuclear spins,⁶ which are supposed to be due to the protons.

It is of interest to see if any known relations, other than those upon which the model is based, agree with the interesting tetrahedral model. Figure 1 gives a representation of the helium-thorium series, taken largely from

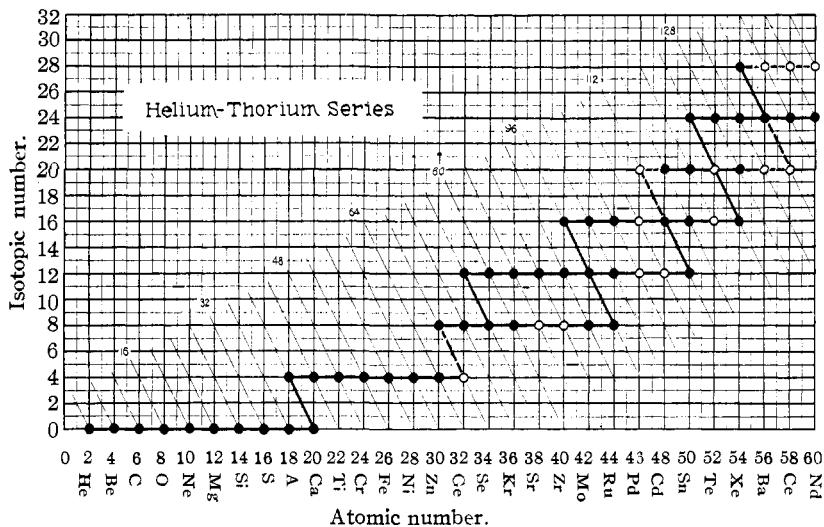


Fig. 1.—Open circles represent species as yet undiscovered.

an early paper,⁷ but extended to fit the most recent data of Aston.⁸ It may be noted that this series is found only on levels 0, 4, 8, 12, etc., which correspond to 0, 1, 2, 3, etc., pairs of extra or cementing electrons. The length of the series at any level will be considered to be given by the number of places for members of the series beginning and ending with known species. The values are collected in Table I.

TABLE I

1	2	3	4
Isotopic number, n	Number of cementing electrons, $n/2$	Number of species in known series	Number of species in Fig. 1
0	0	10	10
4	2	7	8
8	4	8	8
12	6	10	10
16	8	8	8

In explanation of Column 4 it may be said that Fig. 1 represents undiscovered species by open, and known species by black, circles.

⁵ Harkins, *THIS JOURNAL*, 39, 856 (1917); *Proc. Nat. Acad. Sci.*, 2, 216 (1916).

⁶ Harkins, *Phys. Rev.*, 35, 434 (1930).

⁷ Harkins, *J. Franklin Inst.*, 195, 554 (1923).

⁸ Aston, *Nature*, 127, 233 (1931).

Thus the number of species is 10 for either zero or three pairs of cementing electrons, and eight (possibly seven for one pair) for one, two, or four pairs. This agrees with the writer's early idea that the zero level should be a long one, and with Latimer's idea that the level for three pairs of cementing electrons should also be long. While later discoveries may change these limits, they will probably not destroy the validity of the general relations.

It may be noted that Latimer⁹ makes no attempt to explain the most fundamental relation which concerns nuclear stability, the pairing of electrons in the nucleus. Also Dirac's principle of superposition, mentioned by Rodebush,¹⁰ has not been developed to the extent necessary to explain this phenomenon. It is not improbable that the two electrons in an alpha particle move through the whole volume of the particle, but the distribution of electron density is entirely unknown. It is not intended to imply that the electron pairing cannot later be treated in terms of an overlapping of the eigenfunctions of the single electrons.

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WILLIAM D. HARKINS

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THE STRUCTURE OF THE α -PARTICLE

Sir:

In the March number of THIS JOURNAL, W. M. Latimer has written an article in which he refers to a suggestion of mine. Inasmuch as one might infer therefrom that I considered the idea of the tetrahedral form of α -particle to be original with me, may I state that this was not the case. What I did suggest and discuss with Professor Latimer and others was the orientation of the spins of the proton, as used by Latimer, in which the spin of each proton was supposed to point out from the center of the tetrahedron. This was some time ago, and Professor Latimer writes me that our discussion was only recalled to him by our correspondence after this article was in manuscript form.

In view of this paper of Latimer's and recent discussions of nuclear spin [Bartlett, *Phys. Rev.*, **37**, 327 (1931); Gibbs and Kruger, *ibid.*, **37**, 656 (1931)], a word as to my reason for making this suggestion may not be out of place. I wished to have the resultant spin for one, two or three protons the same (and the same as that of the electron, equal to $1/2$ unit), and the spin for four protons equal to zero. This is a natural result of the tetrahedral structure though requiring some "distortion" of the angle (if such language has any meaning) between two protons in the case of two. This would explain the anomalous spin in the case of nitrogen (3 α -particles, 2 extra protons, 1 extra electron, resultant spin

⁹ Latimer, THIS JOURNAL, **53**, 987 (1931).

¹⁰ Rodebush, *ibid.*, **53**, 1611 (1931).

2/2 units) and, in fact, accounts for the spin in all the cases considered by Bartlett. However, these cases will also fit into a scheme in which the electrons have no spin, and the proton spins behave like ordinary electron spins (Bartlett, *loc. cit.*). Both proposals will meet with difficulties in the case of Al (Gibbs and Kruger, *loc. cit.*). I think we must simply admit that we do not know how the spins in nuclei are produced. In the meantime, speculations regarding nuclear structure, such as Latimer's, which are based on other data, are of interest.

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O. K. RICE

THE PREPARATION OF COPPER-CHROMIUM OXIDE CATALYSTS FOR HYDROGENATION

Sir:

The new and very efficient catalyst for the hydrogenation of various organic compounds in the liquid phase [Adkins, Connor and Folkers, THIS JOURNAL, 53, 1091, 1095 (1931)] referred to as "copper chromite" suffers under the disadvantage that in the hydrogenation of certain compounds (ethyl phenylacetate to phenylethyl alcohol, for example), there occurs reduction of the catalyst to a red inactive compound. This undesirable feature is not present in a modified catalyst containing barium, for example, which was prepared by replacing 10% of the copper nitrate with a molecularly equivalent amount of barium nitrate using 750 ml. of water at 70° per mole of nitrate. The preparation of a copper-chromium catalyst as originally described by us was based upon the method patented by Lazier for obtaining catalysts from certain chromates. Recently it has been found in this Laboratory that an equally if not more efficient copper-chromium catalyst may be prepared by a more convenient and simple method which is as follows. Seventy-one grams of ammonium carbonate monohydrate in 400 ml. of water was added to a solution containing 50 g. of copper nitrate trihydrate, 5.4 g. of barium nitrate and 77 g. of chromium nitrate ($\text{Cr}_2(\text{NO}_3)_6 \cdot 15\text{H}_2\text{O}$) in 575 ml. of water. After thorough mixing of the reactants, the precipitate was filtered with suction on a Büchner funnel, and washed twice with 50-ml. portions of water. The solid was dried overnight at 100–110°, ground to a powder and heated to approximately 230° in order to expel ammonia, carbon dioxide, etc. The catalyst was then used as previously described.

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