results. I need not, however, comment any further upon Prof. Richard's private letter to Mr. Gladding, since everything of importance in this controversy is settled by an authority which Prof. Richards will certainly approve of; *viz.*, a passage in his own paper in the *Zeitschrift für anorganische Chemie*, *1895*, **8**, 418, which I translate verbatim:

"Moreover the observation is of interest, that the error caused by occlusion ordinarily just about compensates that caused by the solubility of the sulphate, so that the final corrected result is almost the same as the real weight. The average of the uncorrected results is 0.3215 in lieu of 0.3214 gram."

This, I think, disposes of the aid which Mr. Gladding has solicited from Prof. Richards in his attack upon me.

ZURICH, MAY 23, 1895.

THE PERIODIDES.[1]

BY ALBERT B. PRESCOTT.

Received August 12, 1895.

THE periodides are remarkable as products of extreme additive combination, along with clearly cut crystalline form, distinct physical constants, and instances of rare optical power. They are easily reduced to normal iodides, containing for every atom of iodine firmly bound, one or more iodine atoms loosely bound; therefore they are often and not improperly termed superiodides. Professor Geuther used for them the term polyiodide, perhaps by reason of his view that all their iodine atoms are of equal valence in the molecule.[2] Jörgenson designated them together as superiodides, though including within their structural type certain double polyiodides not understood to contain additive iodine.[3] If these compounds contain, as their behavior has been interpreted to imply, for every atom of iodine that is linked to the base, a number of atoms of iodine linked only to iodine, they offer a striking example of the influence of a basal group upon iodine atoms to which it is not linked. The one iodine atom that is directly united to the nitrogen or other

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[1] Read at the meeting of the American Association for the Advancement of Science, Springfield, Aug. 30, 1895.

[2] A. Geuther, *1887*: *Ann. Chem.* (Liebig), **240**, 82.

[3] M. Jörgenson, *1869*: *Ber. d. chem. Ges.*, **2**, 465.

base-forming element, by virtue of this union, enables a number of other iodine atoms (say from two to eight) to unite with each other together with itself in an iodine group, capable of forming multiples in polybasal molecules. To this view we are led, possibly misled, by the course of theory. In this relation the molecular weight of free iodine is of interest, and has been studied with care, not only in the vapor[1] but in solutions[2] and in the crystals[3] themselves. The relation to the elemental molecules gives to the periodides an interest greater than that of the mixed superhalides, such as iodoperchlorides and iodoperbromides of bases inorganic and organic. The supersulphides, however, present a corresponding instance of additive combination with a single element, as understood. The organic supersulphides[4] are not so ready of formation or so stable as the organic superiodides, though the reverse seems to be true of the corresponding inorganic super compounds. In its elemental states sulphur surpasses iodine in its unusual capacity for polyatomic molecules. And this comparison holds for the hydrides, as hydrogen pentasulphide was reported in 1888[5], while hydrogen diiodide, though holding a name in the earlier handbooks[6] is no longer accounted a chemical individual.[7] Again, the superoxides of organic acid radicals were compared with superiodides by Brodie.

To obtain a general survey of the principal known periodides, they may be provisionally classified, chiefly with respect to their bases, as follows:

1. The periodides of potassium and of mercury. Any double metallic polyiodides containing additive iodine and without other acid.

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[1] V. Meyer, *1880*: *Ber. d. chem. Ges.*, **13**, 1010; Neumann, *1880*: *Ber. d. chem. Ges.*, **13**, 1050.

[2] M. Loeb, *1888*: *J. Chem. Soc.*, **53**, 805; Paterno and Nasini, *1888*: *Ber. d. chem. Ges.*, **21**, 2153; Krüss and Thiele, 1894; *Ztschr. anorgan. Chem.*, **7**, 52; John Conroy, 1874: *Proc. Roy. Soc.*, **25**; 46.

[3] John Conroy, *1876*: *Proc. Roy. Soc.*, **25**, 51; Compare Geuther, *1887*, *Ann. Chem.* (Liebig), **240**, 85.

[4] Palm, 1863: *Phar. Ztschr. Russ.*, **2**, 337, 361, 385; A. W. Hofmann, *1868*: *Ber. d. chem. Ges.*, **1**, 81; E. Schmidt, 1876: *Ann. Chem.* (Liebig), **180**, 287; A. W. Hofmann, again in 1877, *Ber. d. chem. Ges.*, **10**, 1087.

[5] Rebs: *Ann. Chem.* (Liebig), **246**, 356.

[6] Gmelin's Handbook, **2**, 261, *1849*, from Baup, *J. Pharm.*, **9**, 40.

[7] Gmelin-Kraut's Handbuch, I, **2**, 310, *1872*. *J. Chem. Soc.*, **2**, 281, *1876*.

2. Periodides of ammonium. Periodides of arsonium[1] and of stibonium if they have been obtained. Periodides of the metallic derivatives of ammonium. The same of metallic derivatives of arsonium and of stibonium, if they have been obtained.

3. The periodides of organic bases. They are mostly of the quaternary, and the tertiary[2] bases, of the nitrogen-base family, including bases with oxygen and without it. Phosphonium,[3] arsonium,[4] and probably stibonium[5] periodides are known. And, of another type, that of perhalide of a bare amine base, such as $(R_3N)I_2.I$, at least triethyl phosphine periodide[6] and pyridine periodide[7] have been reported. Also a perhalide taken as pyridine dibromide hydrobromide.[8] The nitrogen-base periodides belong in two categories, (1) those of the alkylammonium bases, and (2) those of pyridine and its derivatives. Polyiodides of the vegetable alkaloids belong in the latter division, except the caffeine and theobromine polyiodides.

4. The periodide of iodonium, the organic iodine base obtained by Victor Meyer last year.[9] The normal iodide of iodonium is of structural interest to polyiodides generally.

5. Aromatic sulphon periodides, as found by Kastle and Hill last year.[10]

6. Acid polyiodides, more or less complex, and double base polyiodides, inorganic and organic, including those in which the iodine is not in additive combination, that is, *not* yielding a distinct part of the iodine to reducing agents with a good end reaction.

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[1] Phosphonium *normal* iodide; Labillardiére and Gay Lussac: *Ann. chim. phys.* [2], 6, 304; A. W. Hofmann, *1887*; *Ann. Chem.* (Liebig), 103, 355; 1873: *Ber. d. chem. Ges.*, 6, 286. Inflames by contact with iodine.

[2] In Genther's table, in 1887, of the periodides then known, the only periodides of tertiary bases destitute of oxygen, which appear are a pyridine hydrogen pentiodide, and a quinoline hydrogen tetriodide, both by Dafert (Genther: *Ann. Chem.* (Liebig), **240**, 74). In reporting upon these, in 1883, Dafert says: "Nach den bis jetzt bekannten Thatsachen schientes, dass nur tertiäre und Ammoniumbasen Periodide bilden" (*Monatsh. Chem.*, **4**, 510.)

[3] Tetraethylphosphonium triiodide, Jörgensen, *Ann. Chem.* (Liebig), **240**, 74.

[4] Tetraalkylarsonium triiodides, Cahours, *1860*: *Ann. Chem.* (Liebig), 116, 346; *1862*: *Ibid*, **122**, 215.

[5] Jörgenson, *1869*: *Ber. d. chem. Ges*, **2**, 463.

[6] Masson and Kirkland, *1889*: *J. Chem. Soc.*, **55**, 139.

[7] Mr. Trowbridge and the author in another paper of this date.

[8] Grimaux, *1882*: *Compt. rend.*, **95**, 87; *Bull. Soc. Chim.*, **38**, 127.

[9] *Ber. d. chem. Ges.*, **27**, 1594, *1894*.

[10] *Am. Chem. J.*, 16, 116. A sulphur periodide of another order is that obtained in amorphous condition by Jörgensen, *1869*: *Ber. d. chem. Ges.*, **2**, 464.

Geuther's classification into triiodides, pentaiodides, heptaiodides, and enneaiodides, all with one atom of iodine firmly bound,[1] was of service in his own study of structural features. But Geuther admitted a category of sesqui-, di-, tetra-, and hexaiodides. There is surely a prevailing proportion of *even* numbers of *additive* iodine atoms, making *odd* numbers of *total* atoms of iodine, per "molecule" of the periodide. Generally this is an assumed "molecule" of monobasal proportions. That two or more monovalent groups of the ammonium type should enter into the formation of a periodide molecule, in some cases, is theoretically probable, to say the least, if periodides are individualized in molecules at all. The hypothesis of Jörgenson in 1869,[2] providing for both monammonium and diammonium types of periodides, is not an unreasonable one. Moreover, there is to be considered the probable occurrence of an iodine atom in the fourth position of the organic ammonium group, phosphonium group, etc., with whatever degree of firmness of binding may be determined for it in this position. Take it all in all, therefore, it seems to me that at present we know no law of even or uneven numbers of iodine atoms in superiodides, either to help or to hinder our interpretation of results. With evidence of molecular weight we may gain approach to such a law.

In division 6 of the classification above there are without doubt included certain strictly normal iodides. The iodomercurates as strongly marked double iodides, and the Herapathites as representative acid superiodides come in this division. An interest in the iodomercurates of the nitrogenous bases[3] has been but one among several causes contributing to my own interest in this subject at present. But I have not yet made such an inquiry into the action of deiodinizing agents upon the known double iodides as might reveal what superiodides there are among them. Some of the tabulations of the super-iodine in double inorganic polyiodides given by Geuther[4] seem to invite further inquiry. The acid periodides in many cases undenia-

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[1] *Ann. Chem.* (Liebig), **240**, 74, 80, *1894*.

[2] *Ber. d. chem. Ges.*, **2**, 465, *1869*.

[3] *Am. Chem. J.*, **14**, 607, 1892; **2**, 294, *1880*. *Pharm. Rund.*, **12**, 146.

[4] *Ann. Chem.* (Liebig), **240**, 81.

bly contain additive iodine, but the question of their constitution, like that of mixed halides in general[1] is more complicated and is perhaps of less special significance, than that of the simple polyiodides.

With the exception, then, of the metallic, the iodonium and the sulphon periodides, the formation of superiodides is limited, so far as I have found, to compounds of the nitrogen family of elements.

The first periodide recognized, so far as I find record, may have been that of ammonium, termed by Berzelius the biniodide. After the discovery of iodine the first workers upon the alkaloids seem to have mistaken, in some instances, a produced periodide for a mixed excess of iodine to be taken up by more alkaloid in preparation of the hydriodides.[2] In 1839 Bouchardat,[3] a medical writer in Paris, recounts that, when dogs were being surreptitiously poisoned with strychnine in Paris, and an antidote was asked for, first Guibourt recommended powdered galls, and then Donné advised iodine tincture,[4] whereupon Bouchardat himself, approving the use of iodine, said they should use it in potassium iodide solution. He then set forth some interesting characters of the alkaloid periodides, comparing them with ammonium periodide, quoting for this the name from Berzelius mentioned above. De Vrij has said that Bouchardat anticipated Herapath in production of iodosulphates, A modest memoir of Donné, in connection with the Parisian interest just referred to, upon the use of iodine as an analytical reagent for vegetable bases, was referred for criticism to D'Arcet and Chevreul, who made quite an elaborate report[5] upon the action of free chlorine, bromine, and iodine, in intensive application, with admonition as to undue dependance upon any single analytical reactions. In 1846, in his summary of the distinguishing reactions of the more important

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[1] The Chloriodides of Organic Bases, and Pyridine Chloriodide, Pictet and Krafft, *1892* : *Bull. Soc. Chim.* [3], 7, 72.

[2] Pelletier and Caventou, 1819. *Ann. chim. phys.* [2] 10, 142; *Ann. der Phys. Gilbert*, 63, 306.

[3] Bouchardat, 1839 : *Compt. rend.* 9, 475; *L'Institut*, 7, 358.

[4] Both apparently acting under the opinion, due to that little chemistry which has often brought all chemistry into disrepute, that a precipitant in a test-glass will serve as an antidote in the stomach.

[5] *Ann. chim. phys.* [2] 38, 82.

alkaloids,[1] v. Planta-Richenau specifies for each a precipitation by free iodine. In 1854, shortly after A. W. Hofmann's famous elucidation of organic ammonium bases,[2] Weltzien contributed a full and careful description[3] of the tetramethyl and tetraethyl ammonium triiodides. In 1858 Müller added a good account[4] of quaternary mixed alkyl ammonium triiodides. In 1866 Wagner[5] proposed iodine precipitation and a method of treatment of the periodide precipitates for separation of alkaloids from extractive matters. And Tilden made a contribution in 1866.[6]

The masterly work of Jörgensen, beginning with his dissertation at Copenhagen in 1869, continuing for about nine years[7] in this field, and extending over nearly all relations of polyiodides in general, have had the respect of all chemists, while hardly yet fully assimilated.

In 1887 this subject was taken up by Professor A. Geuther, at Jena, who contributed[8] a good number of new periodides from his own laboratory, with a tabulation of all then obtained, and a vigorous and independent study of the features of structure. The crystallographic investigations were made by Prof. Lüdecke. Prof. Geuther died in 1889.

In 1869 Jörgensen[9] formulated his idea of the probable structure of "these compounds," taking iodine as trivalent, as follows:[10]

$R_4N.I:\begin{array}{c}\mathrm{I}\\ :\\ \mathrm{I}\end{array}$; $R_4N.I:\begin{array}{ccc}\mathrm{I}&.&\mathrm{I}\\ .&&:\\ \mathrm{I}&.&\mathrm{I}\end{array}$; etc., for periodides of uneven numbers of iodine atoms.

$R_4N.I:\begin{array}{ccccc}\mathrm{I}&.&\mathrm{I}&.&\mathrm{I}\\ .&&.&&.\\ \mathrm{I}&.&\mathrm{I}&.&\mathrm{I}\end{array}:I.NR_4$ for those of even iodine numbers.

And $R_4N.I:\begin{array}{c}\mathrm{I}\\ .\\ \mathrm{I}\end{array}:Hg$ for a typical iodomercurate. This simple

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[1] Heidelberg dissertation, 1846. *Ann. Chem. Pharm.*, 74, 245.

[2] *1850-51*: Phil. Trans. 1. 93-131, 357-398.

[3] *Ann. Chem. Pharm.*, 91, 33; 99, 1.

[4] *Ann. Chem. Pharm.*, 108, 1.

[5] *Ztschr. anal. Chem.*, 4, 387.

[6] *J. Chem. Soc.*, 19, 145, *1871*.

[7] *J. prakt. Chem.*, 1870-78, [2] 2, 347, 433; 3, 145, 328; 14, 213, 356; 15, 65, 418; 16, 352. *Ber. d. chem. Ges.*, 2, 460, *1869*.

[8] *Ann. Chem.* (Liebig), 240, 66-91.

[9] *Ber. d. chem. Ges.*, 2, 465, *1869*.

[10] The present writer gives R_4N as an expression for any organic base of nitrogen, instead of "Alk" used by Jörgensen.

conception is, of course, consistent with an iodine valence of five or of seven.

Geuther[1] drew from the optical studies of the color of iodine crystals by Conroy the indication that the molecular mass of the crystalline element is that of $(I_6)_n$. He made this generalization as to color of the periodides, that the tri and hepta iodides were red-brown to violet-blue, and the penta- and enneaiodides green to green-black, the higher iodine numbers giving the deeper shades.[2] He presents structural schemes of orders as follows:

For the triiodides, $(R_6I_6)I_{12} = 6(RI.I_2)$; for the haptaiodides, $(R_2I_2)I_{12} = 2(RI.I_6)$; for the pentaiodides, $(R_4I_4)I_{16} = 4(RI.I_4)$; and for the enneaiodides, $(R_2I_2)I_{16} = 2(RI.I_8)$.

In the laboratory of the writer the preparation of periodides of pyridine is in the hands of Mr. P. F. Trowbridge, and an account of some of these is communicated by both of us in another paper, while he continues the work for pyridine and quinoline. Some work on periodides of the more simple of the aliphatic bases is in other hands. In this subject a pyridine normal polybromide, namely a trimethylene bromide, obtained by Mr. R. F. Flinterman, is reported upon in a paper by him and myself. Therewith it is desired to continue studies of the limit of tertiary base addition to halogen alkyls which are secondary and tertiary. I submit also a note with the observations of several workers upon the preparation and properties of a few pyridine alkyl normal iodides, and Mr. S. H. Baer has some work in progress with me upon pyridine alkyl hydroxides.

ANN ARBOR, MICHIGAN.

AN IMPROVED GAS REGULATOR.

BY F. P. DUNNINGTON.

Received August 7, 1895.

SOME years ago I published[3] a description of a gas-regulator, which is now so modified as to make it less bulky and more reliable. Its arrangement may be understood by reference to the

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[1] *Ann. Chem.* (Liebig), 240, 85.

[2] This generalization, to which Prof. Geuther acknowledged reported exceptions, finds little support in the observations which Mr. Trowbridge and the writer have been able to make.

[3] *Am. Chem. J.*, 4, 2.